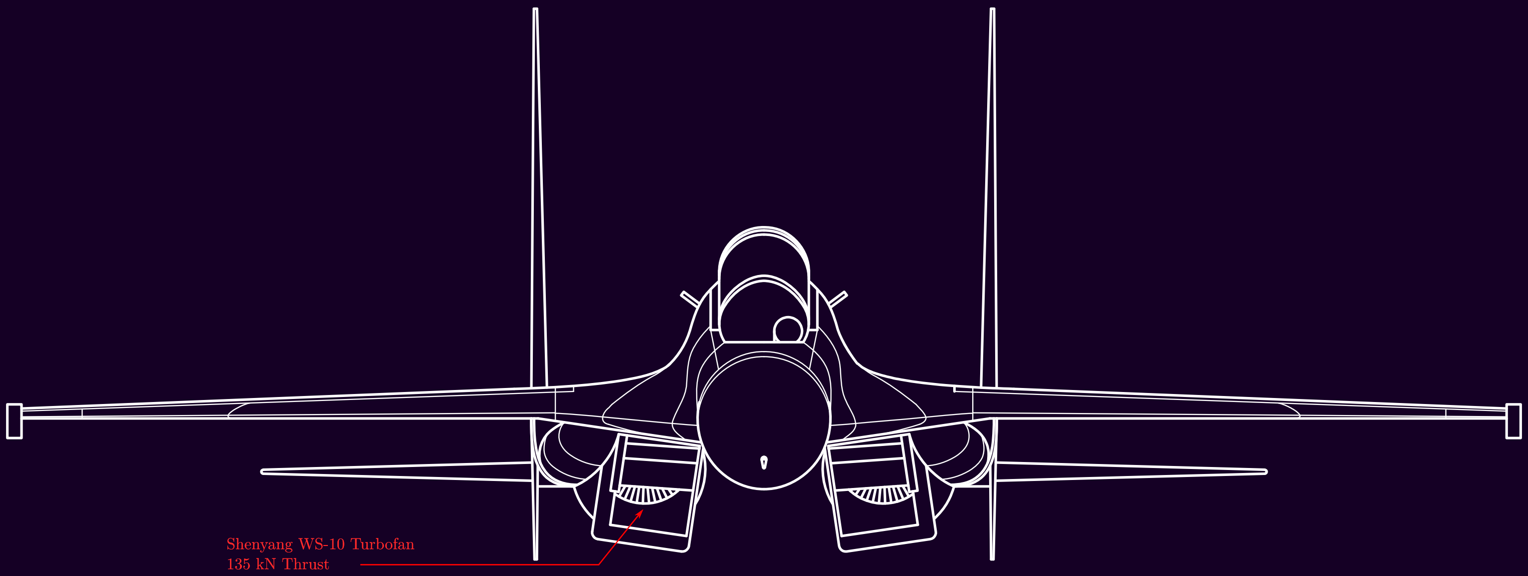

Statistical Physics and Thermodynamics

Mario Lino da Silva

Vol. 1: Theory

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Statistical Physics and Thermodynamics

Mário Lino da Silva

ULisboa School, Shanghai University textbook

last revision: May 22, 2025

Preface

This textbook has been developed for supporting the teaching of undergraduate *Thermodynamics and Statistical Physics* courses with typical duration of one quarter year, awarding 6 ECTS (European Credit Transfer and Accumulation System). Typical courses are structured over 7/10 weeks, with a total time of 40–49 hours split among theoretical lectures and problem-solving/laboratory classes.

The textbook is structured in a fashion that slightly differs from the popular textbooks on the topic. Thermodynamics is a very peculiar discipline where one needs to delve into microscopic phenomena and the fundamentals of the states of matter to fully understand macroscopic thermodynamic processes. However it is often customary for courses and textbooks to give full emphasis to the microscopic aspects of thermodynamics (in more physics-oriented courses) or instead to exclusively focus in the macroscopic aspects of the discipline (in more engineering-oriented courses).

The author has instead striven to achieve a more syncretic approach for the teaching of the discipline, inducing the students into the microscopic world of statistical physics before emerging into the macroscopic world of Thermodynamics (hence why the textbook is named *Statistical Physics and thermodynamics*, mirroring the typical names given to such courses). The problem is that existing textbooks, while extremely rich and detailed, somewhat suffer from being more focused in just one of both aspects of this discipline.

This is why some effort was put into turning these initial lecture notes into a more proper textbook, although in its current state, the teaching material is still a bit dry and synthetic, suited for a classical teaching approach with the transcription of the governing equations and respective demonstrations on the board. This is bound to evolve, as future revisions of the textbook will turn it into a richer resource, ultimately making this a full-fledged textbook suited for the exposition of the discipline in the (differentiated) way it was structured by the author.

Foreword to Students

This textbook provides the theoretical support to topical courses on *Thermodynamics and Statistical Physics*, providing the core of the theoretical concepts that are taught in class (typically by the usual approach of writing on the board, but sometimes supplemented by slideshows). As aforementioned, the textbook –in its current revision– is written synthetically, and should not be considered by the student as the one and definite theoretical resource for the course.

As such, three reference textbooks are suggested to supplement the different chapters of this textbook. These include:

- Blundell, "*Concepts in Thermal Physics*" [1], for Chapters 1–4, providing additional theoretical support on statistical physics, the structure of matter, and on microscopic thermodynamic aspects.
- Cengel, "*Heat Transfer*" [2], for Chapter 5, providing theoretical support on heat transfer phenomena (conduction, convection and radiation).
- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [3], for Chapters 6–10, providing theoretical support on the macroscopic aspects of thermodynamics, in an engineer perspective.

A companion volume, including series of exercises for each chapter, as well as supplementary material for the course (both technical or societal), is also made available for supporting the students study. Thermodynamic tables, generated with the recourse to the latest international standards, are also made available for problem solving exercises.

Foreword to Teachers/Instructors

Thermodynamics is a peculiar discipline in the sense that practical applications predate the foundational definition of the discipline theoretical background, which owes much to the development of statistical physics in the second half of the XIX$^{\text{th}}$ Century. It has been since somewhat customary for thermodynamic courses and textbooks to adhere to this somewhat historical precedent, introducing the teaching of thermodynamic processes, cycles and machines, before moving further to the teaching of the statistical physics aspects of thermodynamics, often induced by the introduction of the concept of entropy.

This textbook instead follows a pedagogical approach where thermodynamics are taught following a more organic approach stemming from the description of microscopic phenomena related to statistic physics and how these microscopic process shape our macroscopic world.

To do so, the textbook firstly considers the definition of all key variables that define matter microscopically and macroscopically, such as mass, volume, density, pressure, and temperature, among others. More specifically, the first three lectures are mostly dedicated to the definition of the concept of temperature, painstakingly approached with the introduction of all the relevant tools used to statistically describe matter at the microscopic level.

The second part of the textbook (from Chapter 6 onwards) approaches the teaching of thermodynamics in a more classic fashion, with a description of fundamental thermodynamic processes, followed by an introduction of thermodynamic cycles and completed by a description of popular cycles in real-world machines.

Prospective teachers/instructors wishing to use this resource should only consider it in case they are willing to follow a teaching approach wherein statistical physics concepts are to be introduced before the discussion of macroscopic thermodynamic processes (and chiefly, fully describing concepts such as temperature at a microscopic level). Otherwise, the textbook is ill-adapted for the more traditional teaching of thermodynamics, where other textbooks will excel at this.

Besides the finer theoretical details that every course of this kind necessarily encompasses, care has been exerted in providing examples of real-life phenomena or applications in relation to the discipline. Namely, societal challenges related to Thermodynamics are discussed in many parts of the course. Also, History is particularly integral to the development of this discipline and as such takes a big part in the additional notes and historical comments that are added around the lecture notes for this Academic Unit.

I have also striven to adhere to the best practices in the contemporary teaching of STEM units, with the liberal sprinkling of themes in relation with Arts and Humanities. Last but not least, some bits of humor, and some anecdotes are liberally sprinkled all around these notes. This fosters student's engagement with the discipline and mitigates some more strenuous parts of the course linked to mathematical derivations and demonstrations.

This textbook is augmented with companion volume, collecting a significant amount of disparate supplementary material, ranging from the more hard topics related to difficult mathematical demonstrations, to the more softer topics on literature and even philosophy.

Material sourcing

A great deal of the theoretical demonstrations and examples for this textbook are borrowed from the comprehensive lecture notes produced and kindly shared by Prof. Vasco Guerra, which has been teaching the same course to Physics Engineering students.

Many figures for these lecture notes have been produced by the author, using the outstanding *libre* vector editing software **inkscape**. Many other figures have been retrieved from online sources available around the World. A few figures are temporarily referenced and taken from other textbooks and will be replaced by newly produced figures in an upcoming revision.

The author wishes to express a heartfelt *thank you* to all the authors that produced and made freely available these high-quality resources which have enriched these lecture notes, and to further express its apologies for not individually crediting every single one of the many authors. Notably, many figures have been retrieved from several *wikipedia* articles on Thermodynamics [4], the `tikz.net` website [5], and the book "*Thermodynamique de l'Ingénieur*" by *Olivier Cleynen* [6]. A series of animations were also taken from the excellent site `animatedengines.com` [7].

All the text and native figures of this textbook may be freely reused, adapted and remixed, without any restriction, and without the need to credit the initial author.

Additional acknowledgements

I further wish to express my gratitude to Prof. Vasco Guerra for firstly sharing his lecture notes that helped shaping the core of this textbook, as well as Dr. António Figueiredo, which has been assisting me with the preparation of the course exercise lists. Last but not least, I wish to express my heartfelt gratitude to all the TA's that helped with the formatting/translation and improvement of many parts of these lecture notes, namely Diogo Costa (2022/2023), Oscar Alves (2023/2024), José Mariano (2023/2025), and Pedro Teigão (2024/2025).

Other recommended textbooks

- Blundell, "*Concepts in Thermal Physics,*" Oxford University Press, 2nd edition, 2010, [1].
- Çengel. "*Heat Transfer, a Practical Approach,*" McGraw Hill, 2nd edition, 2010, [2].
- Moran and Shapiro, "*Fundamentals of Engineering Thermodynamics,*" John Wiley & Sons, 8th edition, 2010, [3].
- Schroeder, "*An Introduction to Thermal Physics,*" Yale University Press, 2021, [8].
- Berry, "*Three Laws of Nature: A Little Book on Thermodynamics,*" Yale University Press, 2019, [9].

References

[1] Stephen J. Blundell and Katherine J. Blundell. *Concepts in Thermal Physics*. 2nd Edition. Oxford University Press, 2010 (cited on page).

[2] Yunus A. Çengel. *Heat Transfer, a Practical Approach*. 2nd Edition. McGraw Hill, 2010 (cited on page).

[3] Michael J. Moran et al. *Fundamentals of Engineering Thermodynamics*. 8th Edition. John Wiley & Sons, 2010 (cited on page).

[4] *Wikipedia.org*. May 17, 2024. URL: `https://www.wikipedia.org` (cited on page).

[5] *tikz.net*. May 17, 2024. URL: `https://tikz.net` (cited on page).

[6] Olivier Cleynien. *Thermodynamique de L'Ingénieur*. 3ème Edition. Edition de l'Auteur, 2021 (cited on page).

[7] *Animated Engines*. May 17, 2024. URL: `https://animatedengines.com/` (cited on page).

[8] Daniel V. Schroeder. *An Introduction to Thermal Physics*. Yale University Press, 2021 (cited on page).

[9] R. Stephen Berry. *Three Laws of Nature: A Little Book on Thermodynamics*. Yale University Press, 2019 (cited on page).

Mário Lino da Silva

Contents

Study Guide

Organization of this Textbook. Teaching Theory and Practice

Thermodynamics, as a discipline, is at the same time inherently practical, providing a set of relationships that govern the behavior of *systems* and their *surroundings*, and how those systems may convert heat into work/motion and motion/work into heat. Concurrently, it is also deeply rooted in intricate fundamental concepts (particularly at the microscopic level) which are essential for a broader understanding of the discipline and our Universe at large.

Therefore, any pedagogical approach needs to strike a balance between the necessary abstractions and complex derivations required for the derivation and presentation for some of the fundamental Laws of the discipline, and the more practical applications of these laws in our everyday life.

A question often forwarded by frustrated students, particularly during the first chapters dealing with statistical physics, is: "***What is the relevance of going through a series of complicated mathematical manipulations to derive ultimately simple expressions for Thermodynamic Laws like for example the ideal gas Law? What does a student gain from learning a demonstration he/she will never apply in his/her practical life?***"

The practical application of all this theoretical "mumbo-jumbo" may seem scarce at first look, with concepts like disembodied forces acting on frictionless pistons appearing as excessively abstract and divorced from engineering applications in everyday life. The astute student could reasonably argue that they will soon forget most of this course materials upon completing it [1], and that there are plenty of available handbooks with a robust set of fundamental and semi-empirical relationships that the professional engineer may quickly consult for his daily problem-solving tasks,

However, reasonable as it may seem, this argument omits the fundamental differences with vocational training such as taught on technical high schools or polytechnic institutes. Whereas the former directly train the student for a specific craft, engineering schools provide a more generic and well rounded formation on general scientific disciplines. More emphasis is put into the more "academic" aspects of teaching, including mathematical formalism and fundamental physical principles. An often used quote is that "*Engineering schools and universities train students on how to learn how to learn*". By looking at complicated derivations of simple equations, even if just once, one delves on the mindsets and thought processes that shape this discipline. In other terms, it is not the result that is important, it is the thought process.

As a future engineer with a solid theoretical background, you will be brought to familiarize yourself with never technologies as progress marches on. And you will able to do this extra training by yourself. You

1: The popular saying that "*One will forget up to 90% of what he learned in the past*" stems from the discredited "learning pyramid" model, see Masters [1]. A recent review work has reported that for studies that do look at longer spans of time, people can lose anywhere between 14% and 85% of their knowledge in just a few years, see Custers [2]

[1]: Masters (2020), *Edgar Dale's Pyramid of Learning in medical education: Further expansion of the myth*

[2]: Custers (2010), *Long-term retention of basic science knowledge: a review study*

will read the new books/technical manuals and self-educate yourself on these new technologies, accounting for the fundamentals you will have learned during your University years.

If you were taught exclusively technical skills from the start of your degree, there would be a strong possibility that your schooling would become obsolete by the time you finished the degree. One great example is Chapter 12 of this textbook, which deals with the thermodynamics of Internal Combustion Engines (ICE), a technology that is quickly becoming obsolete as the result of the ongoing electrification of our economies. The theory that precedes this chapter remains nevertheless perennial, ready to stand the test of Time.

As stated by another author [3]: "*The fundamental principles do not cease to apply in the practical world!*",

[3]: Tatum (2020), *Heat and Thermodynamics*

or better yet:

> *Technologies are ephemeral, Science is eternal.*
>
> Source: g051051 `/r/learnprogramming`

Problem-Solving Techniques

An engineer is tasked with solving problems and coming up with new and innovative designs for systems and machines. Accordingly it shall come as no surprise that the student will be evaluate on his/her capability of applying the theoretical concepts and laws of the discipline towards problem-solving exercises. As with other courses you will be taking concurrently to this one, you will spend most of the time solving several series of exercises in anticipation for those that will be handled to you during the different examination periods for the class. It is therefore important for the instructor to provide some elementary guidelines and techniques for this specific skillset.

A large number of example problems are provided in Volume 2 of this textbook, in the form of seven series of exercises. A great deal of these exercises are provided with detailed solutions, including all the necessary intermediate steps. It is very important that the student **does not** succumb to tentation and review the solutions straightaway, saying to himself/herself "*This makes sense*" and calling it a day. Instead try to work out the problem in a blank page, following the problem-solving steps that are outlined below. If you are still finding it difficult to solve the exercises, then re-check the summaries of the theoretical lectures first, and then the lectures themselves if necessary, alone or with your study group, whatever fits your studying habits best. Refer to the solutions only when you get stuck and have put in a reasonable amount of effort.

Each student will have different personal habits for studying, and that is fine, so I am usually loathe to provide generic advice to students, since its relevance will strongly depend on the person in question. This is perhaps the only exception I will make: **Do try to solve as much exercises as possible, and do it as much as possible without checking the solutions beforehand**.

Problem-solving steps

The **6 steps** outlined below are a rough description of the general methodology that is adopted for engineering problem-solving, and may be found described in the roughly same fashion in all major engineering textbooks. These include:

1. **Problem Statement:**
    a) **Known quantities/variables:** Identify and summarize on your blank page the known quantities/variables that are provided.
    b) **Quantities/variables to be determined:** What are the objectives of the problem? Identify the quantities/variables to be determined.
2. **Schematic of the Problem:** Draw a sketch of the physical system under study, determine if it has any physical boundaries (closed system) or if it is defined as a control volume. Identify any interactions with its surroundings (energy and/or mass exchange). Check for the properties that remain constant/change during a process and identify them on the sketch. Draw any associated diagrams associated to the system, locating key state points (e.g. p–V or T–S thermodynamic diagrams with the initial/final states reported for each individual process).
3. **Assumptions and Approximations:** State any appropriate assumptions and approximations that may allow simplifying the problem and turn it into a tractable exercise. Assume reasonable form missing quantities that might be necessary (write $p = 101.325\,\mathrm{kPa}$ if atmospheric pressure conditions are assumed). Check for any acronyms for reference states and report the corresponding values (e.g. Standard temperature and pressure STP: [0 °C/1 bar]; Standard sea-level conditions SSL: [15 °C/101.325 kPa]; etc...).
4. **Engineering Model:** Describe a model that is appropriate for solving the problem.
    a) **Physical Laws:** Apply the relevant physical laws and principles, writing them with the assumptions and approximations previously listed, crossing out negligible terms. Check that the physical laws are being used in their appropriate range of applicability.
    b) **Properties:** Determine unknown properties at known states from property relations/tables made available to you. Indicate the source for those property relations/tables.
5. **Analysis and Calculations:** Using your Engineering model reduce the appropriate governing equations to forms that will produce the required results. Work as long as possible with analytic expressions, without substitution by their numerical values.
    a) **Rounding:** Round the results to an appropriate number of significant digits (see next section discussion on significant digits).
    b) **Dimensional Analysis:** Carefully check that the set of units being employed is consistent (Verify that you are not comparing "apples to oranges", that you have dimensionless quantities inside ln, exp terms, etc...), and always represent a dimensional quantity with its corresponding unit (else it is meaningless).

Worked example:

Lhasa is a city in Tibet, China, located at an altitude of 3600 m. Find the density of air in Lhasa, if the temperature is $T = 10\,^\circ\mathrm{C}$.

1: Problem statement:
Given: Air temperature in Lhasa
To be found: Density of air

2: Schematic:

Figure 1: Not all problems will require a schematic, and this is the case here. Lets put a nice picture of Lhasa instead

3: Assumptions and Approximations:
Missing information: Atmospheric pressure
Assumption # 1: Take $p = 1\,\mathrm{atm}$ (Inappropriate. Ignores effect of altitude. Will cause more than 30% error.)
Assumption # 2: Consider variable p as a function of height h, with $h = 3600\,\mathrm{m}$. (Appropriate. Ignores only minor effects such as weather.)

4: Engineering Model:
Use barometric formula incorporating pressure and temperature changes with altitude, see Lente and Ősz [4]:

$$p = p_0 \left(1 - \frac{\alpha}{T_0} h\right)^{\frac{gM}{\alpha R}}$$

with $\alpha = 6.49\,\mathrm{K/km}$ and $M = 28.96\,\mathrm{g/mol}$.
Use ideal gas law as a function of density:

$$\rho = \frac{p}{R_{spe} T}$$

5: Calculations:
Convert T to kelvins: $T = 10 + 273.15 = 283.15\,\mathrm{K}$ and calculate p using barometric formula: $p = 66\,413\,\mathrm{Pa}$.
Finally calculate $\rho = 0.817\,\mathrm{kg/m^3}$ using the ideal gas law.

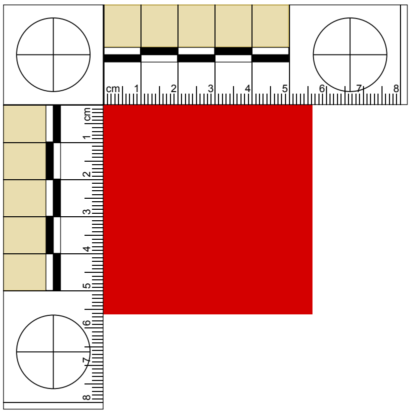
6: Result assessment:
As expected, the density is much lower than the standard density, given the lower pressures ($p = 66.4\,\mathrm{kPa}$ instead of 101.3 kPa), even though the temperature is slightly lower than the reference temperature ($T = 10\,^\circ\mathrm{C}$ instead of 15 °C). Assuming the pressure is the same that at sea level ($h = 0\,\mathrm{km}$) leads to an unacceptable 34% error.

[4]: Lente et al. (2020), *Barometric formulas: various derivations and comparisons to environmentally relevant observations*

6. **Verify and Assess the Results:** Make sure that the obtained results obtained are reasonable, with the appropriate algebraic sign (+/-) and order of magnitude, and verify the validity of the questionable assumptions. Repeat the calculations that resulted in unreasonable values. For example, if you found out that a 1 m long metal bar expands by 0.3 m then you might have made a mistake since thermal expansion of common solids assumes small changes to the reference length.
   State the conclusions and recommendations that can be drawn from the results. Critically assess the significance of the obtained results, and if the assumptions ans approximations applied in 2) are reasonable. If possible, try inferring the relevant trends of the problem through additional "what-if" and parameter sensitivity calculations. Assess any economical and societal impacts of your obtained results (for example how much savings in money/energy may be achieved by insulating some kind of heat reservoir).

Significant digits

Lets say that you have been delivered a cube which has been cut by a very advanced precision machine, and with an unknown side length[2]. You only have a ruler (graded every mm for determining the side length, and you find out that the cube side lies between the 56 mm and the 57 mm mark. Accordingly you assume the length to be $L = 56.5 \pm 0.5$ mm.



Now you want to determine the cube volume, which is simply given by the cube of its side or in other terms:

$$V = L^3 = (56.5\,\text{mm})^3 = 56.5\,\text{mm}\times56.5\,\text{mm}\times56.5\,\text{mm} = 180\,362.125\,\text{mm}^3.$$

However when you measured the cube side, you only knew its side length was between 56 mm and 57 mm or in other terms $L = 56.5 \pm 0.5$ mm and there will be an uncertainty in your volume which will correspond to the differences between the volume of a cube with $L = 56$ mm and $L = 57$ mm:

$$\Delta V = |56^3 - 57^3| = 9577\,\text{mm}^3,$$

[2] Usually these precision-machined parts come with their own metrology certificate, indicating the exact dimensions to many significant digits and one wouldn't need to measure its dimensions.

which corresponds to the fractional uncertainty

$$\frac{\delta V}{|V|} \simeq \frac{\delta x}{|x|} + \frac{\delta y}{|y|} + \frac{\delta z}{|z|} = \frac{3\delta L}{|L|}.$$

Therefore, the uncertainty of the cube volume is almost 10 000 mm^3 and it becomes evident that it is meaningless to report the volume of the cube as $V = 180\,362.125\,\mathrm{mm}^3$ when $\Delta V = 9577\,\mathrm{mm}^3$. Instead, since the orders of magnitude b for the volume and the uncertainty are, respectively $b_1 = 5$ and $b_2 = 2$, it makes sense to report the volume with the same significant digits ($b_1 - b_2$), that is:

$$V = 180 \pm 10 \times 10^3\,\mathrm{mm}^3.$$

As a rule of thumb, **when presenting final results, you should keep the same significant digits than the input variable with the least number of significant digits**. Naturally, it is appropriate to retain all the digits during intermediary calculations, avoiding the propagation of rounding errors, and to only round the final result.

General rules for expressing quantities

s.d. refers to "significant digits"

1. **Zero digits on the left do not count for the number of s.d.**
   Example: 0.00044 (2 s.d.)
2. **Zero digits on the right count for the number of s.d.**
   Example: 12.00 (4 s.d.)
3. **Digits 1–9 and zeros among them are always s.d.**
   Example: 1203.4 (5 s.d.)
4. **Powers of 10 are ambiguous and should be represented using scientific notation**
   Example: 800 is ambiguous, 8.00×10^2 is correct (3 s.d.)
5. **Constants have an arbitrary number of s.d.**
6. **Addition and Subtraction:** The result should have the same s.d. that the operand with the least s.d.
   Example: $105.4 + 0.2869 + 34.27 = 139.9569 = 140.0 = 1.400 \times 10^2$.
7. **Multiplication and Division:** The result should also have the same s.d. that the operand with the least s.d.
   Example: $7.325 \times 8.14 = 59.6255 = 59.6$.
8. **Square Roots, Exponentials amd Logarithms:** The result should also have the same s.d. that the operand.
   Example: $\sqrt{92} = 9.59166 = 9.6$.

INTRODUCTION

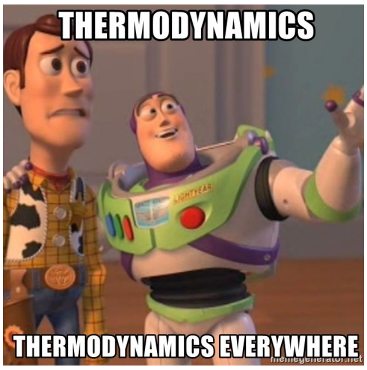
Introduction

> *Thermodynamics is the study of the relations between heat, work, temperature, and energy. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings.*
>
> Encyclopedia Britannica

Thermodynamics and You

Why it is relevant to You:

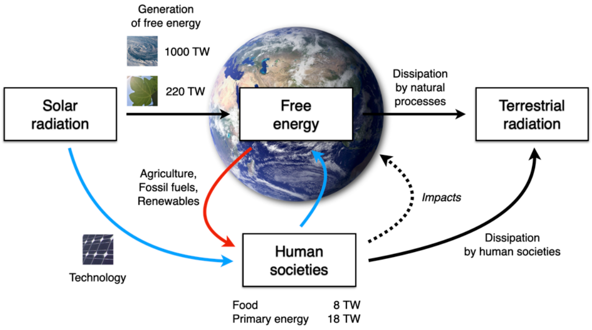
- A discipline as fundamental to a scientist/engineer as mathematics and general physics
- Thermodynamic laws govern all the scales of the universe (from macroscopic to microscopic)
- As engineers, you will apply this discipline for solving many real-life problems/designing cool stuff



Thermodynamics is a discipline whose Laws apply to all the scales of our Universe:

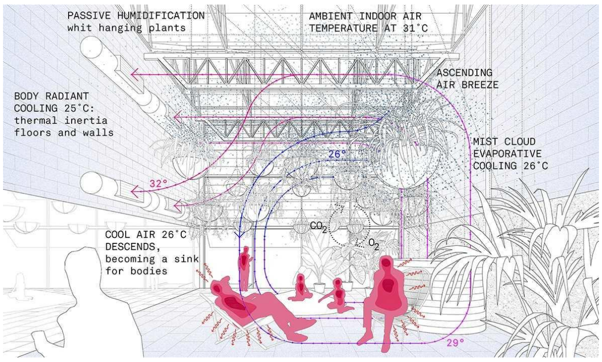
Macroscopic Scales

Thermodynamics govern the whole Universe

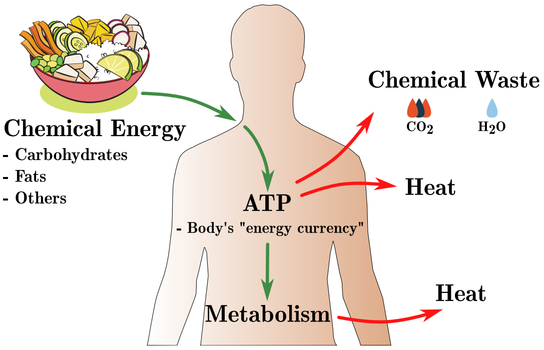


The Sun-Earth pair is a thermodynamic system

Mesoscopic Scales

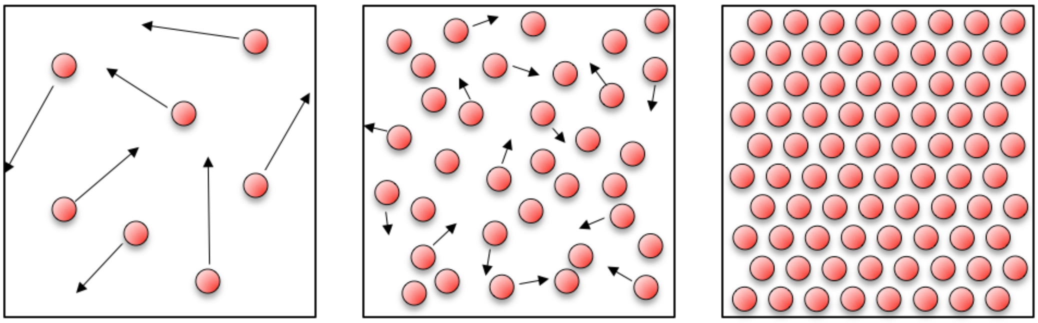


Thermal regulation of buildings



Life is also a thermodynamic system

Microscopic Scales



gas liquid solid

The fabric of matter is also defined by the Laws of Thermodynamics in their statistical interpretation.

Thermodynamics and Statistical Physics

A complete understanding of thermodynamic processes cannot be achieved without delving into the microscopic properties and dynamics of matter.

- When observing the behavior and motion of macroscopic objects (ball, car, bullet, etc. . .), we may describe them as **discrete** objects and use the Newton laws of motion.
- This is no longer true for modeling the microscopic motion of particles. The large number of elements (1L of gas contains 2.7×10^{22} particles in standard conditions) mandate a **statistical treatment** for their motion.

We will use statistical physics to describe the microscopic world and we will understand how this translates into the macroscopic world.

Throughout the course we will be traveling between **worlds of different sizes**, just like Gulliver...

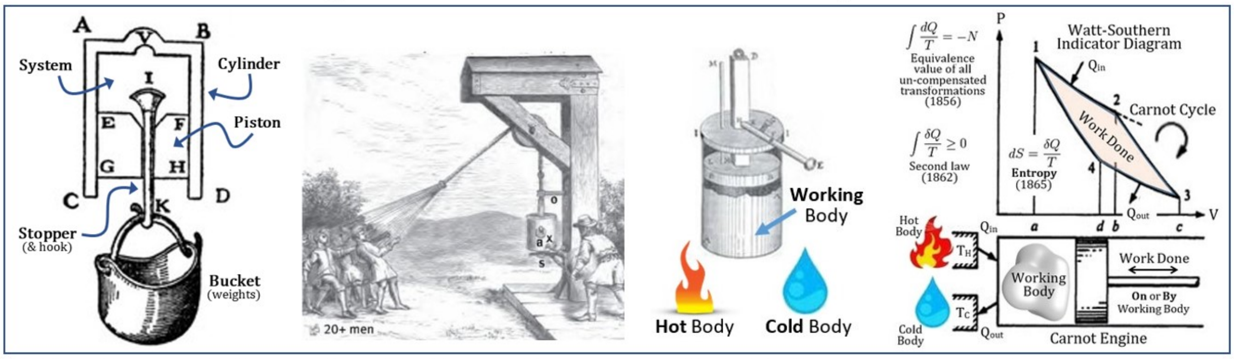
...and we will unravel the underlying fabric of our physical world

How did Thermodynamics came to be?

- Traditional paradigm: basic-to-applied. Flow of concepts from basic science to applications
  - Theory of relativity ⟶ atomic bombs ⟶ nuclear energy
  - Solid-state physics ⟶ transistors ⟶ electronics/informatics
- The discipline of thermodynamics is remarkable in that if followed the opposite concept: applied-to-basic.
  - Thermodynamic machines were firstly invented (18th-early 19th Century), and thermodynamic laws were firstly formulated as empirical laws.
  - The rigorous theoretical framework was developed later through the development of statistical physics (second half of 19th Century).

See Berry, Three Laws of Nature, Chap. 3, 2019

History of Thermodynamics – Concepts



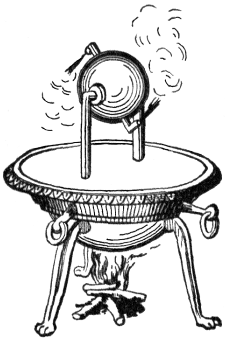
Galileo Vacuum Device
(1632)

Guericke Vacuum Engine
(c.1670)

Papin Engine
(1690)

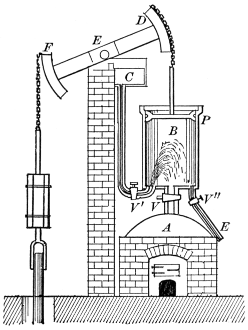
Carnot Engine
(1824)

History of Thermodynamics – Engines



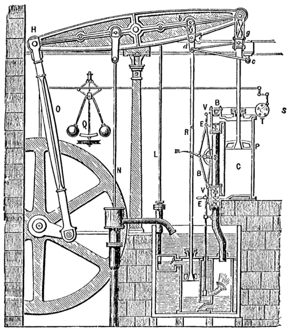
Hero's engine

(Aeolipile)
1st Century



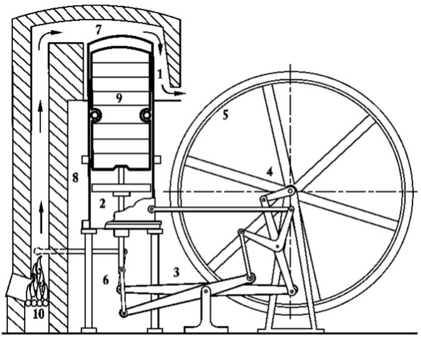
Newcomen engine

1772



Watt engine

1784

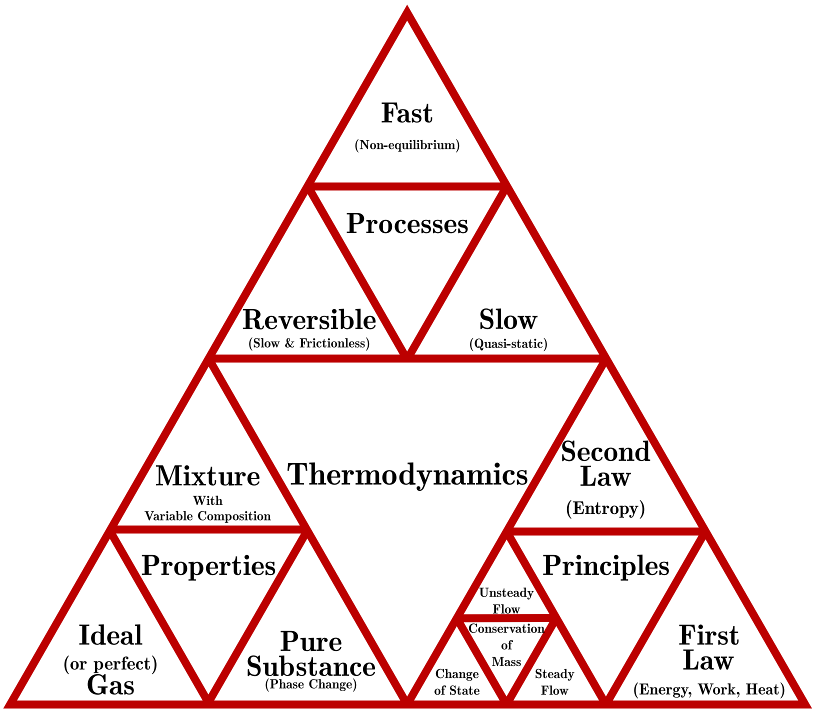


Stirling engine

1816

Steam Engines heralded Thermodynamics and the Industrial revolution in the 19th Century

Thermodynamics – Principles, Properties and Processes



1 Basic Concepts

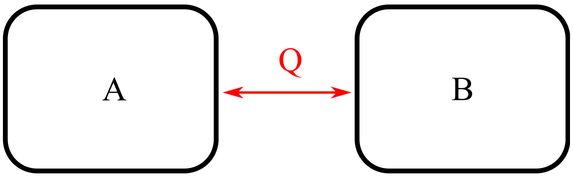
Thermodynamics: Studies the movement (flow) of energy, and how energy may create movement.

It is an universal theory (unlike for example **Newton Laws** which only apply for non-relativistic velocities), whose laws are applicable from sub-microscopic scales until the scale of the Universe (see slides from Lecture 1a).

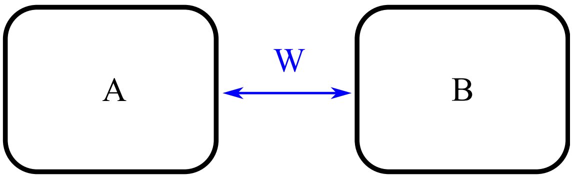
With this said, thermodynamics does not deal with anything properly “tangible". The objects of study are systematically idealized as “systems” with a given **Energy** E, which is quantified (with the units **Joules** J), and which may be transferred or transformed inside the system, or alternatively exchange with the surroundings of the system (for the example of a heater inside a room, the heater represents the system, and the room the surroundings of the system).

Energy exchanges takes on two different forms:

- **Heat** Q which corresponds to the flowing Energy E. This energy is exchanged in a **disordered** fashion between two systems.



- **Work** W which corresponds to energy is exchanged in an **ordered** fashion between two systems.



1.1 Mechanical Energy Conservation

Mechanical Energy E_m: Sum of the **potential U and kinetic K energies** of a mechanical system: $E_m = U + K$.

For an isolated system only actioned by conservative forces, the mechanical energy remains constant ($E_m = \text{const}$).

Conservative Forces: The total work done in moving an object between two points is independent of the taken path.

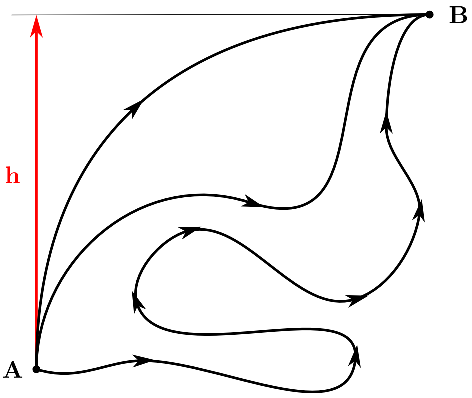


Figure 1.1: Example for a gravitational potential with $E_m = mgh$

Non-Conservative Forces: The total work done will depend on the taken path.

Example: Friction. If we take the shortest route, we lose the less energy through friction forces.

⚠ : Key concept that will be revisited more ahead.

Kinetic Energy K: Energy that an object possesses due to its motion.

$$K = \frac{1}{2}mv^2 \tag{1.1}$$

Demonstration:

The **Work W** of a **Force F** exerted at a distance l parallel to F is:

$$W = F \cdot l \tag{1.2}$$

From Newton's 2$^{\text{nd}}$ Law:

$$F = ma \tag{1.3}$$

We consider the relationships between distance l, speed v, and acceleration a:

$$\frac{d^2l}{dt^2} = \frac{dv}{dt} = a \tag{1.4}$$

Integrating eq. 1.4 we have:

$$\begin{aligned} d^2l &= adt^2 \\ l &= a\frac{t^2}{2} \\ v &= at \end{aligned} \tag{1.5}$$

We may now rework eq. 1.2:

$$\begin{aligned} W &= F \cdot l \\ &= ma \cdot l \\ &= ma \cdot a\frac{t^2}{2} \\ &= m\frac{(at)^2}{2} \end{aligned} \tag{1.6}$$

since $v = at$ we may write:

$$W = m\frac{(v)^2}{2} = K \tag{1.7}$$

For a rotating object, the kinetic energy is written as:

$$K = \frac{1}{2}I\omega^2 \tag{1.8}$$

With I the rotational moment of inertia and ω the angular velocity.

Potential Energy U: Energy that an object possesses owing to its position relative to other objects, stresses within itself, its electric charge, or other factors.

Example for a gravitic potential:

$$\left.\begin{aligned} F_{\text{grav}} &= mg \\ W &= F \cdot l \end{aligned}\right\} W = mgh = U \tag{1.9}$$

(here we consider $l = h$ where h is the height difference between the initial and final position.)

Internal Energy E_{int}: Energy contained within the system, measured as the quantity of energy necessary to bring the system from its standard internal state to its present internal state of interest, accounting for the gains and losses of energy due to changes in its internal state.

Examples: Energy in a deformed elastic medium (spring); chemical energy (fuel).

Mechanical energy conservation example:

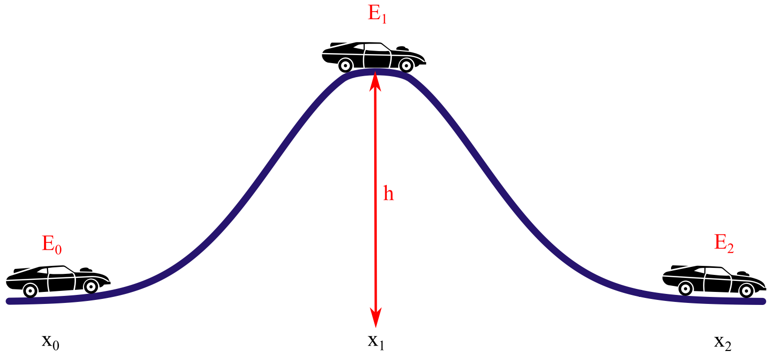


Figure 1.2: Energy balance for a car driving up and down a hill

We assume:

- The car maintains constant velocity over the climb to the mountain.
- No losses from friction.
- Perfect efficiency (100%) in the conversion of internal energy into kinetic/potential energy[1].

Applying the previous relationships one may determine the values for the different energies of the car at locations x_0, x_1 and x_2, as well as its velocity. These are summarized in table 1.1. The vehicle spends part of its internal energy (fuel) that is converted into potential energy as it climbs the hill. The potential energy is then converted into additional kinetic energy as the car descends the hill.

Table 1.1: Energy balance for the car

	E_{int}	E_{pot} (U)	E_{kin} (K)	v (m/s)
x_0	X	0	$m\frac{v_0^2}{2}$	v_0
x_1	$X - mgh$	mgh	$m\frac{v_0^2}{2}$	v_0
x_2	$X - mgh$	0	$m\frac{v_0^2}{2} + mgh$	$v_0 + \sqrt{2gh}$

Another example: marble bouncing on a wall

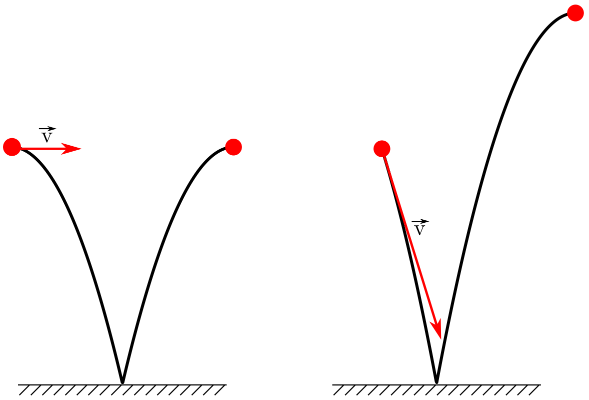


Figure 1.3: a marble moving with initial velocity parallel to the floor will bounce back to the same height (assuming no friction losses in its trajectory), but a marble moving with an initial negative vertical component of velocity will bounce to a higher height, again assuming that there are no friction losses.

1.2 Energy Dissipation

Friction: this is an example of a dissipative phenomena, and a reason why mechanical energy is lost (it is said that the energy is degraded).

⚠: Dissipation processes like friction are key to the understanding of thermodynamics and will again be discussed more ahead.

We will see more ahead that Thermodynamics allows reconciling these inconsistencies of classical mechanics.

- Historically, James Prescott Joule first discovered in 1843 that mechanical energy lost through friction was converted in heat.
- The concept of energy degradation (entropy increase) will be more rigorously discussed later in the course.

We now can return to the concept of Energy E, Heat Q, and Work W in the thermodynamic sense. Namely, we can now understand that the concept of energy E is more general in the thermodynamic sense and encompasses the concept of Mechanical Energy E_m derived from classical

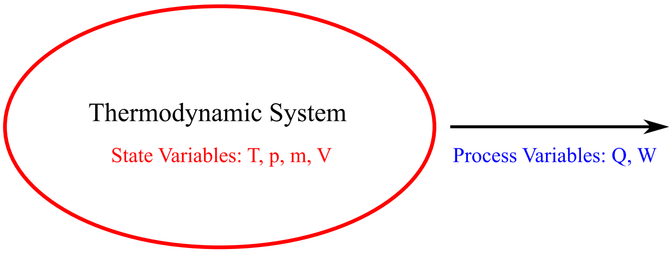
[1] Thermodynamics teaches us that this is totally wrong as we will see during the course

mechanics. Further, since Work W corresponds to an ordered exchange of energy between systems, we can correlate W with E_m, and intuitively introduce the concept of Heat Q as somewhat being related to the losses in mechanical systems (for example, our hands heat-up if we friction them in a vigorous fashion, or bicycle/car brakes heat-up when we are braking the vehicle).

Since we know that Q and W correspond to different forms of flowing energy, we may define the appropriate dimensions for such variables:

$$[Q] \Leftrightarrow [W] \Leftrightarrow [1/2mv^2](\text{Kinetic energy}) \Leftrightarrow [\text{J}] \tag{1.10}$$

Heat Q and Work W are therefore two forms of energy associated to a process of energy exchange. They are called **Process Variables**. Other variables are then needed to define the states of the different systems exchanging energy. These are called **State Variables**.



If further the system is isolated, energy E cannot be exchanged, and it will be considered a state variable as well

1.3 Equilibrium

Definition of a system in equilibrium: The properties of the system are invariant over the timescale into consideration.

Example: A volume of air outside can be considered in equilibrium over a short 10 min timescale (if meteoreological conditions allow so). The Temperature T, Pressure p won't change significantly over the time period between 12:00 and 12:10.

However, if we consider a larger 12 h timescale (from 12:00 to 00:00) one may no longer consider this system to be in equilibrium, as the day/night cycles will alter significantly the properties of the atmospheric air (among other possible phenomena).

We may still consider an averaged day/night value for those variables over say one wheel. We then have another condition for equilibrium, which again won't be valid if we further extend the timescale to a full month, as seasonal changes will contribute to changing the average properties of outside air. However, we may again average those properties over a year and so on...

One needs to point out that Thermodynamics may also be used for describing the time-dependent behavior of systems in non-equilibrium, but the underlying relations are significantly more complicated. In the scope of this course, we will restrict ourselves to equilibrium/steady-state systems.

This so-called "**Classical Thermodynamics**" provides us with a set of rigorous rules about what kind of processes may be allowed for a system evolving from an equilibrium state to another, and those who are disallowed.

1.4 State Variables

We discriminate between extensive and intensive variables:

- Extensive variables have well-defined frontiers. Examples: Mass m and Volume V
- Intensive variables do not rely on well-defined frontiers. Examples: Pressure p, Density ρ, and Temperature T

Figure 1.4: Water in a glass (left) has a well-defined Volume V and Mass m, whereas outside air (right) does not have a defined Volume V/Mass m, however, it has a defined Temperature T, Pressure p, and Density ρ

- In the **Macroscopic world** we use extensive (m, V) and intensive variables (T, p, ρ)
- In the **Microscopic world** we use additional extensive variables (m, V and $x_{x,y,z}$; $v_{x,y,z}$; $\omega_{x,y,z}$ corresponding, respectively to the position, velocity and angular velocity in 3D coordinates). No intensive variables exist.

1.4.1 State Variables Definitions

Mass m: [2] Defined in kg. Fundamental measure of how much matter an object contains.

Mole: Quantity of matter which contains as much objects (atoms, molecules, etc...) as the number of atoms contained in exactly 12 g of ^{12}C carbon.

1 mole has the Avogadro number N_a of atoms/molecules such that $N_a = 6.02214076 \times 10^{23}$. The molar mass M is defined as the mass of a mole of a substance such that $M = m \times N_a$.

Volume V: Self-explanatory. The Density ρ is defined as:

$$\rho = \frac{m}{V} = \frac{[\mathrm{kg}]}{[\mathrm{m}^3]} \tag{1.11}$$

[2] ⚠ Mass ≠ Weight.

Example:

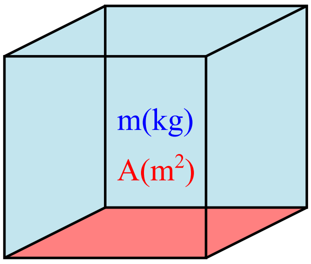
$F^{\mathrm{Earth}}_{\mathrm{gravity}} = 9.81\,\mathrm{m/s^2}$

$F^{\mathrm{Mars}}_{\mathrm{gravity}} = 3.71\,\mathrm{m/s^2}$

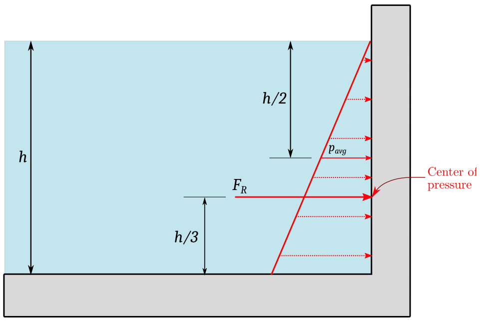
A 1 kg object on Earth will also have a mass of 1 kg on Mars. Such an object will weight 9.81 N on Earth, but only 3.72 N on Mars.

Pressure p: Force applied perpendicular to the surface of an object per unit area over which that force is distributed.

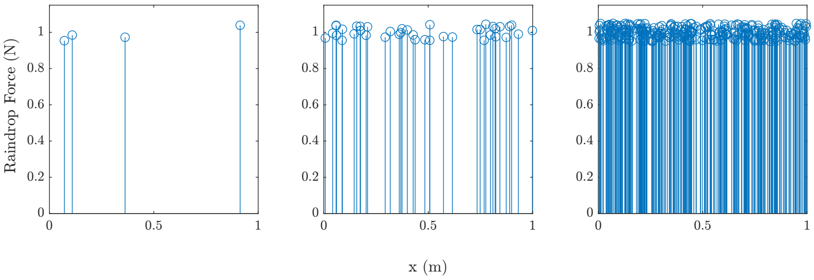
- Solid object: $p = F/A = mg/A$. Units: [Pa] = [N]/[m^2].



- Colum of water: Hydrostatic pressure: $p = \rho g h$.[3] (Associated concept: Pascal's principle, see appendix 1.A of this chapter)



- Gases: Thermodynamic limit: [4]. The gases produce pressure akin to heavy rain pouring on a rooftop.



Temperature T: There is more than meets the eye...

We have discussed the concept of Heat $\underline{Q}$ who corresponds to Energy $\underline{E}$ in transit, but then what does "Temperature" exactly mean? Intuitively, we can assume that a given object with a temperature T_1 is going to have more energy $\underline{E}$ than the same object at a lower T_2 temperature.

A Temperature can therefore define the "intensity of Heat", but this doesn't explain how we can quantitatively define and measure Temperature.

With this said, if we grab a metal bar at ambient temperature, we will feel more cold than if we grab a wooden bar. On the same reasoning, if

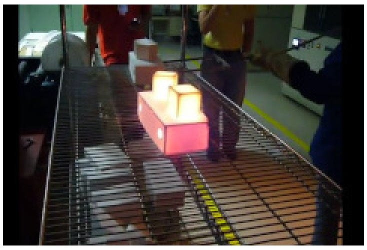
---

[3] with h the height of the column of water above the object

[4] see also *Blundell, "Concepts in Thermal Physics", pp. 4 section 1.2*

we drop the same amount of water/alcohol in our hands, we will feel more cold with alcohol.

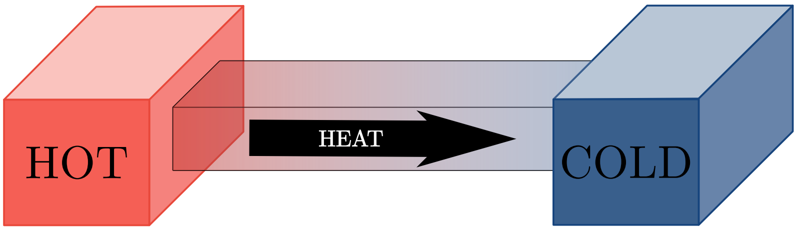
see also video of people grabbing a red hot Space Shuttle tile with their bare hands



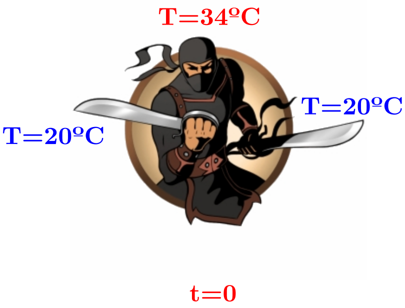
Something is up! Although the examples above are intriguing, we do have thermometers (and very simple ones) which are capable of measuring temperatures...

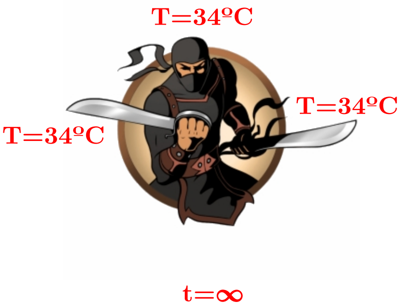
What is happening is that when we grab a metal bar at ambient temperature 20 °C, and with metal being a good heat conductor, the heat from our body (at 34 °C) will flow to the metal bar up and until this one reaches the same temperature as our body. The cold sensation is therefore nothing more than the Heat Q exiting our body!

Heat flows from a hotter to a colder body



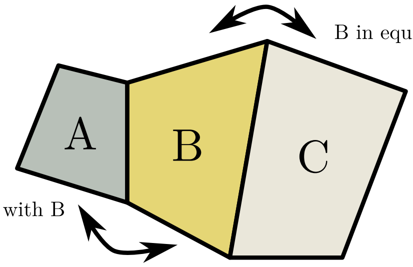
Now if we place another metal bar in our other hand, heat will identically flow from our body towards the metal bar, up and until it reaches our body temperature.





The two metal bars will reach the same temperature, in equilibrium with our body temperature.

This concept stands for the Law 0 of Thermodynamics

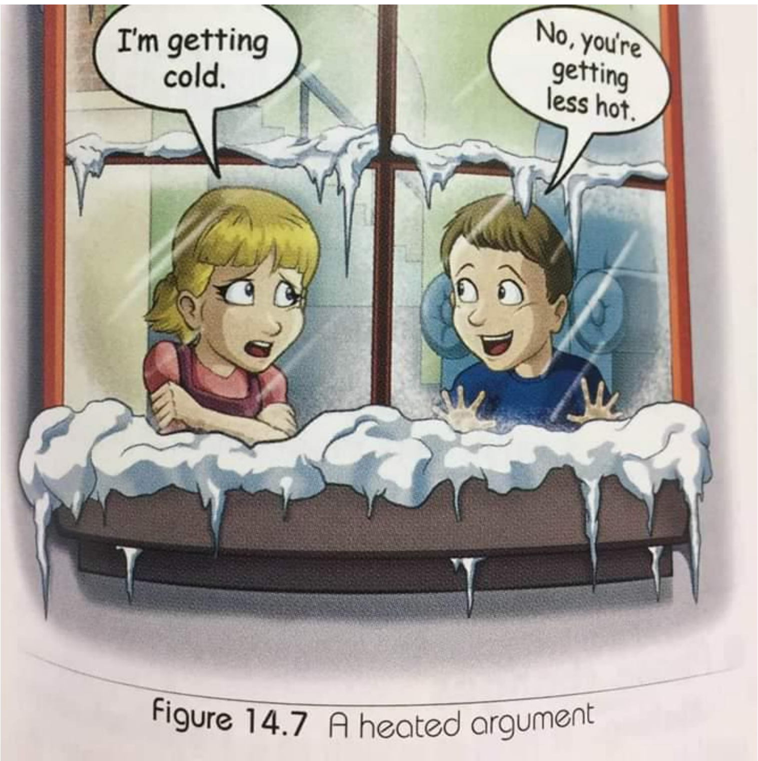


B in equilibrium with C

Therefore A and C are in thermal equilibrium. If they were brought into contact, there would be no net heat transfer.

A in equilibrium with B

Remember: Heat flows from the hotter body towards the colder body, it is NOT cold that moves from the colder body towards the hotter body



1.A Pascal's principle

We may show[5] through a force balance analysis that the hydrostatic pressure for a fluid element is

$$\Delta p = p_2 - p_1 = \rho g \Delta z$$

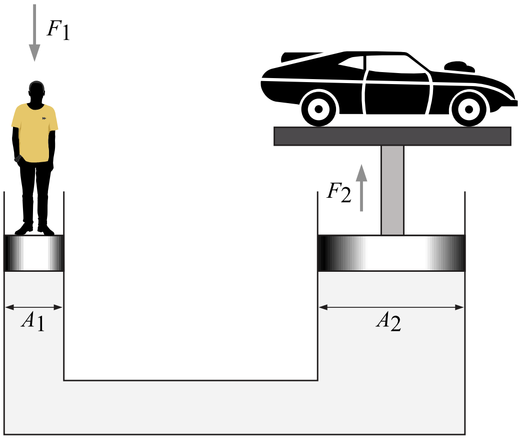
Consequently, pressure in a fluid does not change over the horizontal direction. In the vertical direction, as a consequence of the gravitational pull, the pressure difference between two points is proportional to their vertical distance Δz and the fluid density ρ.[6]

1.A.1 Definition

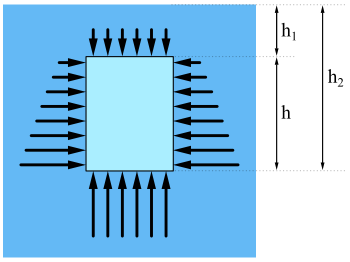
We have shown that pressure in a fluid remains constant in the horizontal direction. We may accordingly state the principle of transmission of fluid pressure, named after Blaise Pascal (1623–1662). It states that:

> *"Pressure applied to an incompressible fluid is transmitted equally to all points in all directions throughout the whole fluid, and that the force due to the pressure acts at right angles to the enclosing walls."*

This principle has very useful engineering applications such as hydraulic jacks, which allow multiplying applied forces (for example if we apply a small force F_1 over a small area A_1, we may retrieve a large force F_2 elsewhere if we put this fluid in contact with a large area A_2 since $p_1 = p2$ and $p = F/A$, which yields $F_1/A_1 = F_2/A_2$.



[5] Demonstration: $\sum F_z = ma_z = 0$ since the flow element is in equilibrium: Accordingly, the force exerted on the bottom of the fluid element is in equilibrium with the force exerted on top of the fluid element plus the gravity force of the fluid element: $p_{\text{down}}\Delta x - p_{\text{top}}\Delta x - \rho g \Delta x \Delta z = 0$, where $W = mg = \Delta x \Delta z$.



[6] Example: For air, which has a density of about 1 kg/m^3, the Δp for a 1 m column height will be negligible (9.8 Pa) whereas the Δp for a 1 m column height of water will be 1,000 times higher (9.8 kPa), since the density of water is 1,000 times higher (about 1000 kg/m^3).

Nomenclature

Variables:

- E: Energy [J]
- Q: Heat [J]
- W: Work [J]
- E_m: Mechanical energy [J]
- K: Kinetic energy [J]
- U: Potential Energy [J]
- F: Force [N]
- t: Time [s]
- l: Length [m]
- x: Position [m]
- v: Velocity [m/s]
- a: Acceleration [m/s^2]
- g: Acceleration of gravity [m/s^2]
- I: Moment of rotational inertia [kg $\cdot$ m^2]
- m: Mass [kg]
- M: Molar Mass [g/mol]
- V: Volume [m^3]
- ρ: Density [kg/m^3]
- p: Pressure [Pa]
- T: Temperature [K]

Constants:

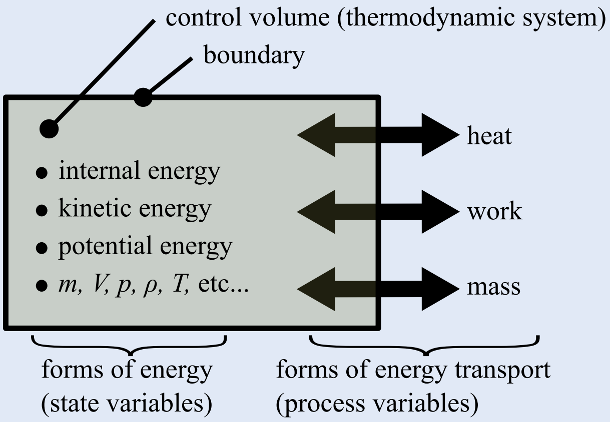
- $N_A = 6.02214076 \times 10^{23}$ [mol^{-1}]: Avogadro Number/Constant

Acronyms, subscripts and superscripts

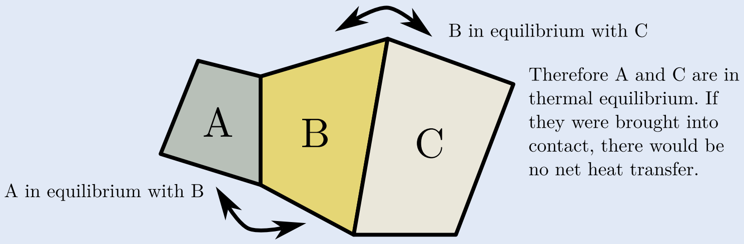
- int: Internal
- kin: Kinetic
- pot: Potential
- $const$: Constant

Chapter Summary

- Heat Q and Work W: Energy U in transit.
- Q: Energy E exchanged between systems in a disordered fashion.
- W: Energy E exchanged between systems in an ordered fashion.
- System Variables:
- Mechanical Energy E_m = Kinetic Energy K + Potential Energy U.
- Mechanical Energy E_m is conserved if the forces are conservative (e.g. no friction, etc...).
- Thermodynamic Equilibrium: System is invariant in time (may be an instantaneous time or a time average).
    - Process variables: Energy transport (+ mass transport for control volumes, discussed in lecture more ahead).
    - State Variables: Define the characteristics of the system.
    - Definitions for m, V (extensive varibles) and p, ρ, T (intensive variables).



- Zero Law of Thermodynamics: If the systems (A–B) and (A–C) are in equilibrium, then systems (B–C) are in equilibrium too.



Recommended readings

- Blundell, "*Concepts in Thermal Physics*", Chapters 1, 2, 3 (partially).
- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*", Chapters 1, 2.1.

Thermodynamics and Culture: Relevant Works

Chapter 1 discusses the universality of the foundations of Thermodynamics, which are equally applicable at large macroscopic scales down to microscopic scales, unlike other disciplines like for example classical mechanics which is only valid at macroscopic scales, or quantum mechanics, only valid at microscopic scales. A relevant literary work is

Jonathan Swift, "*Gulliver Travels*", 1726,

a novel about a man named Gulliver and his voyages to Lilliput (a land populated by tiny people, 15 cm tall on average) and Brobdingnag (a land populated by huge people, over 20 m tall).

Gulliver enjoying a meal on Lilliput

"It was the marvellous imaginary voyages of Lemuel Gulliver which made us see a world of petty six-inch patriots, or of sixty-foot people, large-minded and generous. Dean Swift was not writing science, but he lighted for our minds the meaning of size in our perception and in all human affairs.

In science the scale of things is often decisive. We human beings can view the world from one scale only, our own. But in that world are ants and whales, mountains and seas, planets, stars and atoms. A great deal of their nature is explainable as the consequence of their magnitude, for the fundamental building bricks of all the world, the particles of the physicist, fix a size built somehow into everything material."

Philip Morrison, Physicist, Royal Institution Lectures, 1968

`https://www.rigb.org/explore-science/explore/video/gullivers-travels-world-captain-gulliver-1968`

STATISTICAL PHYSICS

2 Temperature: A Statistical Definition

We have learned from the previous lecture that the concept of Temperature T “is complicated”.

Many textbooks refer to T as the “heat intensity” since we know that a body at high T is “very intense” (or in other terms, we burn ourselves). However, if we touch a body which is very cold instead (say $T = -100\,^{\circ}\mathrm{C}$) we also get burned! We call this *“frostbite”*[1].

To clearly grasp the concept of Temperature, we have no other choice but to “go down the rabbit hole”...

... and land in the microscopic world (either Lilliput, or the world from Alice in Wonderland, as the microscopic world does not follow the same set of rules than our macroscopic world).

To get our bearings in this very special place, we are going to resort to the powerful tool which is **Statistical Physics**...

---

[1] we acknowledge burning as coming from very hot as well as very cold objects as these have “extreme” Temperatures compared to our 34 °C body surface temperature, leading to excessive Heat transfer Q in one or another direction

... a Powerful, yet **Dangerous** tool!

Perhaps it would be wise to approach the subject cautiously...

In preparation of our trip to the microscopic world, lets (re-)introduce the binomial distribution (which the student has probably already been induced to in a more detailed and rigorous fashion in the probability and statistics unit).

The binomial distribution corresponds to the probability of obtaining a given outcome by performing a series of tests to which there are only two possible results.

The example of the repeated tossing of a coin in the air N times (which we will use more ahead), and the analysis for the odds of having x outcomes of heads/tails, is obtained utilizing the binomial distribution[2]:

$$P(x) = \left(\begin{array}{c} N \\ x \end{array} \right) p^x q^{(N-x)} = \frac{N!}{(N-x)!x!} p^x q^{(N-x)}. \tag{2.1}$$

Here the term $\left(\begin{array}{c} N \\ x \end{array} \right) = \frac{N!}{(N-x)!x!}$ corresponds to all the possible combinations of heads/tails tosses.

For the case of equivalent outcome probabilities $p = q = 1/2$ such as a coin toss, we have $p^x q^{(N-x)} = p^N$.

This particular case was studied by Blaise Pascal (1623–1662), who provided tabulated values of the corresponding binomial coefficients in what is now recognised as "Pascal's Triangle". A ludical/pedagogical

[2] reminder: $N! = N \times (N-1) \times (N-2) \times \ldots \times 2 \times 1$

for large N one may use the Stirling approximation

$N! \sim N^N e^{-N} \sqrt{2\pi N}$,
or its slightly less accurate version $\ln(N!) \sim N \ln(N) - N$

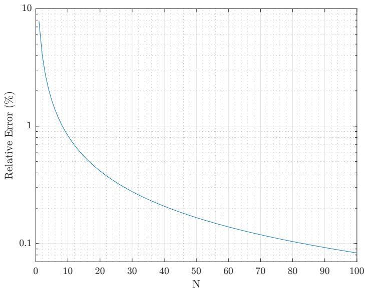


Figure 2.1: Error plot (in %) for the Stirling approximation, as a function of N.

illustration of the binomial distribution is the Galton board, devised in 1873.[3]

Some mathematical terms for the binomial distribution are:

- Average: $\mu = E(x) = Np$.
- Variance: $\sigma^2 = Np(1-p)$
- Standard Deviation: $\sigma = \sqrt{Np(1-p)}$

In physics the binomial distribution is applied to many relevant cases. This will also apply to the object of our study (Thermodynamics).

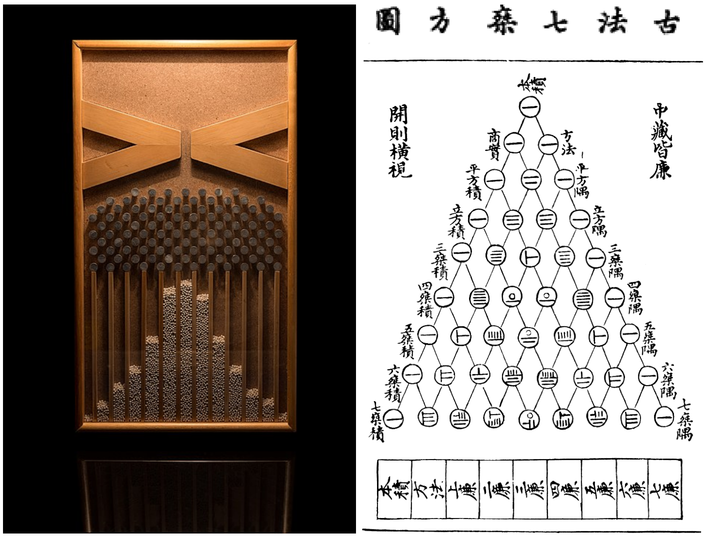
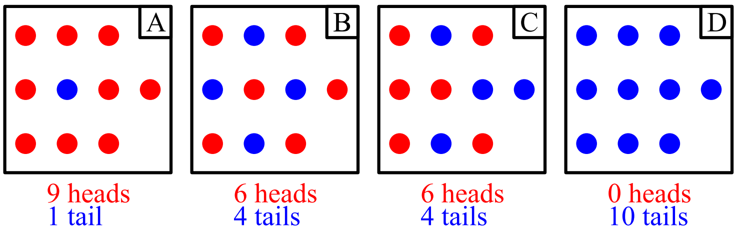


Figure 2.2: Left: Galton board. **Right:** Knowledge of Pascal's triangle has also been shown to have existed in China centuries before Pascal. Drawing of Pascal's Triangle published in C.E.1303 by Zhu Shijie. It was called Jia Xian triangle or Yanghui Triangle by the Chinese, after the mathematician Jia Xian & Yang Hui.

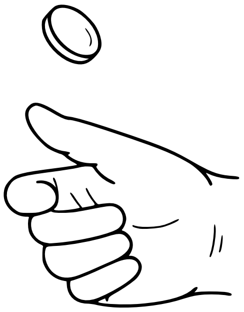
2.1 Microstates, Macrostates, Canonical Ensembles, Boltzmann distribution, and a statistical definition of Temperature

Let's go back to our coin-tossing exercise.

We toss 100 coins on a table. A few will randomly land as heads, other as tails. Let us examine the possible combinations (here we will just draw 10 coins for the sake of simplicity), representing heads as red and tails as blue.



(there are obviously plenty more combinations possible)



This chapter part is adapted from Blundell, "*Concepts in Thermal Physics*", 2nd Ed., Part 1, Chap. 4, pp. 35–45).

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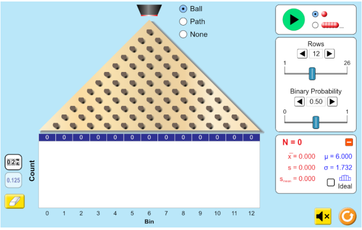
[3] See the online Galton board simulation (link in text & image)



Each of the boxes (A, B, C, D, ...) is an unique state which is labelled a **microstate**.

However we may notice a particular case presented by states/boxes $\boxed{\text{B}}$ and $\boxed{\text{C}}$ which both have 6 heads and 4 tails. If we ignore the spatial arrangement of the coins and only consider if they are showing heads or tails, then states $\boxed{\text{B}}$ and $\boxed{\text{C}}$ are indistinguishable and are combined into an unique **macrostate**.

Coming back to our 100-coin tossing example, we have $2^{100} \simeq 1.2677\times10^{30}$ possible box arrangements (or in other terms 1.2677×10^{30} **microstates**), but only 100 possibilities of N heads and $N - 100$ tails (or in other terms 100 **macrostates**), whose odds follow a binomial distribution.

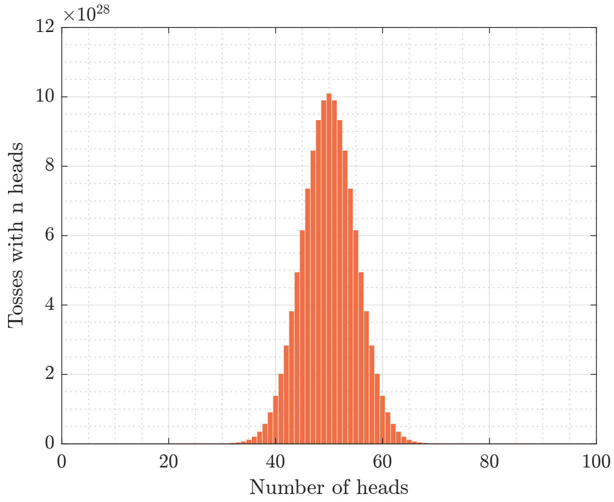


Figure 2.3: Number of heads obtained for $2^{100} \simeq 1.2677 \times 10^{30}$ coin tosses

Now we move from our macroscopic world to the microscopic world proper.

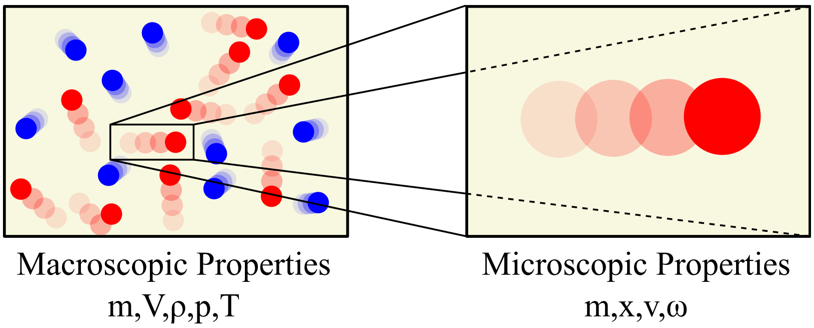
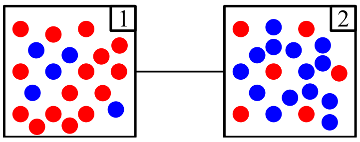
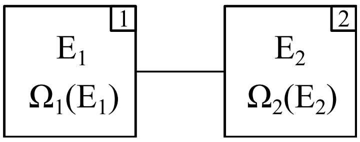


Figure 2.4: Left: Macroscopic properties: Mass m, Volume V, Density ρ, Pressure p, Temperature T. Right: Microscopic properties: Mass m, Position x, Velocity v, Angular Velocity ω

2.1.1 A statistical definition of Temperature

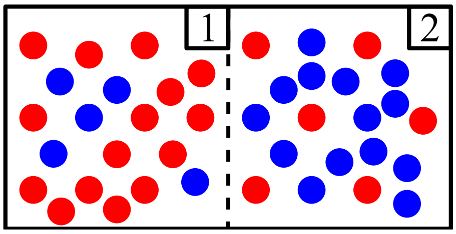
Let us now consider two systems with coins/particles. Keeping our heads/tails analogy, we will consider that the coin/particle with the state heads has a larger energy than the state tails. Inside each box, the coins are constantly flipping between heads/tails, but with the overal ratio of heads/tails constant (energy is conserved).





Box $\boxed{1}$ and box $\boxed{2}$ have quantified and constant Energies E_1 and E_2, respectively. They also have a certain amount of microstates $\Omega_1(E_1)$ and $\Omega_2(E_2)$.

We now join the boxes:

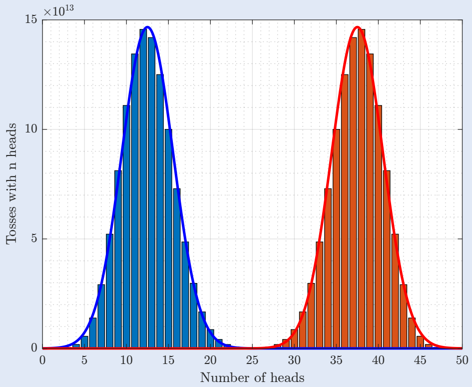


This larger ensemble will have an energy $E = E_1 + E_2$. However this system also has much more accessible microstates, each with the same probability of occurring.

The system will occupy all the possible microstates, remaining the same amount of time in each of them. This is called the **ergodic hypothesis**.

Macroscopically, the most probable state inside the new box will be the macrostate that encompasses the larger number of microstates.

Example: Sum of two independent binomial distributions
Let us now "cheat" a little bit in our coin toss exercise and procure two "biased" coins: one which is "biased" towards heads, yielding heads 3 tosses out of 4, and one which is "biased" towards tails, only yielding heads 1 toss out of 4. We sequencially toss each coin 50 times and report the overall outcomes (e.g. how much times we got heads and tails during the 50+50 coin toss exercise).



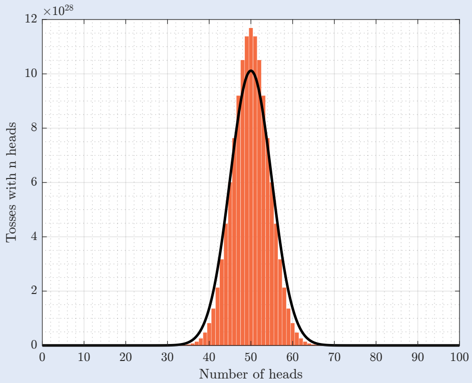
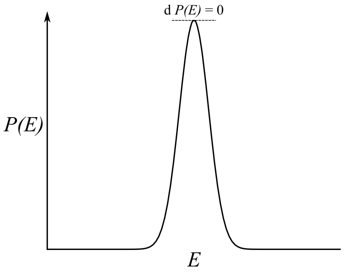


Figure 2.5: Individual probability distribution functions for the 50 coin tosses with a bias towards heads (red) and the 50 coin tosses with a bias towards tails (blue) (top) and compounded probability distribution function for the sum of the two coin toss events (orange) with a binomial distribution for an unbiased ($p = 1/2$) 100 coin toss exercise displayed for comparison purposes.

The energy (in this example assimilated to the number of heads vs. tails where we arbitrarily assume that heads (red) have are high energy states and tails (blue) are low energy states) is in the middle (with $N = 50$ being the most probable outcome), as would be expected since the two sequencial coin tossing exercises had opposite bias towards heads and tails. One may also note that the maximum number of idential microstates has increased dramatically, from $2^{50} \simeq 1.1259 \times 10^{15}$ to $2^{100} \simeq 1.2677 \times 10^{30}$.

Note that the convolution of the two binomial distributions would only be a binomial distribution itself in case both would have the same probability p which is not the case, and hence this result is to be expected. One may intuitively understand this outcome if we consider the more extreme case of 50 coin tosses with a coin fully biased to heads ($p = 1$), followed by 50 coin tosses with a coin fully biased to tails ($p = 0$). One would *always* retrieve 50 heads and 50 tails at the end of the exercise and the probability distribution function would be the shape of a dirac with $P(N = 50) = 1$ and $P(N \neq= 50) = 0$

We will now mathematically determine the most probable macrostate.



If we consider the macrostates as in the binomial distribution (see Fig. 2.3) and we consider the function to be continuous, the maximum of the function will correspond to its zero derivative:

$$\frac{d}{dE_1}[\Omega_1(E_1)\Omega_2(E_2)] = 0 \tag{2.2}$$

We now differentiate the product $(fq)' = fg' + f'g$:

$$\Omega_2(E_2)\frac{d\Omega_1(E_1)}{dE_1} + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1} = 0$$

Since $E = E_1 + E_2 =$ constant we have $dE_1 = -dE_2$ and:

$$\frac{dE_2}{dE_1} = -1 \tag{2.3}$$

We now simplify Eq. 2.2 using Eq. 2.3:

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dE_1} - \frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2} = 0. \tag{2.4}$$

Since $1/x\mathrm{d}x = \mathrm{d}ln(x)$ we have

$$\frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2}, \tag{2.5}$$

the condition which defines the most probable division of energy between two systems which are able to exchange energy. We also have by definition $T_1 = T_2$ since the two systems exchange energy and achieve an identical temperature[4]. If we define a constant k_B (the meaning of we will explain later on), we may simplify the above expression to

$$\frac{1}{k_B T_1} = \frac{1}{k_B T_2}.$$

If we further consider Eq. 2.4 we can write:

$$\boxed{\beta\left\{\frac{1}{k_B T_1} = \frac{d\ln\Omega}{dE}\right.} \tag{2.6}$$

which provides us with a clear physical meaning of Temperature.

(well, not really. Yet, although it may sound confusing now, it will make sense soon enough! Meanwhile, we need a few more definitions...)

2.1.2 The Boltzmann distribution

We define:

- **The Micro-canonical ensemble:** Statistical ensemble of systems with the same fixed energy.
- **The Canonical ensemble:** Statistical ensemble of systems which can all exchange energy with a large reservoir of heat.
- **The Grand Canonical ensemble:** Statistical ensemble of systems which can all exchange energy and particles with a large reservoir.

We will now introduce the **Boltzmann distribution** definition:

The probability for a canonical system having an energy ϵ is given by the Boltzmann distribution:

$$\boxed{P(\epsilon) \propto \exp\left(-\epsilon/k_B T\right),} \tag{2.7}$$

with $\beta = 1/k_B T$ (see Eq. 2.6).

In this chapter, we will derive this distribution in an intuitive fashion, playing a little game. The corresponding mathematical demonstration is also presented next below.

Note to instructors: Play the game of an Karl–Marx-to-Boltzmann distribution on the board, and run the corresponding Matlab/Python simulation. See Appendix E.1 for the script printout.

[4] remember the two-swords ninja from lecture 1b

Derivation of the Boltzmann distribution:

We will make use of a few simplifying assumptions:

- Each allowed energy of the system contains only a single microstate ($\Omega = 1$).
- The total Energy of the system & reservoir is E, with ϵ the energy of the system and $E - \epsilon$ the energy of the reservoir.

The probability $P(\epsilon)$ that the system has energy epsilon ϵ is proportional to the product of microstates accessible to the reservoir and the system:

$$P(\epsilon) \propto \Omega(E - \epsilon) \times 1 \tag{2.8}$$

Taking Eq. 2.6, and considering that $\epsilon \ll E$, we may perform a Taylor expansion of $\ln \Omega(E - \epsilon)$ around $\epsilon = 0$, such that

$$\ln \Omega(E - \epsilon) = \ln \Omega(E) - \frac{d \ln \Omega(E)}{dE}\epsilon + \cdots ,$$

Substituting Eq. 2.6 into the equation above we have

$$\ln \Omega(E - \epsilon) = \ln \Omega(E) - \frac{\epsilon}{k_B T}, \tag{2.9}$$

where T is the Temperature of the reservoir.
Higher-order terms of the Taylor expansion may be neglected (see Exercise 4.4 in Blundell)

$$\frac{d^2 \ln \Omega(E)}{dE^2}\epsilon^2 \ll \frac{d \ln \Omega(E)}{dE}\epsilon,$$

and Eq. 2.9 becomes

$$\Omega(E - \epsilon) = \Omega(E) \exp\left(-\epsilon / k_B T\right).$$

Considering Eq. 2.8 we can derive the probability distribution describing the system, given by

$$P(\epsilon) \propto \exp\left(-\epsilon / k_B T\right) \tag{2.10}$$

2.2 The Maxwell–Boltzmann distribution

Let us now apply the Boltzmann distribution to the movement of a particle[5]:

We first consider that the particle moves at a velocity v and has the corresponding kinetic energy $E = 1/2mv^2$.

We may decompose the velocity onto its different components such as $v^2 = v_x^2 + v_y^2 + v_z^2$ (Pythagorean theorem), and we may accordingly write:

$$E = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

We will now apply Boltzmann's equation to each of the components for the velocity, starting with v_x.

[5] The term "particle" refers to gaseous particles only (atoms or molecules) in this context

As the velocity is directly correlated with the energy, we have

$$P(\epsilon) \propto \mathrm{e}^{-\beta\epsilon}$$

For the coordinate x we have $E_x = \frac{1}{2}mv_x^2$ and we also have $\beta = 1/k_BT$.

If we substitute $(\underline{\epsilon}, \underline{\beta})$ by $(\underline{E_x}, \underline{1/k_BT})$, respectively, we then have:

$$P(E_x) \propto \exp\left(-\frac{mv_x^2}{2k_BT}\right)$$

Since a particle with the energy E_x will have the corresponding velocity $g(x)$ we may write

$$g(v_x) \propto \exp\left(-\frac{mv_x^2}{2k_BT}\right)$$

We now normalize the expression above using the Gaussian Integral (see appendix A.2, eq. A.3), with $\alpha = m/2k_BT$:

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}$$

and we now may write exactly:

$$g(v_x) = \sqrt{\frac{m}{2\pi k_BT}} \exp\left(-\frac{mv_x^2}{2k_BT}\right) \tag{2.11}$$

with $\sqrt{\frac{m}{2\pi k_BT}}$ the normalization function.

We may naturally proceed in an equal fashion for the functions $g(v_y)$ and $g(v_z)$.

Let us now determine the fractions of particles with velocities comprised between (v_x, v_y, v_z) and $(v_x + \mathrm{d}v_x, v_y + \mathrm{d}v_y, v_z + \mathrm{d}v_z)$,[6] using $g(v_{x,y,z}) \propto \exp\left(-\frac{mv_{x,y,z}^2}{2k_BT}\right)$.

We may write (considering $v^2 = v_x^2 + v_y^2 + v_z^2$):

$$\begin{aligned}
&g(v_x)\mathrm{d}v_x g(v_y)\mathrm{d}v_y g(v_z)\mathrm{d}v_z \\
&\qquad \propto \exp\left(-\frac{mv_x^2}{2k_BT}\right)\mathrm{d}v_x \exp\left(-\frac{mv_y^2}{2k_BT}\right)\mathrm{d}v_y \exp\left(-\frac{mv_z^2}{2k_BT}\right)\mathrm{d}v_z \\
&\qquad \propto \exp\left(-\frac{mv^2}{2k_BT}\right)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z
\end{aligned}$$

Let us now replace $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ by $\mathrm{d}v$. We may do so through the representation of the 3D velocity space as a sphere. In such a representation, $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ corresponds to an "onion peel" of the sphere's exterior.

[6] This will correspond to the product of the fractions of particles in each sub-dimension velocity space $g(v_i)\mathrm{d}v_i$, with $i = (x, y, z)$

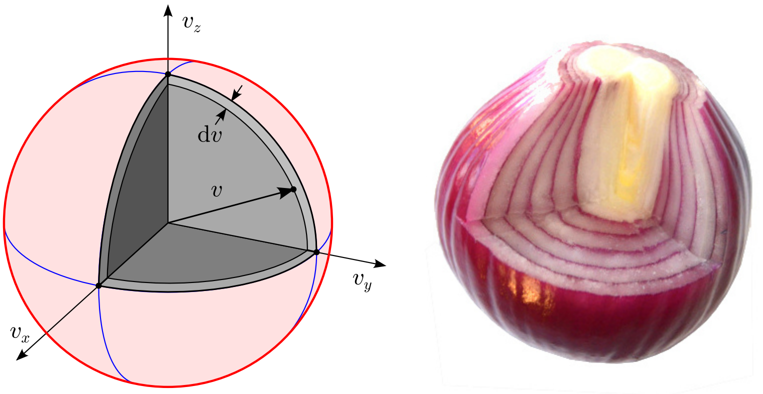


Figure 2.6: Left: Velocity space; Right: Onion peel

This volume may be written as:

$$\begin{aligned}V &= \frac{4}{3}\pi(v+dv)^3 - \frac{4}{3}\pi(v)^3\\ &= \frac{4}{3}\pi\left[(v+dv)^3 - v^3\right]\\ &\langle \text{expansion of } (v+dv)^3 \rangle\\ &= 4\pi\left[v^2dv + 3vdv^2 + \frac{dv^3}{3}\right]\end{aligned}$$

We now may resort to infinitesimal approximations, as d$v \longrightarrow 0$, we have d$v \gg$ d$v^2 \gg$ dv^3, and we may ignore the two last terms:

$$V = 4\pi v^2 \mathrm{d}v, \tag{2.12}$$

and

$$\mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z = 4\pi v^2 \mathrm{d}v.$$

If we now absorb the constant 4π in the proportionality coefficient, we have:

$$f(v)\mathrm{d}v \propto v^2 \mathrm{d}v \exp\left(-\frac{mv^2}{2k_BT}\right), \tag{2.13}$$

where $f(v)$dv corresponds to the fraction of particles with velocities comprised between v and v + dv.

We again normalize this function using the integral (see appendix A.2, eq. A.9):

$$\int_{-\infty}^{+\infty} x^2 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}$$

and we may again write exactly:

$$\boxed{f(v)\mathrm{d}v = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right)\mathrm{d}v} \tag{2.14}$$

with $\frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}$ the normalization function.

Eq. 2.14 corresponds to the **Maxwell–Boltzmann** distribution, which correlates Temperature T and the Velocity Distribution $f(v)dv$ of a gas.

We see that the velocity distribution function of a gas will depend not only on the particles Mass m, but also the factor $k_BT = 1/\beta$ which was previously introduced and corresponds to a measure of the system energy.

If we define several values for k_BT, the corresponding function $f(v)$ will have the following shapes:

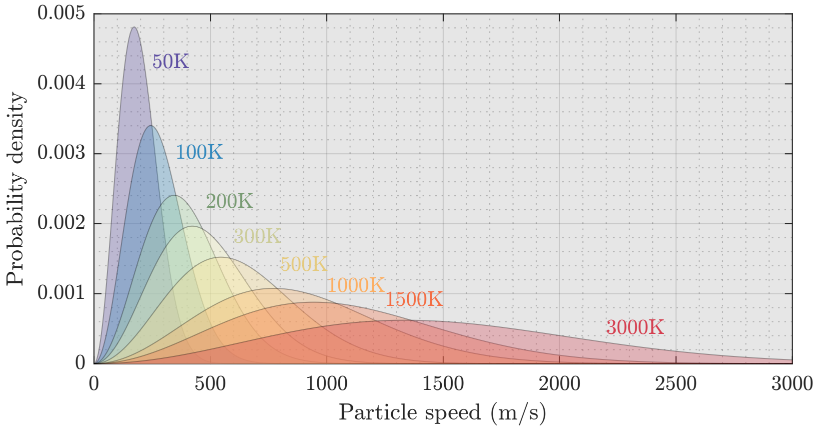


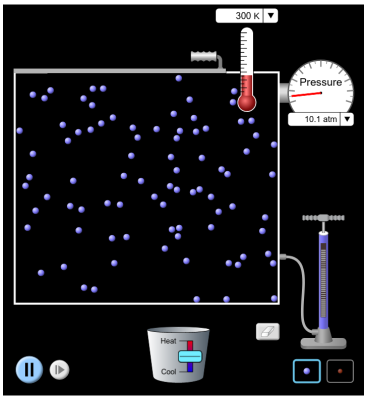
Figure 2.7: Sample Maxwell–Boltzmann distributions

with $\beta_1 > \beta_2 > \beta_3$ (or $T_1 < T_2 < T_3$).

Why is the probability of having a particle with zero velocity zero? Several reasonings:

- Mathematically-speaking, this is because the integral of Eq. 2.12 tends to 0 as $v \longrightarrow 0$.
- One may also superpose funtions $g(v_x)$ and $g(v_y)$ in a 2D space. Even if the probability of having v_x is maximal, the probability of having $v_y = 0$ at the same time is infinitesimally small.
- We may reason in terms of macrostates and microstates: if we sample the space of velocities v_x as [0, 1, 2, ...] and do so also for v_y and v_z we see that there is only one microstate for $v = 0$, whereas the number of possible microstates for increasing velocities increases exponentially.
- Still not convinced? Try colliding two moving balls and have one of them fully stop post-collision...

See the online simulation of a gas as a collection of small hard-sphere particles colliding with each other (link in text & image)



2.2.1 A few useful properties of the Maxwell-Boltzmann distribution

- **Most probable velocity:** $v_p \Rightarrow \dfrac{\mathrm{d}f(v)}{\mathrm{d}v} = 0$

$$\frac{\mathrm{d}f(v)}{\mathrm{d}v} = -8\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v \left(\frac{mv^2}{k_B T} - 1\right) \exp\left(\frac{-mv^2}{2k_B T}\right) = 0$$

which admits the solution: $\frac{mv^2}{k_BT} = 1$.

$$\boxed{v_p = \sqrt{\frac{2k_BT}{m}}} \tag{2.15}$$

- **Average velocity:** $\langle v \rangle = \int_0^{+\infty} v f(v)\mathrm{d}v$. If we hold $b = \frac{m}{2k_BT}$;

and we again consider the analytical integral (see appendix A.2, eq. A.13):

$$\int_{-\infty}^{+\infty} x^3 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2\alpha^2}$$

We obtain:

$$\begin{aligned} \langle v \rangle &= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \int_0^{+\infty} v^3 \mathrm{e}^{-bv^2} \mathrm{d}v \\ &= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \frac{1}{2b^2} = \sqrt{\frac{4}{\pi b}} = \sqrt{\frac{8k_BT}{\pi m}} \end{aligned}$$

$$\boxed{\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}}} \tag{2.16}$$

- **Average quadratic velocity:** $v_{rms} = \sqrt{\langle v^2 \rangle} = \left[\int_0^{+\infty} v^2 f(v) \mathrm{d}v\right]^{1/2}$.
  Holding again $b = \frac{m}{2k_BT}$;
  and again considering the analytical integral (see appendix A.2, eq. A.10):

$$\int_{-\infty}^{+\infty} x^4 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}}$$

We obtain:

$$\begin{aligned} \sqrt{\langle v^2 \rangle} &= \left[4\pi \left(\frac{b}{\pi}\right)^{3/2} \int_0^{+\infty} v^4 \mathrm{e}^{-bv^2} \mathrm{d}v\right]^{1/2} \\ &= \left[4\pi \left(\frac{b}{\pi}\right)^{3/2} \frac{3}{8}\sqrt{\frac{\pi}{b^5}}\right]^{1/2} = \sqrt{\frac{3}{2b}} = \sqrt{\frac{3k_BT}{m}} \end{aligned}$$

$$\boxed{v_{rms} = \sqrt{\frac{3k_BT}{m}}} \tag{2.17}$$

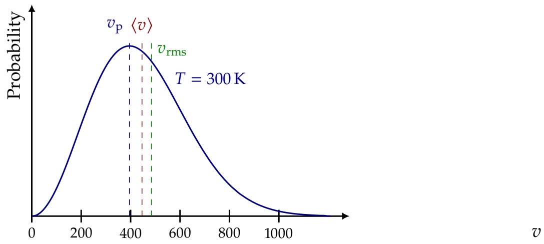


Figure 2.8: v_p, $\langle v \rangle$ and v_{rms} for a Maxwell–Boltzmann distribution of O_2 at T = 300 K

Nomenclature

Variables:

- n: Number of coin tosses
- x: Number of coin heads outcomes
- p: Probability for an outcome
- μ: Probability average
- σ: Probability standard deviation
- σ^2: Probability variance

- E: Energy of a system (macroscopic energy) [J]
- ϵ: Energy of a particle (microscopic energy) [J]
- Ω: Microstate
- T: Temperature [K]
- β: $\beta = 1/k_B T$

- m: Mass [kg]
- v: Velocity [m/s]
- $\langle v \rangle$: Average velocity for a set of particles [m/s]

Constants:

- k_B: Some constant yet to be defined

Acronyms, subscripts and superscripts

- x: x coordinate [m]
- y: y coordinate [m]
- z: z coordinate [m]
- rms: Root mean square

Chapter Summary

- Definition of Macrostates and microstates, definition of binomial distribution.
- Boltzmann distribution for the occupation probability of the different energy states of a system.

$$P(\epsilon_i) \propto exp(-\epsilon_i/k_B T)$$

- Maxwell-Boltzmann distribution for the particle velocities with an average energy $< E >$; Statistical definition of temperature T.

$$f(v)\mathrm{d}v = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right)\mathrm{d}v$$

Recommended readings

- Blundell, “*Concepts in Thermal Physics*”, Chapters 4–5

Thermodynamics and Culture: Relevant Works

Chapter 2 discusses the motion of gas particles at microscopic level. The movements of individual particles are seemingly chaotic, and there aree too many particles for one to be able to describe the movements of all particles using discrete equations of motion. A statistical analysis is required, which then yields meaningful averaged properties for these chaotic movements when particles are observed individually. It may seem at first sight disconcerting that structure and rules may arise from such chaotic movements, and as such a very relevant literary work is

Lewis Carroll, "*Alice Adventures in Wonderland*", 1865,

a novel about Alice, a young girl who, while falling asleep outside on a golden afternoon, sees a white rabbit and follows it into a rabbit hole. When she falls down the rabbit hole, she begins her fantastical adventures in Wonderland.

Her adventures include distortions of time and proportion. Throughout the story she shrinks and grows repeatedly as she meets characters of all kinds and sizes, including the Caterpillar who asks *"Who are you?"* and Cheshire Cat who asks her *"Where do you want to go?"*

Alice in Wonderland, digital painting by Daniel Revoy, 2010. see `https://simple.wikipedia.org/wiki/File:Alice-in-Wonderland_by-David-Revoy_2010-07-21.jpg`

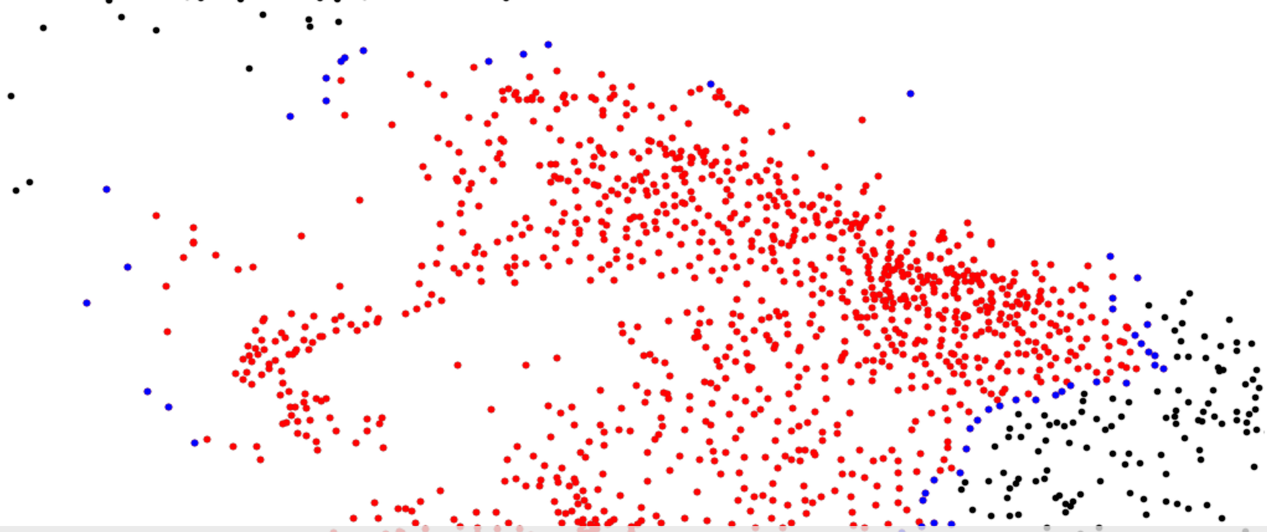
All the worlds/universes, real or imaginary, macroscopic or microscopic, are governed by a set of rules/laws. These may make sense to the observer or not, but they do exist and should be observed at all times!

"Alice's Wonderland is a place where the only rule is that the rules will keep changing. One offering makes you larger, another makes you small; it's always teatime because there's no time; and the rabbit, with his broken watch, is always late. The rules of Wonderland fail to offer what is so beloved about rules, which is the increase of what Daston terms the "radius of predictability." This may not be equivalent to the good. But the predictable is as much a human need as are ruptures from the predictable."

Rivka Galchen, The New Yorker, 6th July 2022.

`https://www.newyorker.com/science/elements/why-do-we-obey-rules`

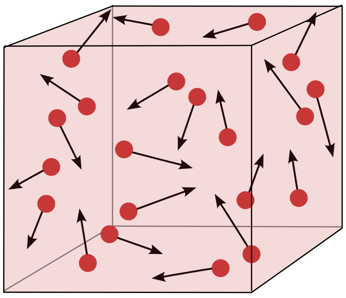
"Down the Rabbit Hole" is nowadays a synonym of *"ending up in a strange place"*. On the 1999 movie **"The Matrix"**, Morpheus gifts Neo the **red pill** and adds: *"You stay in Wonderland, and I show you how deep the rabbit hole goes."*



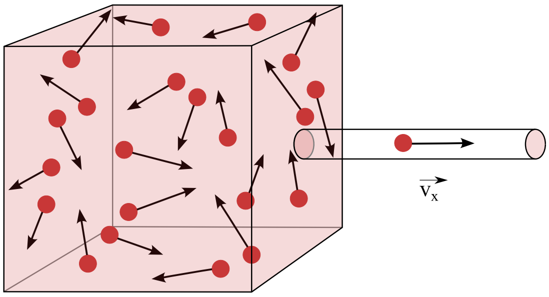
3 Statistical Physics of Solids, Liquids, and Gases

3.1 The Equipartition theorem

In the previous class, we have determine that the particles moving in a box with a given energy E, follow a Maxwell–Boltzmann distribution, randomly moving in a 3D space.



Let us now constrain a particle in a small corridor, effectively rendering its movement **one-dimensional**. This corridor is connected to the aforementioned particle reservoir with a total energy E much larger than the energy of the individual particle:



Let us also assume that this particle remains confined to this tube, colliding at its border with the volume of energy E. The particles of this volume will randomly collide with ths particle, randomly adding/subtracting energy to it.

After a given amount of time, the average energy $\langle \epsilon \rangle$ of the particle will be in equilibrium with the average energy of the particles in the volume $\langle E \rangle$.

We may accordingly determine this value of $\langle \epsilon \rangle$: The average velocity of the particle will be $\langle v_x \rangle$ and its kinetic energy $\epsilon = 1/2mv_x^2$.

The probability for the particle having a given energy ϵ_i is given by the Boltzmann distribution (using $\beta = 1/k_B T$):

$$P(\epsilon) \propto \exp(-\beta\epsilon) = \exp\left(-\frac{1/2mv_x^2}{k_B T}\right)$$

We now normalize this probability[1]:

$$P(\epsilon) = \frac{\exp\left(-\frac{1/2mv_x^2}{k_B T}\right)}{\int_{-\infty}^{+\infty} \exp\left(-\frac{1/2mv_x^2}{k_B T}\right) \mathrm{d}v_x}$$

The average energy $\langle E \rangle$ is by definition:

$$\begin{aligned}\langle \epsilon \rangle &= \int_{-\infty}^{+\infty} \epsilon P(v_x) \mathrm{d}v_x \\ &= \frac{\int_{-\infty}^{+\infty} 1/2mv_x^2 \exp\left(-\frac{1/2mv_x^2}{k_B T}\right) \mathrm{d}v_x}{\int_{-\infty}^{+\infty} \exp\left(-\frac{1/2mv_x^2}{k_B T}\right) \mathrm{d}v_x}\end{aligned}$$

’ Defining $a = 1/2m$ and $b = m/2k_B T$, and using two of the integrals introduced in chapter 2:[2]

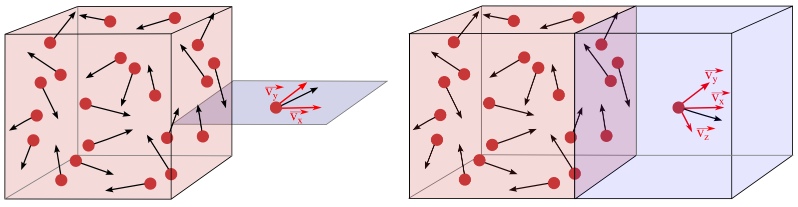
$$\begin{aligned}\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x &= \sqrt{\frac{\pi}{\alpha}} \\ \int_{-\infty}^{+\infty} x^2 \mathrm{e}^{-\alpha x^2} \mathrm{d}x &= \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}},\end{aligned}$$

we may write

$$\begin{aligned}\langle \epsilon \rangle &= \frac{\int_{-\infty}^{+\infty} a v_x^2 \exp\left(-b v_x^2\right) \mathrm{d}v_x}{\exp\left(-b v_x^2\right)} \\ &= \frac{a/2\sqrt{\pi/b^3}}{\pi/b} = \frac{a/2}{\sqrt{b^2}} = \boxed{\frac{1}{2} k_B T}\end{aligned}$$

The **average energy** of a particle with **one** degree of freedom is **$\frac{1}{2} k_B T$**.

We may extend this result to other degrees of freedom:



(a) 2 degrees of freedom: x, y
$\langle \epsilon \rangle = \frac{2}{2} k_B T$

(b) 3 degrees of freedom: x, y, z
$\langle \epsilon \rangle = \frac{3}{2} k_B T$

[1] we consider the intervals $[-\infty \leftrightarrow +\infty]$ for v_x as it can have a negative value in this system of coordinates (in other terms the particle might be travelling left or right)

[2] See also appendix A.2, eqs. A.3 and A.7)

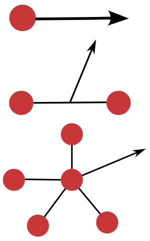
This defines the **Equipartition Theorem**

The energy of a classical system with N degrees of freedom, in contact with a reservoir at Temperature T, is $E = N \times \frac{1}{2} k_B T$

3.1.1 Applications for the Equipartition Theorem

There are different kinds of gases:

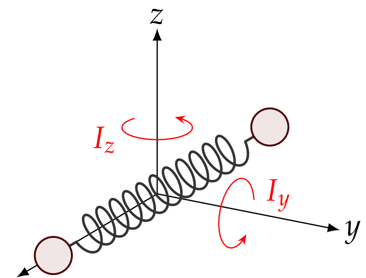
- Atomic (ex: He, Ar, Kr, ...)
- Diatomic (ex: N_2, O_2, CO, ...)
- Polyatomic (ex: CH_4, O_2, H_2O, ...)



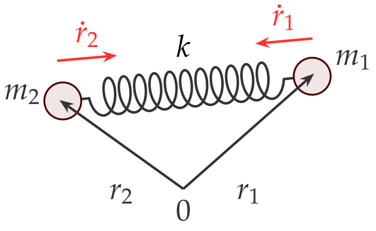
All gaseous species have **3 translational** (x, y, z) degrees of freedom.

Diatomic and **Polyatomic** molecules have additional degrees of freedom: **Rotation** and **Vibration**[3]

Example for a diatomic molecule fully excited rotationally and vibrationally:



Rotational motion



Vibrational motion

The total energy for the molecule is:

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{1}{2} \mu (\dot{r}_1 - \dot{r}_2) + \frac{1}{2} k (r_1 - r_2) \quad (3.1)$$

and its average energy:

$$\langle E \rangle = (3 + 2 + 2) \times \frac{1}{2} k_B T = \frac{7}{2} k_B T, \quad (3.2)$$

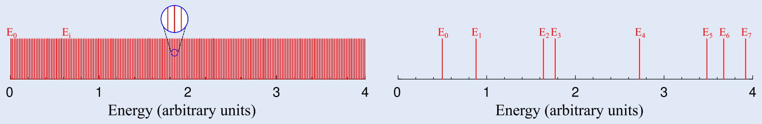
(since the equipartition theorem only cares about the number of modes in the system)

A walk on the wild side, some more "quantum things", and how there's more than meets the eye:

The so-called "Quantum revolution" was initiated around 1905, when it was first acknowledged by Einstein (following the ground-lying

[3] There are additional degrees of freedom associated to the electron cloud of the chemical species but these are "quantum things" that only apply at very high temperatures, and which we will leave "untouched" in the scope of this textbook.

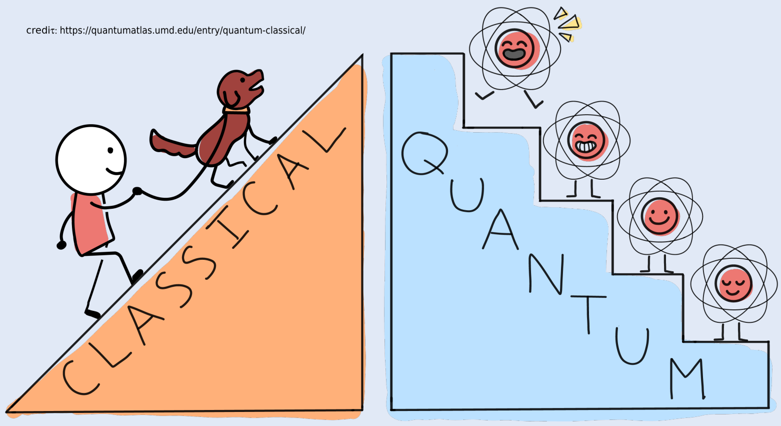
work of Planck) that the energy states of a particle are quantified, which means that particles (in fact any body) jump from a state to another by discrete jumps instead of a continuum.



Continuum states
Classical Mechanics

Discrete states
Quantum Mechanics

credit: https://quantumatlas.umd.edu/entry/quantum-classical/



The microscopic quantum world is hidden from us living at the macroscopic level, since typical energy jumps are of the order of magnitude of 5×10^{-23} J for jumps between adjacent rotational levels, and 5×10^{-20} J for jumps between adjacent vibrational levels. However, at the microscopic level, the energy transferred by a particle during a collision with another one is of this order of magnitude: $E = \frac{N}{2} k_B T$ (with $N = -3 - 7$). For low enough Temperatures T, this energy exchange becomes too low to trigger a quantum jump.

⇒ it stems from the above that a minimum temperature is required to excite the rotational and vibrational modes of a molecule (typically 2–90 K for rotation and 3,000–6000 K for vibration - Note: We will see more ahead that 0 °C=273.15 K)

Figures 3.3 and 3.4 show the temperature dependence of the energy capacity for the N_2 and O_2 molecules, respectively. We transition from molecules wich are only capable of moving in the 3D coordinates with an average energy $\langle E \rangle = 3/2 k_B T$ up to $2 - 100$ K, after which rotational motion is unfrozen, with the average energy becoming $\langle E \rangle = 5/2 k_B T$. Then, around $1500 - 5000$ K, vibrational motion is also frozen, with the average energy becoming $\langle E \rangle = 7/2 k_B T$
We may note that the rotational and vibrational modes are excited at different critical temperatures, depending on the molecule. This is because the atomic masses and electronic configurations differ for both molecules (the latest being particularly important for the vibrational excitation temperature).

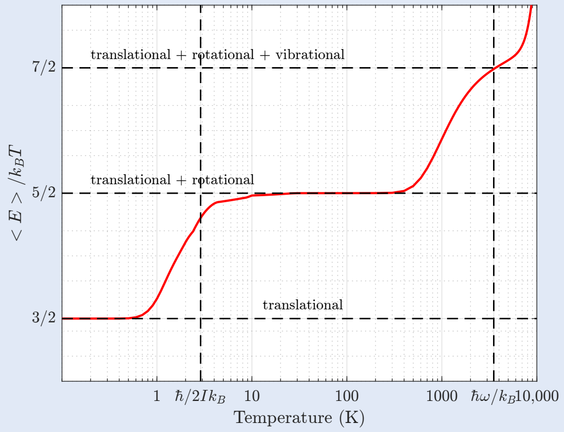


Figure 3.3: Temperature-dependent Average energy for molecular nitrogen N_2

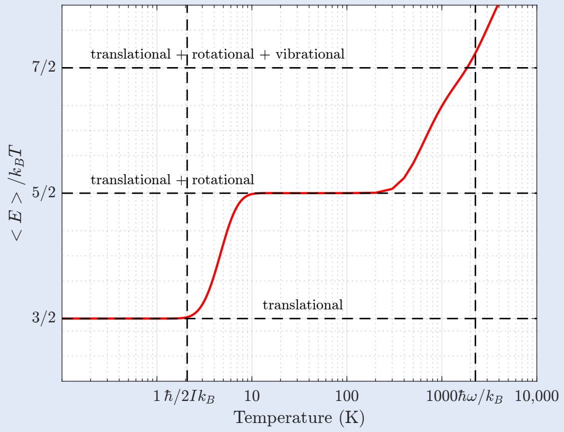


Figure 3.4: Temperature-dependent Average energy for molecular oxygen O_2

In practical terms, and in the scope of this academic unit which will treat thermal engines whose minimum temperatures are usually above $T = -100\,°\text{C}$ and below $T = 1000\,°\text{C}$, we will consider that **the rotation of molecules is always activated** whereas **the vibration of molecules is never activated**.

We therefore **always** consider:

- $\langle E \rangle$ for an atomic particle: $\frac{3}{2}k_BT$
- $\langle E \rangle$ for a diatomic particle: $\frac{5}{2}k_BT$

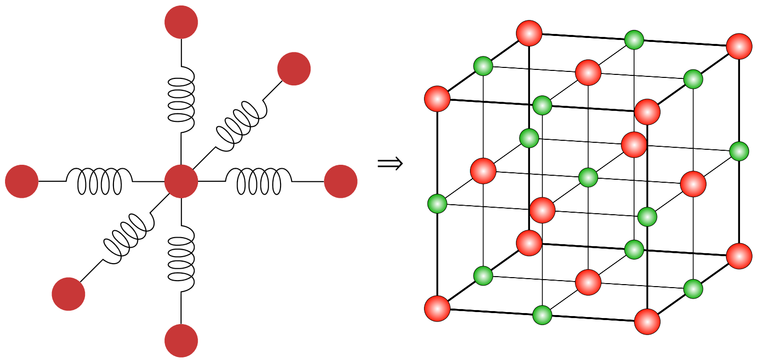
3.1.2 Degrees of freedom for liquids

Too complicated for this course. Lets skip this...

3.1.3 Degrees of freedom for solids

In a solid, the atoms are embedded into a lattice which disallows free motion. However the atoms may vibrate over their equilibrium position.

The atom in the lattice may move in 6 directions, therefore a solid has 6 degrees of freedom and $\langle E \rangle = \frac{6}{2}k_BT$.



3.2 Where we finally get to define what Temperature really stands for

We have been arguing since chapter 1 that the concept of Temperature "is complicated". We arbitrarily introduced the variable $\beta = 1/k_B T$ during our discussion about microstates and macrostates, and the Boltzmann distribution.

If we finally want to settle this matter once and for all, properly defining Temperature T (and by the way what does the constant k_B stands for), we need to go back to our history books:

The concept of Temperature was devised much before the development of statistical physics, with the development of the first thermometers where a liquid (usually mercury) dilates/contracts (more onto this in the next class) in a vertical column.

The unit of 1 °C (or 1 K) stems from the definition of a temperature scale where the most precious chemical element in the World (Water H_2O) was used as a standard, with 0 °C set as the Temperature below which water is frozen (at standard atmospheric pressure, more on this in a future lecture), and 100 °C set as the Temperature above which water is vaporized[4].

Later on, the constant volume heat capacity $C_v = \partial\langle E\rangle/\partial T$ of water was approximately determined as being 4.186 J/(g K). Knowing that a mole of H_2O has a mass of 18.015 g, and that liquid water has 9 degrees of freedom (don't ask), we may write for the heat capacity of one molecule of liquid water:

$$\begin{aligned} C_v &= 4.186[\mathrm{J/(g\,K)}] \\ &= \frac{4.186[\mathrm{J/(g\,K)}] \times 18.015[\mathrm{g/mol}]}{9N_A[1/\mathrm{mol}]} \\ &\simeq 1.391 \times 10^{-23}[\mathrm{J/K}] \end{aligned}$$

which is approximately[5] the value for the Boltzmann constant $k_B = 1.3806488 \times 10^{-23}$.

We may therefore acknowledge the Boltzmann constant as a simple conversion factor which correlates Temperature T which was originally scaled against the properties of water and the Joule energy units.

We now put to rest our debate concerning temperatures:

[4] we note that there are other possible scales proposed in the past (and used up until today) such as Fahrenheit and Rankine units, however these are not accepted as standard units - SI units

[5] The value is not exact as the C_v value for water is slightly dependent on Temperature T, even in the liquid state

A volume of gas comprised of a given amount of particles with N degrees of freedom will have an average energy for each particle equal to $\langle E\rangle = \frac{N}{2}k_BT$, and a velocity distribution function following the Maxwell–Boltzmann equation, depending on the mass m of the particles and the macroscopic Temperature T of the gas.

or in simpler terms:

The Temperature T of a gas is a measure of its "intensity of energy", and its value allows us to determine the velocity distribution of its constituent particles through the Maxwell–Boltzmann distribution.

We may now conceptually describe heat flowing from higher temperatures to lower temperatures as heat spreading out from higher to lower concentrations. Similarly to Temperature being described as the "intensity of energy/heat" we may also describe pressure as the intensity of force applied by matter to another matter ($p = F/A$). Then, for a fluid in movement, we may observe the same spreading out of regions with higher intensities of force (higher pressures) to the regions with lower intensities of force (lower pressures).

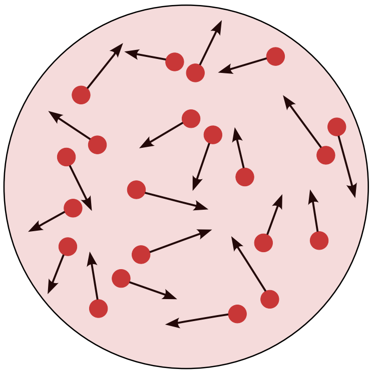
To summarize these important definition for Temperature T and pressure p:

- Temperature T is the "**intensity of energy/heat**";
- Pressure p is the "**intensity of force**".

3.3 Ideal gas law

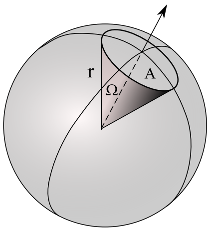
Now that we have appropriate microscopic definitions for Pressure p and Temperature T, we may try to correlate both these identities in the scope of gaseous interactions.

Let us again consider an arbitrary Volume V with a series of moving gas particles, but this time with a spherical form:

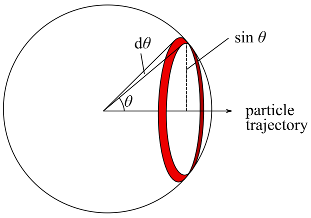


We may start by defining the solid angle in its usual fashion:

We consider the movement of the particles to be isotropic (independent of the angle). Then the fraction of trajectories in an elementary solid angle $\mathrm{d}\Omega$ is equal to $\mathrm{d}\Omega/4\pi$ (since the full solid angle is 4π).



$$\Omega = \frac{A}{r^2}$$

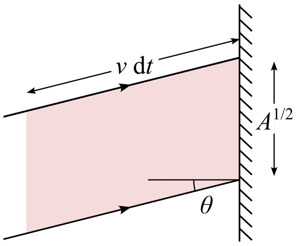


Next the quantity of particles which move with angles comprised between θ and $\theta + \mathrm{d}\theta$ relative to the wall normal in this solid angle Ω is:

$$\begin{aligned} &\mathrm{d}\Omega = 2\pi \sin\theta \mathrm{d}\theta \\ &\Rightarrow \\ &\frac{\mathrm{d}\Omega}{4\pi} = \frac{1}{2}\sin\theta\mathrm{d}\theta \end{aligned}$$

and we may determine the number of particles with velocity $[v, v + \mathrm{d}v]$ moving with angles $[\theta, \theta + \mathrm{d}\theta]$:

$$nf(v)\mathrm{d}v\frac{1}{2}\sin\theta\mathrm{d}\theta \tag{3.3}$$

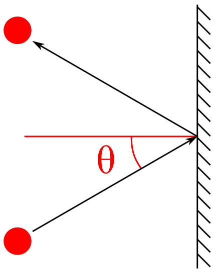


If we now consider the collisions of the particles impacting the wall, we firstly verify that the particles who travel at an angle θ from the wall normal, in a time interval dt, cross the volume

$$Av\mathrm{d}t\cos\theta$$

If we multiply this expression by Eq. 3.3, we find the number of particles which hit the wall of area A during the time interval dt:

$$Av\mathrm{d}t\cos\theta nf(v)\mathrm{d}v\frac{1}{2}\sin\theta\mathrm{d}\theta$$



and the number of particles with velocity $[v, v + \mathrm{d}v]$ moving with angles $[\theta, \theta + \mathrm{d}\theta]$ which hit an unit area A over an unit time dt is given by:

$$v\cos\theta nf(v)\mathrm{d}v\frac{1}{2}\sin\theta\mathrm{d}\theta \tag{3.4}$$

We finally account that a particle hitting a wall has a momentum change of $2mv\cos\theta$

and we integrate[6]:

$$\begin{cases} v \text{ from } 0 \text{ to } \infty \\ \theta \text{ from } 0 \text{ to } \pi/2 \end{cases}$$

[6] the θ integral is only carried in the region $[0 - \pi/2]$ since the particles with $\theta = [\pi/2 - \pi]$ are moving away from the wall and will not collide with it

This finally allows us to derive the pressure as:

$$p = \int_0^\infty \int_0^{\pi/2} \text{variation of moment} \times \text{number of particles } \mathrm{d}v\mathrm{d}\theta$$
$$p = \int_0^\infty \int_0^{\pi/2} 2mv\cos\theta \times v\cos\theta n f(v)\mathrm{d}v \frac{1}{2}\sin\theta \mathrm{d}\theta$$
$$p = mn\int_0^\infty v^2 f(v)\mathrm{d}v \int_0^{\pi/2} \cos^2\theta \sin\theta \mathrm{d}\theta.$$

Acknowledging that $\int_0^\infty v^2 f(v)\mathrm{d}v = \langle v^2\rangle$ and considering the exact solution for the second term: $\int_0^{\pi/2}\cos^2\theta\sin\theta\mathrm{d}\theta = \frac{1}{3}$ we may write:

$$p = \frac{1}{3}mn\langle v^2\rangle \tag{3.5}$$

Finally, considering the overall number of particles N on the Volume V $(N = nV)$, and the Maxwell–Boltzmann relationship for a three degrees-of-freedom particle movement $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$, we have:

$$\boxed{pV = Nk_BT} \tag{3.6}$$

The Ideal Gas Law!

Equivalent forms of the Ideal Gas Law

Dividing both sides of Eq. 3.6 by Volume V we have

$$p = nk_BT \tag{3.7}$$

where $n = N/V$ is the number of particles per unit volume.
We may wish to define the number of particles in its molar form (more adapted to our macroscopic world) with $n_m = n/N_a$. The corresponding version of Eq. 3.6 is:

$$pV = n_mRT, \tag{3.8}$$

with $R = N_Ak_B = 8.314\,47\,\mathrm{J/(K\,mol)}$ the Universal Gas Constant.
If we want to express the Ideal Gas Law in terms of Mass, we may write $n_m = m/M$ where m is the mass of the gas and M its molar mass. Replacing n_m by m/M in Eq. 3.8, and introducing the density $\rho = m/V$ (in [Kg/m^3], we get

$$p = \rho R_mT, \tag{3.9}$$

with $R_m = R/M$ the Specific Gas Constant.

Nomenclature

Variables:

- E: Energy of a system (macroscopic energy) [J]
- I: Rotational momentum of Inertia [kg m^2]
- L: Angular momentum [kg m^2/s]
- k: Spring constant [N/m]
- m: Mass [kg]
- M: Molar Mass [g/mol]
- N: Number of particles [-]
- n: Number of particles per unit Volume $n = N/V$ [m^3]
- n_m: Number of moles per unit Volume $n_m = n/N_A$ [mol/m^3]
- μ: Reduced mass: $\mu = \frac{m_1 m_2}{m_1+m_2}$ [kg]
- p: Pressure [Pa]
- ρ: Density [kg/m^3]
- r: Distance [m]
- T: Temperature [K]
- t: Time [s]
- v: Velocity [m/s]
- V: Volume [m^3]
- $f(v)$: Maxwell–Boltzmann velocity distribution function
- R_m: Specific Gas Constant $R_m = R/M$ [J/(kg K)]

- C_v: Heat Capacity [J/(kg K)]

- β: $\beta = 1/k_B T$
- ϵ: Energy of a particle (microscopic energy) [J]

- θ: Angle [rad]
- Ω: Solid Angle [sr]

Constants:

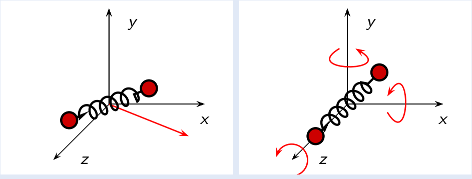
- $k_B = 1.3806488 \times 10^{-23}$ [J/K]: Boltzmann Constant
- $N_A = 6.02214076 \times 10^{23}$ [1/mol]: Avogadro Number/Constant
- $R = 8.31447$ [J/(mol K)]: Universal Gas Constant

Acronyms, subscripts and superscripts

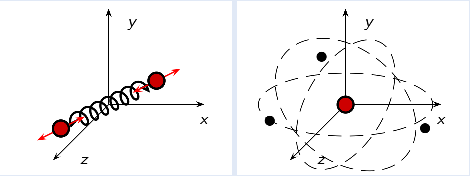
- x: x coordinate [m]
- y: y coordinate [m]
- z: z coordinate [m]
- rms: Root mean square
- $\langle X \rangle$: Average value of variable X for a set of particles

Chapter Summary

- Equipartition Theorem: $< E >= N \times 1/2 k_B T$
  - N: system degrees of freedom
- Particle degrees of freedom:
  - Atomic: $N = 3$
    - 3 translational degrees of freedom x, y, z.
  - Diatomic: $N = 5$
    - 3 translational degrees of freedom x, y, z.
    - 2 rotational degrees of freedom.
    - 2 vibrational degrees of freedom inactive at low temperatures
    - also additional degree of freedom for the electron cloud, also inactive at low temperatures

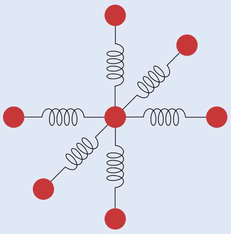


translational mode rotational mode



vibrational mode electronic mode

- Degrees of freedom for a solid: $N = 6$ (Law of Dulong–Petit).



- Statistical definition of temperature T (continued.) and definition of the Boltzmann constant k_B.
- Perfect Gas Law: $pV = N k_B T$.

Recommended readings

- Blundell, “*Concepts in Thermal Physics*”, Chapters 19 and 6.

Thermodynamics and Culture: Relevant Works

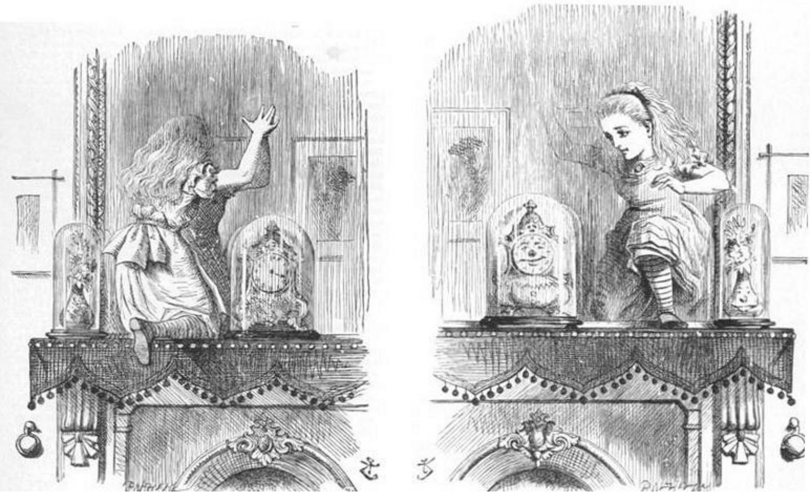
Chapter 3 continues our travels through the microscopic world of particles, with an outlook on their internal properties and the behaviour of their movement. We are still in the world of Wonderland and as such the chapter literary work is

Lewis Caroll, "*Through the Looking-Glass*", 1871,

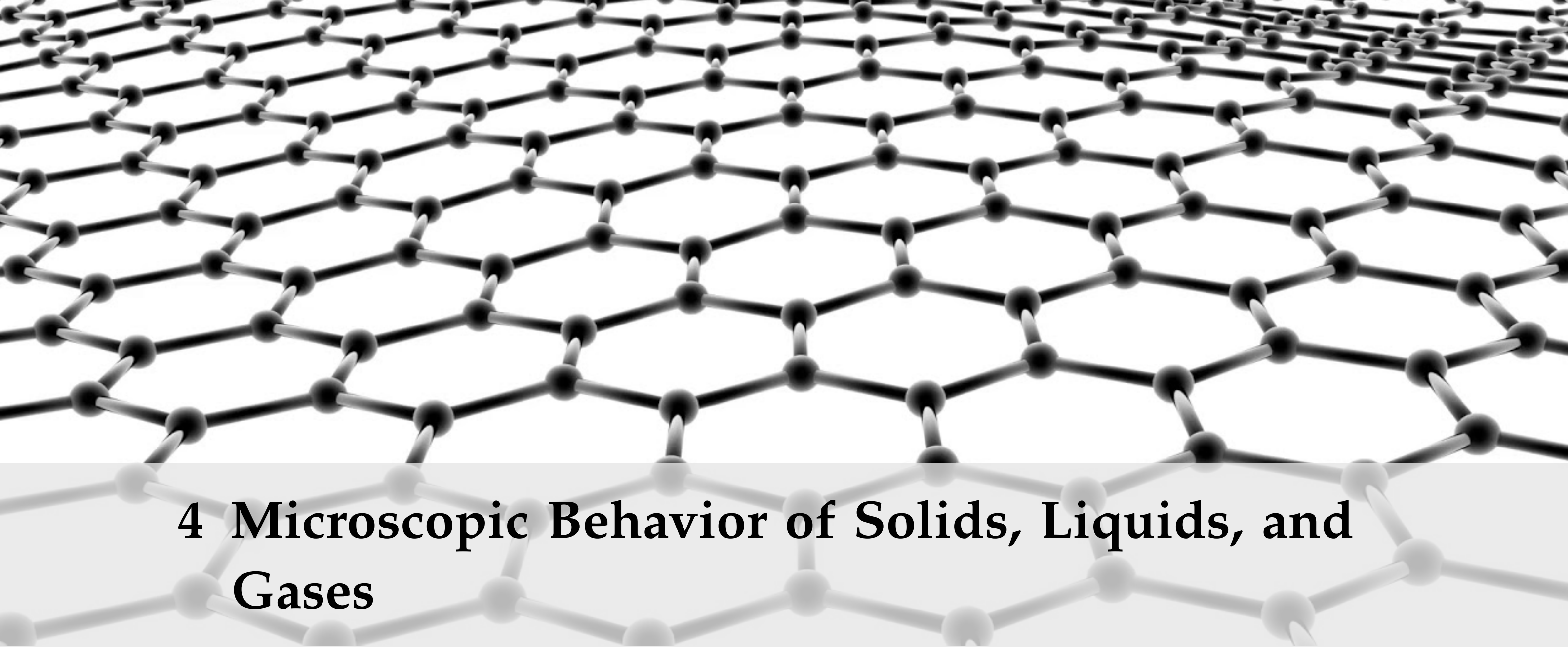
a sequel of *Alice's Adventures in Wonderland*, written and published in part because of the widespread success the former novel garnered.

The book is comprised of a series of dream-like fantasy episodes. The theme which ties them together is Alice's journey as a pawn from the start of a fantasy game of chess until she reaches the eighth rank and becomes a queen.

Alice again enters a fantastical world, this time by climbing through a mirror into the world that she can see beyond it. There she finds that, just like a reflection, everything is reversed, including logic (for example, running helps one remain stationary, walking away from something brings one towards it, chessmen are alive, nursery rhyme characters exist, and so on).

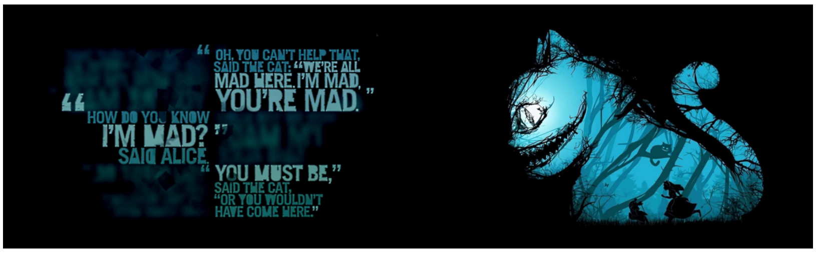


Alice entering the looking-glass.



4 Microscopic Behavior of Solids, Liquids, and Gases

In this Chapter we will continue our walk through the microscopic world...



with an emphasis on chemistry and an outlook into intramolecular and intermolecular forces.

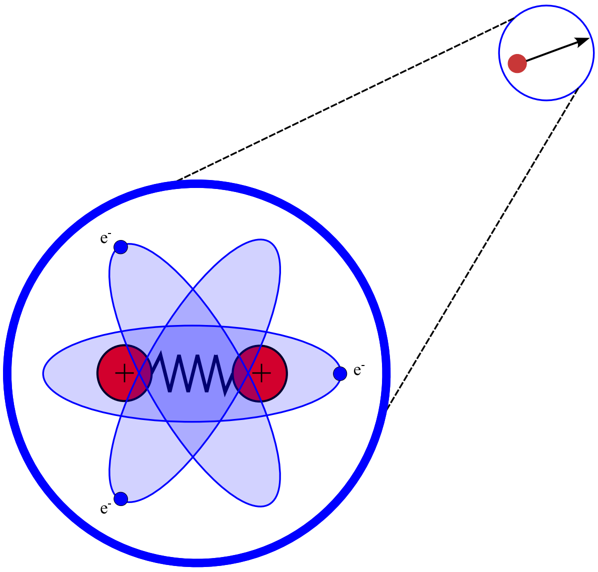
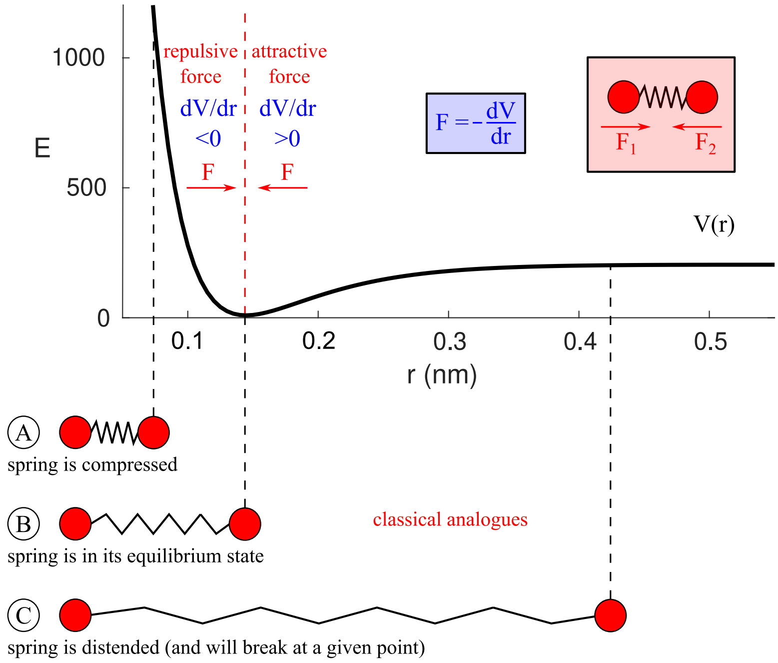


Figure 4.1: Schematic view of a diatomic molecule and its cloud of electrons

We will briefly discuss the interactions and forces (a) inside a molecule, and (b) between two molecules.

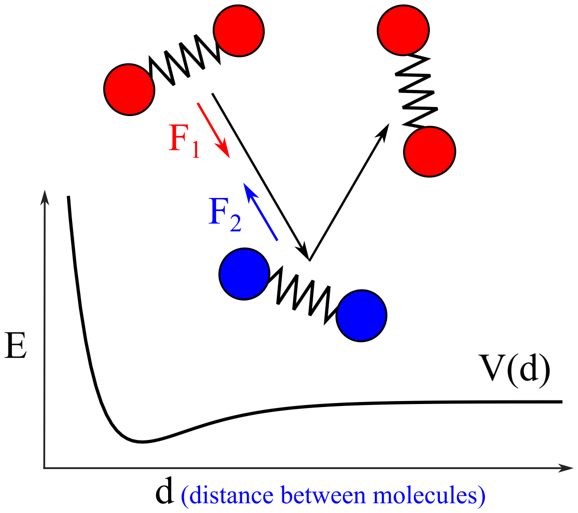
Force interactions within a molecule (intramolecular forces):



What happens when

- **Case** Ⓐ : When pushing the two atoms of a molecule together, the electrostatic forces of both *nuclei* repel themselves.
- **Case** Ⓑ : The repulsive electrostatic forces of the two *nuclei* are offset by the attractive forces of their electron cloud, which maintain an equilibrium between these forces.
- **Case** Ⓒ : When stretching the *nuclei* we also stretch the electron cloud up an until the electrons “choose” one of both *nuclei* for orbiting around. The molecule is said to be “broken”, e.g. it dissociated into two atoms: $N_2 \longrightarrow N + N$.

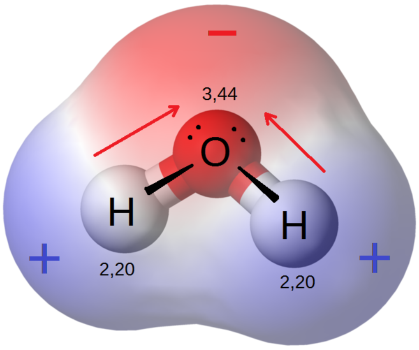
Force interactions between two molecules (intermolecular forces):



We have the same pattern of forces.

Why is that? Aren't non-ionized molecules electrostatically neutral beyond some point? (this is the so-called Debye length)

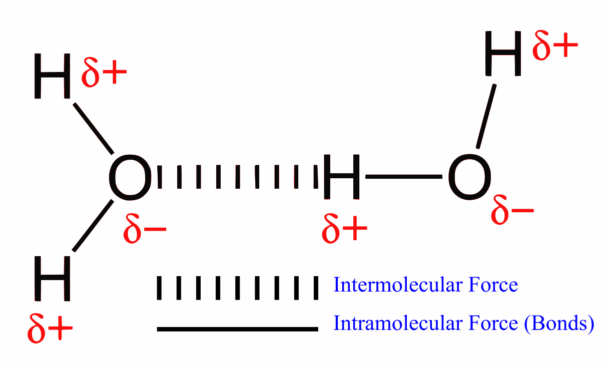
Indeed! Yet the issue lies that for some molecules, the spatial distribution of its charges may differ. Let us examine again the case of the most important chemical component in the Universe (Water H_2O):



For water, the electron cloud tends to be denser around its O constituent atom and scarcer around both its constituent H atoms. These are called polar molecules (in opposition to non-polar molecules) as their electron charge is anisotropic (it will depend on the orientation of the molecule).

It is precisely this anisotropic distribution of charges which is going to allow for molecules to have small long-distance attractive forces, while remaining repulsive at short distance.

Let us keep with the example of H_2O. We see that the O atom (⊕ charge) of H_2O will be attracted to another H_2O molecule H atom (⊖ charge):



These intermolecular forces allow for phase transitions and for the liquid and solid states of matter. If particles move at low enough speeds, during a collision process between two of them, these forces may interact long enough that they may prevent departure after the encounter. We then have the formation of a liquid or a solid where the molecules will find optimal geometrical arrangements among them. An example for the liquid and solid phases for H_2O at molecular level are presented in the figure below.

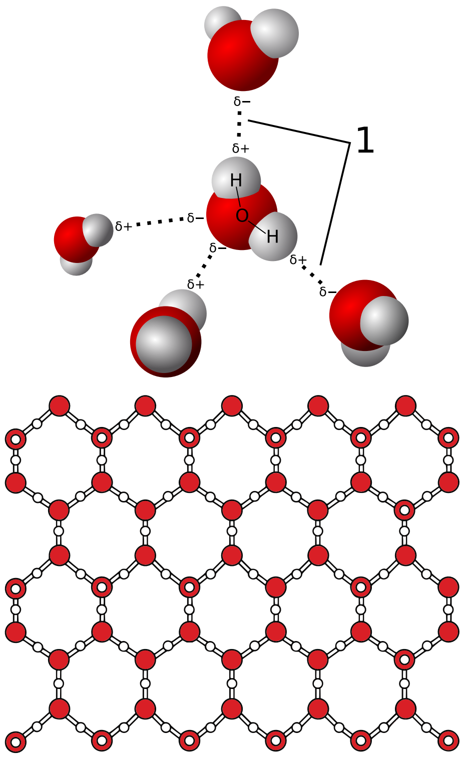
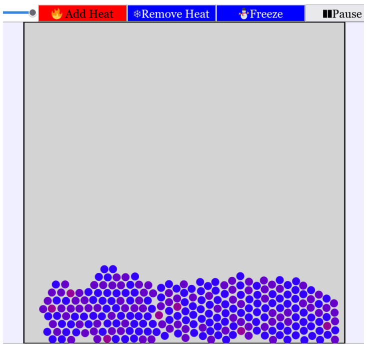


Figure 4.2: O-H bonds in liquid water (left), and in frozen water (ice, right)

Attractive forces work as sticky glue in our billiard balls model.

- In the **gaseous phase** (high Temperatures), the impulse of a collision is much stronger than attractive forces, and these may be neglected (on a first approach), considering a full "rigid spheres" collision model.
- In the **liquid phase** (intermediate Temperatures), the average speeds are lower, and the attractive forces "dampen" movement in a more noticeable fashion. We may say that particles "slide" among them.
- In the **solid phase** (low Temperatures), the particles no longer have a significant movement and attractive forces get to shape the structure of the formed solid.

see also the online simulation of phase transitions between solids, liquids, and gases at microscopic level (link in text & image)



Definition of impulse:

$$\text{Impulse} = F_{avg}\Delta t = m\Delta v$$

$\Rightarrow$

$$F_{avg} = m\frac{\Delta v}{\Delta t}$$

with $\Delta v = \vec{v}_f - \vec{v}_i$ of the particle.

Note: **intramolecular** attractive forces are typically stronger than **intermolecular** attractive forces.

Lets see an example, again for H_2O:

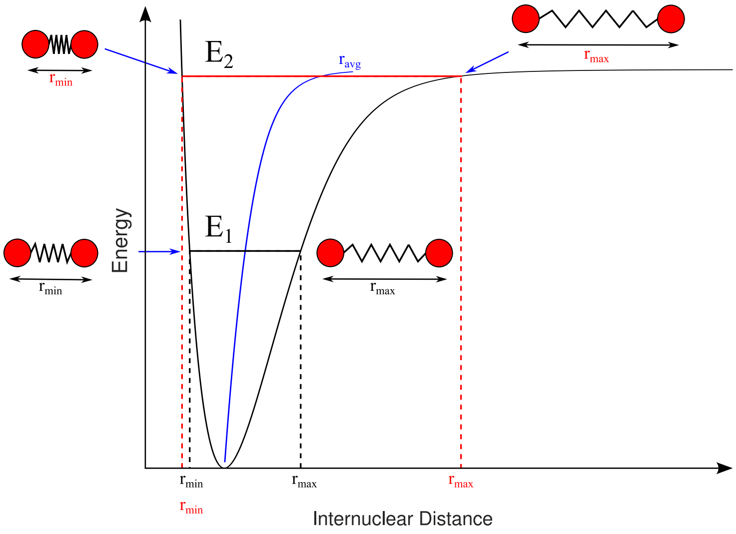
- energy for melting a mole of ice: 6010 J
- energy for vaporizing a mole of water: 40 700 J

- energy for dissociating a mole of vapour: 425 900 J

Water melts at 0 °C, vaporizes at 100 °C, and dissociates at 2000–3000 °C.

4.1 Expansion of solids, liquids, and gases

We saw in Chapter 3 that the constituent particles of a solid will vibrate with a given amplitude. This is true for any state of matter, and the amplitude of vibration will be a function of the solid's temperature (intensity of energy). Let us examine the intramolecular potential of a pair of isolated atoms (essentially a diatomic molecule). This potential has the following functional shape:

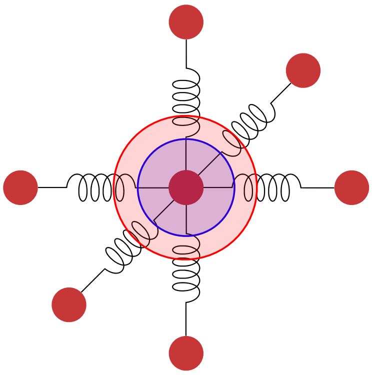


The average intranuclear separation between the constituent atoms of a molecule increases with its energy of vibration E, which increases as a function of Temperature T (owing to the equipartition theorem $E = N/2k_BT$):

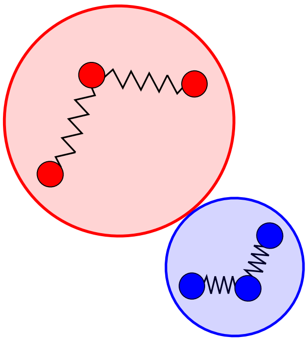
$$r_2^{avg} = \frac{r_2^{min} + r_2^{max}}{2} > r_1^{avg} = \frac{r_1^{min} + r_1^{max}}{2}$$

Consequences for the different phases (again using the water molecule as example):

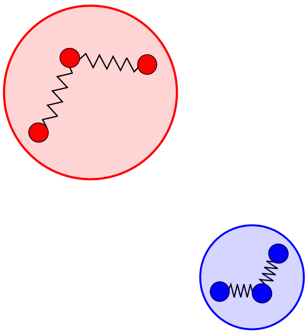
- **Solids**: The vibrating atom of a solid will occupy more space ⇒ The solid expands at higher Temperatures



- **Liquids**: The moving molecules will also occupy more space ⇒ The liquid expands at higher Temperatures



- **Gases**: There is plenty of room between molecules, therefore the increase in molecule occupation volume is irrelevant. There is only a slight increase of the collision cross-section between two molecules.



4.1.1 Macroscopic relationships

Linear Thermal Expansion (1D case):

$$\alpha = \frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}T} \simeq \frac{\Delta L}{T_0}\frac{1}{\Delta T}, \quad \text{if } \Delta L \ll L \tag{4.1}$$

with $\Delta L = L_1 - L_0$; $\Delta T = T_1 - T_0$

$$\begin{aligned} \alpha L \propto L_0 \Delta T \longrightarrow L_1 &\simeq L_0 + \alpha L_0 (T_1 - T_0) \\ L_1 &\simeq L_0 + [1 + \alpha(T_1 - T_0)] \end{aligned}$$

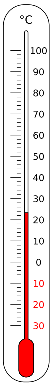


Figure 4.3: A thermometer makes use of the 1D thermal expansion of a liquid to display temperatures.

Derivation of the Linear Expansion Relation:

More rigorously, from $\alpha = \frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}T}$ we have $\frac{\mathrm{d}L}{\mathrm{d}T} = \alpha L$.

$$\frac{\mathrm{d}L}{L} = \alpha \mathrm{d}T; \quad \int_0^1 \frac{\mathrm{d}L}{L} = \alpha \int_0^1 \mathrm{d}T; \quad \ln\left(\frac{L_1}{L_0}\right) = \alpha(T_1 - T_0)$$

$$L_1 = L_0 \exp\left[\alpha(T_1 - T_0)\right] = L_0 \exp\left(\alpha \Delta T\right)$$

Note that alternatively we could have solved:

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \alpha L \;\longrightarrow\; L(T) = C\exp(\alpha T),$$

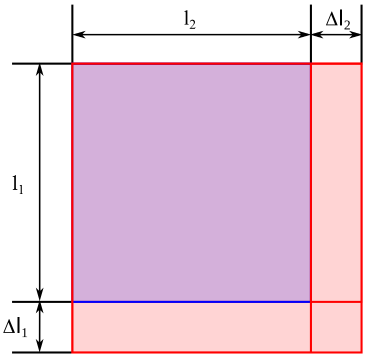
$$L(T_0) = L_0 \;\longrightarrow\; C\exp(\alpha T_0) = L_0; \quad C = L_0\exp(-\alpha T_0)$$

$$L_T = L_0 \exp\left[\alpha\left(L - L_0\right)T\right]$$

for small x we have $\mathrm{e}^x \simeq 1 + x$:

$$L_1 = L_0 \exp\left(\alpha \Delta T\right) \simeq L_0\left(1 + \alpha \Delta T\right)$$

For a thin sheet of an isotropic solid (2D case):



$$\begin{aligned}
\frac{\Delta A}{A} &= \frac{\Delta\left(l_1 l_2\right)}{l_1 l_2} \\
&= \frac{\left(l_1 + \Delta l_1\right)\left(l_2 + \Delta l_2\right) - l_1 l_2}{l_1 l_2} \\
&= \frac{l_1 l_2 + l_1 \Delta l_2 + \Delta l_1 l_2 + \Delta l_1 \Delta l_2 - l_1 l_2}{l_1 l_2}
\end{aligned}$$

ignoring the terms in $(\Delta l)^2$ since $\Delta l \ll l$:

$$\frac{\Delta A}{A} \simeq \frac{\Delta l_1}{l_1} + \frac{\Delta l_2}{l_2} = 2\alpha \Delta T$$

with $\frac{\Delta l_1}{l_1} = \alpha \Delta T$ and $\frac{\Delta l_2}{l_2} = \alpha \Delta T$.

Some properties of α:

- α may vary with temperature T, but usually we can neglect this over a large range of T.
- For anisotropic solids (crystals), α may vary with orientation

- For some materials, we may have α_x positive and α_y negative (example: Calcite expands in one direction and contracts in the opposite when the Temperature T increases

For thermal expansion in a volume (3D case):

$$\beta = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T},$$

with β the volumetric expansion coefficient.

$$\beta = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} \simeq \frac{1}{V_0}\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{\Delta V}{V_0}\frac{1}{dT} = 3\alpha\frac{\Delta T}{\Delta T} = 3\alpha$$

Generally $\beta > 0$.

Expression for gases

Unlike liquids and solids, which may be mostly assumed as incompressible[1], gases are strongly compressible.

It is also unusual to apply the expressions for thermal expansion for gases (since these do not assume a given volume, instead filling all the space available). One may still define the isobaric thermal expansion coefficient as

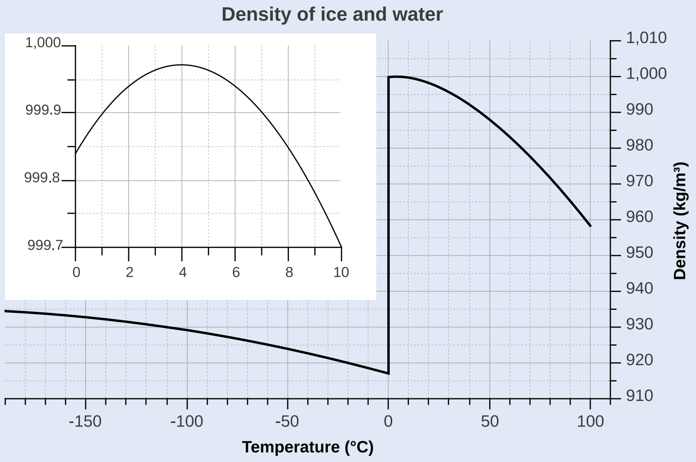
$$\beta = \frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p, \tag{4.2}$$

where the subscript p stands for constant pressure.

If we assume an ideal gas then we obtain [2]

$$\beta = \frac{1}{T}$$

Water and Ice: A special case, and why it matters in the Grand scheme of things.

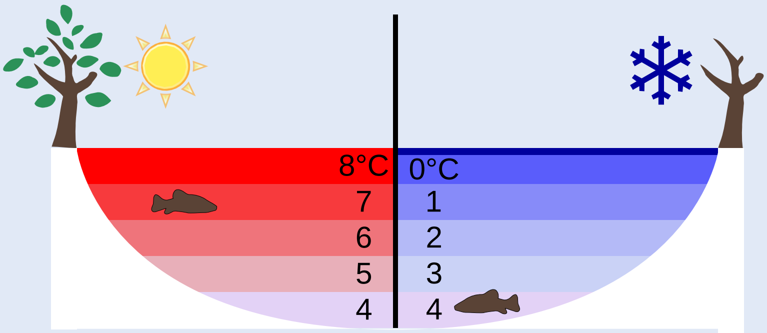


The hexagonal arrangement of water ice is "wasteful in terms of space, since it leaves hexagonal gaps large enough to potentially contain

[1] for solids this excludes elastomers, and liquids are still slightly compressible if you significantly increase the pressure

[2] We differentiate the ideal gas expression to $p\mathrm{d}V + V\mathrm{d}p = nk_B\mathrm{d}T$, then simplify it since we are isobaric ($V\mathrm{d}p = 0$), and replacing $\mathrm{d}V/\mathrm{d}T$ by Nk_B/p in Eq. 4.2. We finally recognize that $Nk_B/pV = 1/T$ and simplify the expression.

additional molecules of water. This is what happens when increasing temperature in the range 0–4 °C. The breaking of hydrogen bonds on melting allows for a denser molecular packing in which some of the lattice cavities are filled by water molecules, hence increasing the density up to 4 °C. Above this value, thermal expansion effects become dominant again.
As a result of this more sparse arrangement of the solid, Ice is about 9% less denser than liquid water, which is why ice rocks float over water.



This is a key feature for Life on our planet since these peculiar properties of water allow for lakes and the bottom of the sea maintaining a constant temperature of 4 °C, allowing for the insulation of life from harsher meteorological conditions at its surface. Water also has a very large volumetric heat capacity, larger than most common metals, and it acts as a very efficient heat reservoir (which is why coastal areas near the sea have more temperate temperatures).

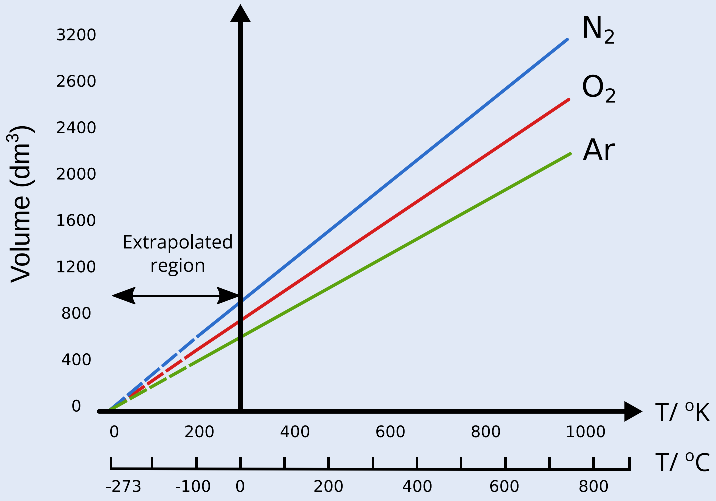
It is believed that without these very favorable thermodynamic properties of water, it would have been impossible for complex and ultimately intelligent life to appear on Earth.

Historical note: The determination of the “absolute zero”.

As we previously discussed, the temperature scale was initially defined through the energy differences of solid/liquid equilibrium for water (0 °C), and the corresponding liquid/vapor equilibrium (100 °C).

Between 1787 and 1802, Jacques Charles in France, John Dalton in the United Kingdom, and Joseph Louis Gay–Lussac in France discovered that ideal gases expand/contract in a linear fashion (Charle’s Law) by approximately 1/273 parts per Celsius (with measurements carried out between 0 °C and 100 °C).

This would imply that the volume of a gas frozen down to −273 °C would have a Volume $V = 0$, which was remarkably close to the real value (−273.15 °C).



We note that it was acknowledged by Gay–Lussac that Charles Law would need to be extrapolated down to absolute zero, since the measured gases would inevitably liquefy before reaching this point. Later in 1848, William Thomson (Lord Kelvin) defined in a more rigorous fashion the temperature scale which would bear his name: The Kelvin

$$\boxed{T(°\mathrm{C}) = T(\mathrm{K}) + 273.15} \tag{4.3}$$

(Note that Kelvin units omit the symbol (°) in the temperature (K)

4.2 Specific Heat, Latent Heat, Heat Capacity

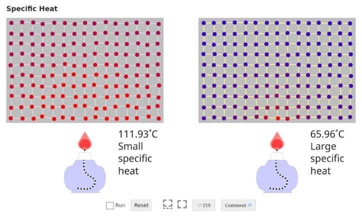
Reminder:

Specific Heat: Heat quantity necessary for increasing by 1 °C the temperature of 1 g of a given substance.

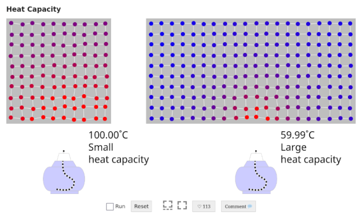
$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} [\mathrm{J/K}]]$$

(for an object with m mass)

see the online simulation of specific heat (link in text & image)



and the online simulation of heat capacity (link in text & image)



We may then define the **heat capacity of a substance**.

We start by defining c as: C[J/K] = m[kg] × c[J/kg/K].

We then have:

$$C = mc\frac{\Delta Q}{\Delta T} \longrightarrow \Delta Q = mc\Delta T = C\Delta T$$

or

$$\mathrm{d}Q = mc\mathrm{d}T = C\mathrm{d}T \tag{4.4}$$

If c is not constant in the temperature interval ΔT we have, considering Eq. 4.4:

$$\Delta Q = m\int_{T_i}^{T_f} c(T)\mathrm{d}T = m\bar{c}\left(T_f - T_i\right),$$

where $\bar{c}$ is the average specific heat.

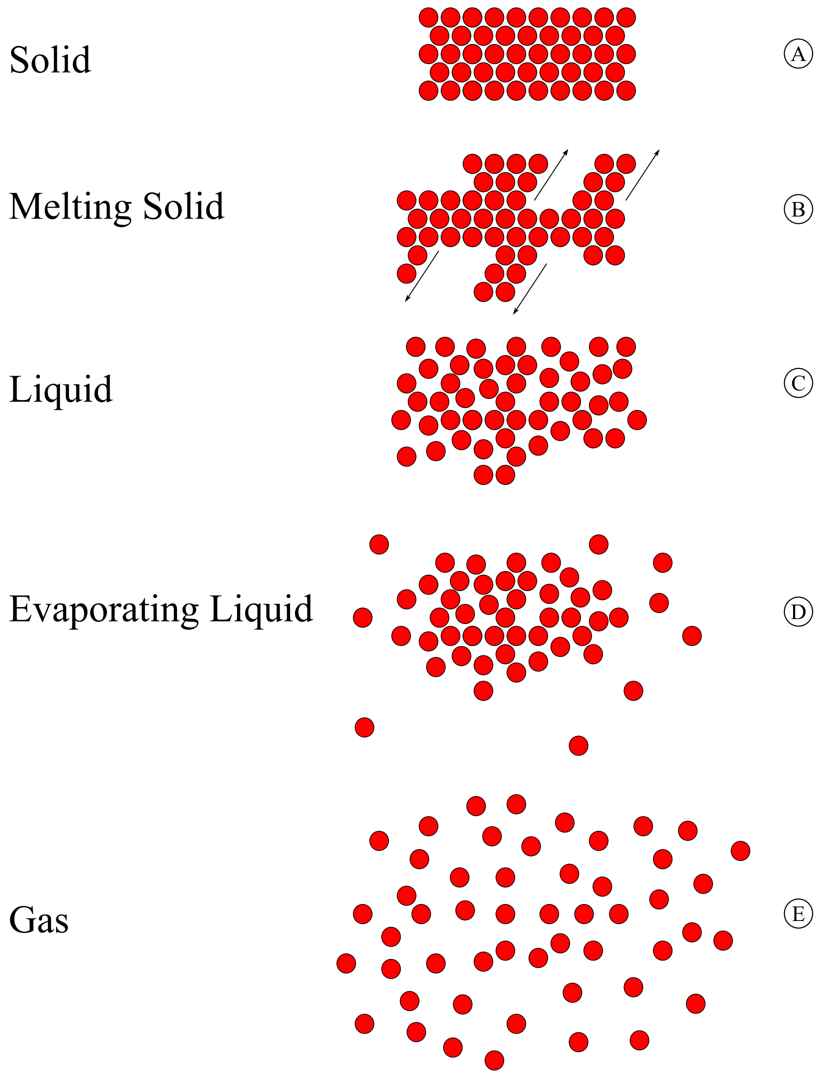
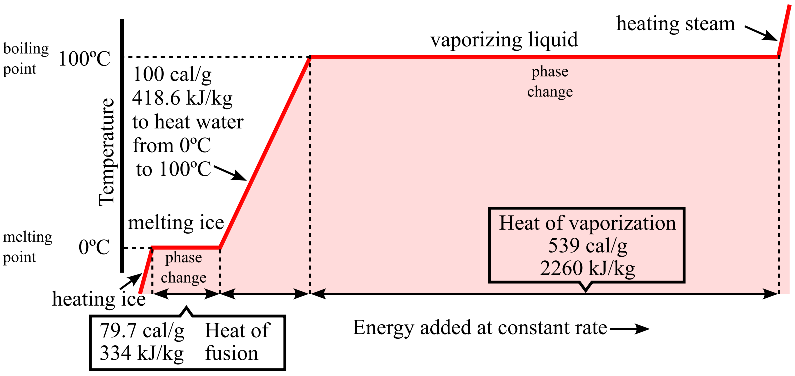


Figure 4.4: Substance phases seen at microscopic level

Latent Heat: When we are in transition between phases (see Fig. 4.4, cases Ⓑ and Ⓓ), the temperature (agitation energy) remains constant and the process of heating/cooling destroys/creates chemical bonds between the particles which release/constrain their movements melting/freezing solids or vaporizing/condensing liquids.

$$\Delta Q = m\lambda \tag{4.5}$$

with λ[J/kg]: latent heat.

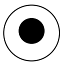


4.3 Real Gas Law (van der Waals equation)

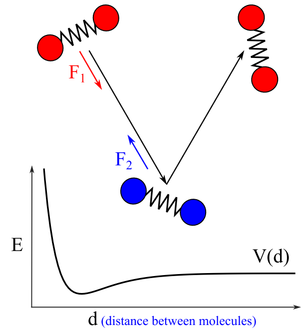
We have seen in the previous class that the Ideal Gas Law is written as $pV = Nk_BT$, which entails a "hard-sphere/billiard balls"-like collision model, where the collisions are fully elastic and the particles are treated as point sources.

This is a simplistic model since:

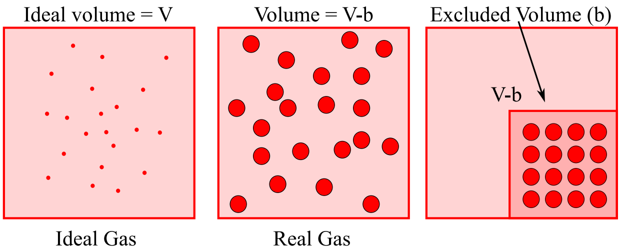
1. Particles occupy a certain amount of space:



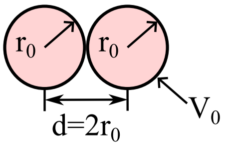
2. There are short-range attractive forces



Case ① (occupation of the space): Let us calculate the exclusion volume.



The minimum distance between particles is $d = 2r_0$:



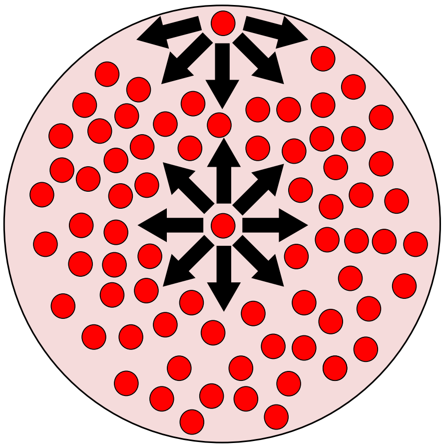
Which corresponds to an "exclusion volume" $V = \frac{4}{3}\pi d^3 = 8\frac{4}{3}\pi r_0^3 = 8V_0$.

If we have N molecules in a volume V, the available volume for the path of the center mass of a particle is: $V - 8(N-1)V_0 \simeq V - 8NV_0$.

If we define $8V_0 = b$ we then have $V \longrightarrow V - nb$, where $pV = Nk_BT \longrightarrow$ $\boxed{p(V - Nb) = Nk_BT}$.

Case ② (attractive interactions):

The attractive effects between molecules average themselves in the gas (they are roughly isotropic resulting in no net force). This is no longer valid near the walls:



For a fixed V, the number of particles in the volume is proportional to N/V, which means $F_{vdW} \propto N/V$.

The number of molecules that are affected by this attraction is also $\propto N/V$, which results in a decrease of pressure $\propto (N/V)^2$, $\Delta p = -a\frac{N^2}{V^2}$, $a > 0$.

We finally may write the **Real Gas (van der Waals) Equation** as:

$$\boxed{\left[p + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT} \tag{4.6}$$

Nomenclature

Variables:

- A: Area [m^2]
- a: van der Waals constant [Pam^6/mol^2]
- b: van der Waals constant [m^3/mol]
- F: Force [N]
- L: Length [m]
- m: Mass [kg]
- M: Molar Mass [g/mol]
- n: Number of particles per unit Volume $n = N/V$ [1/m^3]
- n_m: Number of moles per unit Volume $n_m = n/N_A$ [mol/m^3]
- N: Number of particles [-]
- p: Pressure [Pa]
- ρ: Density [kg/m^3]
- R_m: Specific Gas Constant $R_m = R/M$ [J/(kg K)]
- T: Temperature [K]
- t: Time [s]
- v: Velocity [m/s]
- V: Volume [m^3]

- C: Heat Capacity [J/K]
- c: Specific Heat of a substance [J/(kg K)]
- λ: Latent Heat [J/kg]

- α: Linear expansion coefficient [1/K]
- β: Volumetric expansion coefficient [1/K]

Constants:

- $k_B = 1.3806488 \times 10^{-23}$ [J/K]: Boltzmann Constant
- $N_A = 6.02214076 \times 10^{23}$ [1/mol]: Avogadro Number/Constant
- $R = 8.31447$ [J/(mol K)]: Universal Gas Constant

Acronyms, subscripts and superscripts

- i: initial
- f: final
- avg: Average
- vdW: van der Waals

Chapter Summary

- Intermolecular Potentials.
- Microscopic concepts of Solids, Liquids, and Gases.
- Microscopic concept of Solids and Liquids Thermal Expansion.
- Thermal expansion laws for solids:
    - **1D**: Linear Expansion Coefficient: $\alpha = 1/L \times \mathrm{d}L/\mathrm{d}T$
    - **2D**: Sheet/Plate/Area Expansion Coefficient: $\alpha' = 1/A \times \mathrm{d}A/\mathrm{d}T, \alpha' = 2\alpha$
    - **3D**: Volumetric Expansion Coefficient: $\beta = 1/V \times \mathrm{d}V/\mathrm{d}T, \beta = 3\alpha$
- Specific Heats, Latent Heats, Heat Capacities.
- Real Gas Law (van der Waals Law).
    - $\left[p + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT$

Recommended readings

- Blundell, "*Concepts in Thermal Physics*", Chapters 26 and 28 (partially).

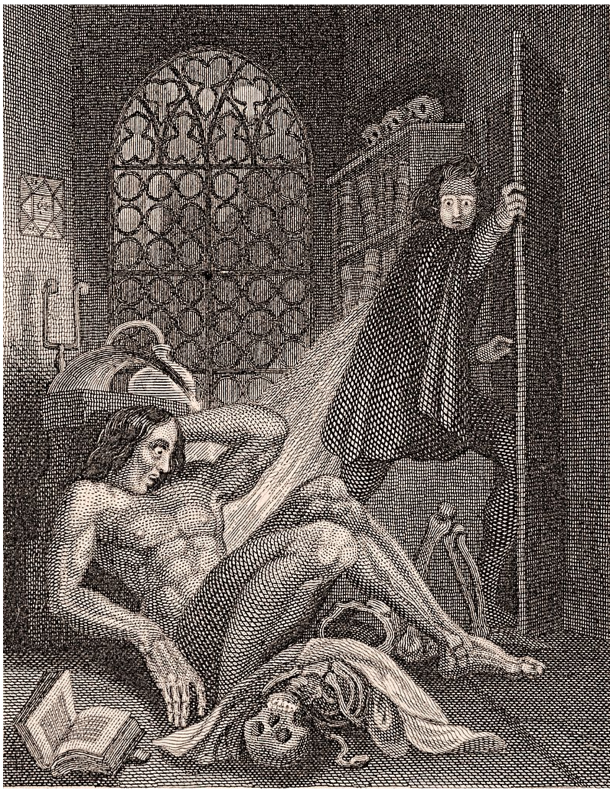
Thermodynamics and Culture: Relevant Works

Chapter 4 discusses how individual particles (atoms and molecules) interact to form compounds, giving rise to the more well known states of matter (solid, liquid and gaseous), owing to electrostatic forces and interactions which are extensively studied in physical chemistry disciplines. A relevant literary work is

Mary Shelley, "***Frankenstein or the Modern Prometheus***",
1818,

a novel about about a "mad scientist" (Victor Frankenstein) who wants to create life itself. He stitches together parts from the dead bodies and brings his creation to life during an electrical storm.

The young Mary Shelley wrote her seminal novel (and one of the first science-fiction novels) at the age of 18, partly as a consequence for her fascination with chemistry and electricity (galvanism), two popular topics in the 19th Century, where science was coming to understand that chemistry held the keys to the phenomena of life. In this context, electricity was understood as a fluid as any other, yet imbued with energizing and vitalizing powers.



Frontispiece to Frankenstein, 1831 Edition

"The teenage Shelley showed uncanny prescience by intimating that life was fundamentally a chemical affair. In the early part of the century, chemists such as Jacob Berzelius and Justus Liebig began to establish organic chemistry as the link between the living and the abiotic, and to erode the need for any 'vital force'. Soon, even Charles Darwin was speculating about life's chemical origins, while his ally Thomas Henry Huxley considered there to be a kind of universal living substance called protoplasm. In the early 20th century the focus of this nascent biochemistry came to be the issue of organization, not mere composition – but one could say that molecular biology never looked back."

Phillip Ball, "*The Making of a Modern Prometheus*", ChemistryWorld. url: `https://www.chemistryworld.com/opinion/how-frankenstein-left-chemistry-with-a-monstrous-reputation/1017377.article`

5 Heat Transfer

There are 3 main energy transfer processes[1]:

$$\left\{\begin{array}{l}\text{Conduction:}\\ \text{Convection:}\\ \text{Radiation:}\end{array}\right\} \left\{\text{Energy Transfer}\right\} \begin{array}{l}\left\{\text{in a material medium}\right\}\\ \left\{\text{in a transparent medium}\right\}\end{array} \left\{\begin{array}{l}\text{without movement}\\ \text{with movement}\\ \text{with photons at } v = c\end{array}\right\}$$

Figure 5.1: conduction, convection, radiation

Note: Convection refers to the combined effect of heat diffusion (conduction) and heat transfer from $A \longrightarrow B$ thorough movement of the fluid which transports heat (advection)[2]. In this textbook, we will consider the simplified version of convection as heat transfer through a moving fluid.

Heat transfer processes

5.1 Conduction

Conduction is the heat transfer through a material medium at rest, under the effect of temperature differences.

- Energy flows from T_1 to T_2 woth $T_1 > T_2$ (from higher energies towards lower energies).
- The amount of heat transfered in an interval Δt will depend/be proportional to the following (using the analogy of a boiling pot):

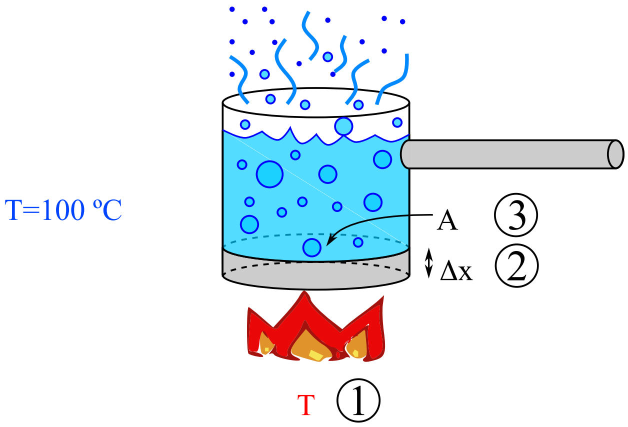
---

[1] A 4th energy transfer mechanism has recently been discovered, allowing heat transfer through quantum fluctuations, including in vacuum, though valid only at very short scales (~ 100 nm), see Fong et al. [1]

[1]: Fong et al. (2019), *Phonon Heat Transfer Across a Vacuum Through Quantum Fluctuations*

[2] both effects are also referred as "natural" and "forced" convection

1. $\propto \Delta T = T_2 - T_1$ (water will heat faster if the flame temperature is higher)
2. $\propto \frac{1}{\Delta x}$ (the thicker the bottom of the pot, the longer it will take to boil water)
3. $\propto A$ (higher areas for energy transfer will lead to thigher heat transfer; consider the flame occupying all the bottom of the pot, or just part of it)
4. $\propto t$ (time-dependence is self-evident)



Accounting for all the proportionality relations we may write[3]:

$$\frac{dQ}{dt} = -kA\frac{dT}{dx} \tag{5.1}$$

which is the **Fourier Law** for heat transfer (in its unidimensional form).

Property ③ has plenty of engineering applications. For building efficient heat dissipators, one may simply increase the contact area A.

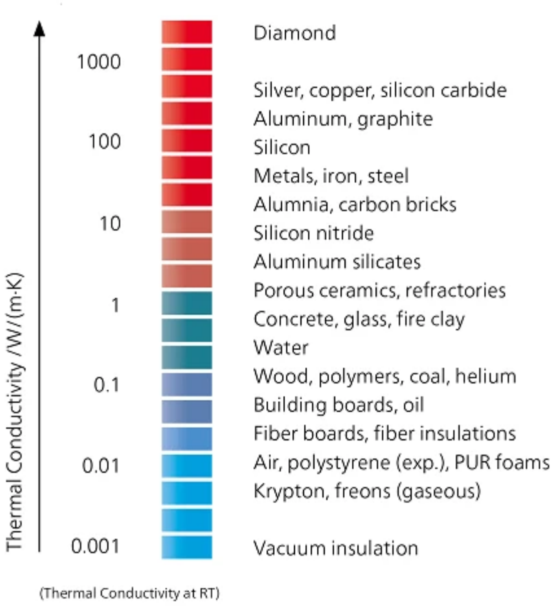
Figure 5.2: car radiator (left) and graphics card heat dissipator (right)

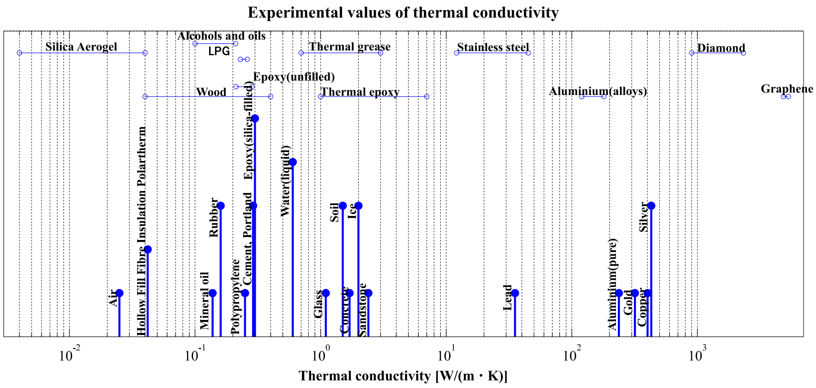
5.1.1 Heat conductivity of different materials

- **Gases:** Very bad conductors (the distance between particles is too large)
- **Liquids:** Mediocre conductors, but extremely efficient for convective heat transfer (good mobility, good heat capacity)
- **Solid metals:** Excellent conductors (the "free electrons" move in the metal and transport energy). Conduction is the result of both atomic vibrations and the movement of electrons'

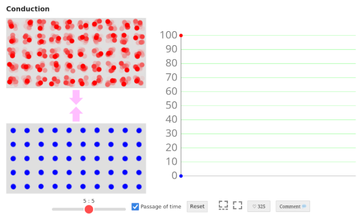
---

[3] with k the thermal conductivity coefficient replacing the proportionality term $\propto$

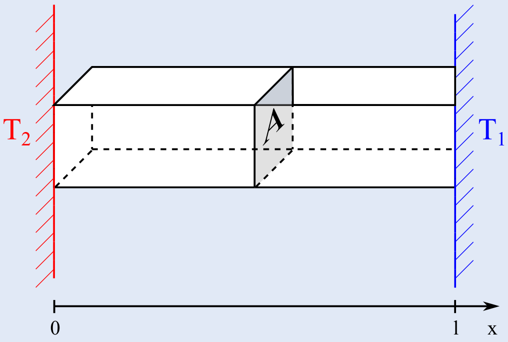




See the microscopic visualization of heat conduction from a hot to a cold solid (link in text & image)



Example: Conduction in an homogenous bar
We consider an homogeneous bar, with cross-section A, length l, conductivity k, and boundaries in contact with a heat source at T_1 and a heat sink at T_2.
Let us also consider that the bar is in stationary regime, which means that $\frac{dQ}{dt}$ is independent of x, and hence $\frac{dT}{dx}$ = c (constant).



This differential equation has the trivial solution:

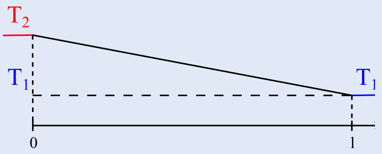
$$T(x) = c_1 x + c_2$$

And we may now simply determine the equation constants from the constraints at the edge of the bar:

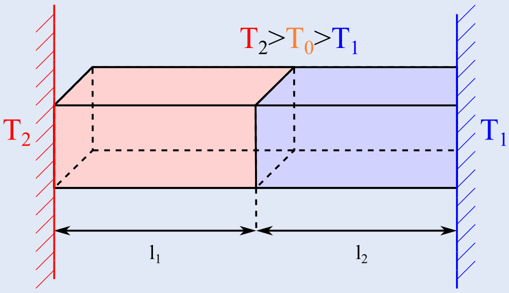
$$\begin{aligned} T(x=0) = T_2 &\quad\longrightarrow\quad c_2 = T_2 \\ T(x=l) = T_1 &\quad\longrightarrow\quad c_1 l + T_2 = T_1 \end{aligned}$$

and we have the solution

$$T(x) = -\frac{T_2 - T_1}{l}x + T_2$$



Example: Conduction in two homogenous bars
We consider two homogeneous bars, with the same cross-section A, but with lengths l_1 and l_2, and conductivities k_1 and k_2.
As usual, the bars are in the stationary regime, $\frac{dT}{dx}$ = c (constant) in any section.



$$\frac{dQ}{dt} = c_1 = -k_1 A \frac{dT}{dx}_{(0<x<l_1)} = k_2 A \frac{dT}{dx}_{(l_1<x<l_2)}$$

We solve for $(0 < x < l_1)$ and $(l_1 < x < l_2)$:

$$\left.\begin{array}{l} \frac{dT}{dx} = \frac{T_0 - T_2}{l_1} \\ \frac{dT}{dx} = \frac{T_1 - T_0}{l_2} \end{array}\right\} k_1 \frac{T_0 - T_2}{l_1} = k_2 \frac{T_1 - T_0}{l_2}$$

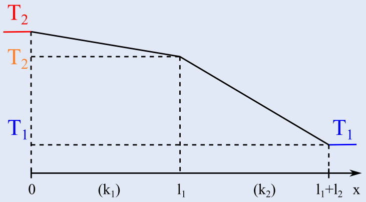
→

$$\begin{aligned} k_2 l_2 T_0 - k_1 l_2 T_2 &= -k_2 l_1 T_0 + k_2 l_1 T_1 \\ T_0(k_1 l_2 + k_2 l_1) &= k_1 l_2 T_2 + k_2 l_1 T_1 \end{aligned}$$

and

$$T_0 = \frac{k_1 l_2 T_2 + k_2 l_1 T_1}{k_1 l_2 + k_2 l_1}$$

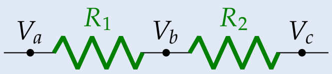
$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}t} &= -\frac{k_1 A}{l_1}\left[\frac{k_1 l_2 T_2 + k_2 l_1 T_1}{k_1 l_2 + k_2 l_1} - T_2\right] \\ &= -\frac{k_1 A}{l_1}\frac{-k_2 l_1 T_2 + k_2 l_1 T_1}{k_1 l_2 + k_2 l_1} \\ &= \frac{k_1 k_2 l_1 A}{l_1}\frac{T_2 - T_1}{k_1 l_2 + k_2 l_1} \\ &= A\frac{T_2 - T_1}{\frac{l_2}{k_2} + \frac{l_1}{k_1}}\end{aligned}$$



If $l_1 = l_2$, T_0 will be closer to T_2 if $k_1 > k_2$. If $k_1 = k_2$ and $l_1 = l_2$, $T_0 = \frac{T_1+T_2}{2}$.

[we may remark from the previous solution that if we want to minimize $\frac{\mathrm{d}Q}{\mathrm{d}t}$, for example to minimize the heat losses of a house wall, improving its insulation, we may do so if we add a thick wall ($l \nearrow$) with low thermal conductivity ($k \searrow$)]

Note: these calculations are analogue to the ones carried out when pairing electrical resistances:



$$\Delta V = (R_1 + R_2)I$$

We may write similarly:

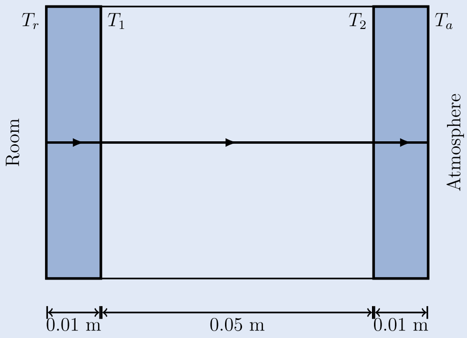
$$\Delta T = \left(\frac{l_1}{k_1 A} + \frac{l_1}{k_1 A}\right)\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{5.2}$$

→

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = A\frac{1}{\frac{l_1}{k_1} + \frac{l_2}{k_2}}\Delta T \equiv \frac{1}{R_1 + R_2}\Delta T,$$

defining $R = l/k$.

Example: Double-pane window used for insulating a room
A double-pane window used for insulating a room thermally from the outside consists of two glass sheets each of area 1 m^2 and thickness 0.01 m separated by a 0.05 m thick stagnant air space. In the steady state, the room glass interface and the glass-outdoor interface are at constant temperature of 27° and 0°, respectively.
Calculate the rate of heat flow through the window pane and find the temperature for each interface. Assume the thermal conductivities of glass and air as 0.8 and 0.08 W/(m K), respectively.



Solution:

The rate of heat flow through the room-side glass is

$$\frac{\mathrm{d}Q_{g1}}{\mathrm{d}t} = \frac{k_g A(T_r - T_1)}{x_g}, \tag{5.3}$$

and through the air-space is

$$\frac{\mathrm{d}Q_a}{\mathrm{d}t} = \frac{k_a A(T_1 - T_2)}{x_a}, \tag{5.4}$$

and through the outside glass is

$$\frac{\mathrm{d}Q_{g2}}{\mathrm{d}t} = \frac{k_g A(T_2 - T_a)}{x_g}. \tag{5.5}$$

In the steady-state, $\mathrm{d}Q_{g1}/\mathrm{d}t = \mathrm{d}Q_a/\mathrm{d}t$. Solving Eq. 5.3 and Eq. 5.4 in the same fashion than for the last exercise we get

$$k_g x_a(T_r - T_1) = k_a x_g(T_1 - T_2) \tag{5.6}$$

In the same fashion, $\mathrm{d}Q_{g2}/\mathrm{d}t = \mathrm{d}Q_a/\mathrm{d}t$. Solving Eq. 5.4 and Eq. 5.5 yields

$$k_a x_g(T_1 - T_2) = k_g x_a(T_2 - T_a) \tag{5.7}$$

combining 5.6 and Eq. 5.7 we get

$$(T_r - T_1) = (T_2 - T_a) \tag{5.8}$$

Solving these last two equations (Eq. 5.7 and Eq. 5.8) we get

$$\begin{aligned} T_1 &= \frac{(k_g x_a + k_a x_g)T_r + k_a x_g T_a}{2k_a x_g + k_g x_a} \\ &= 26.48\,^\circ\mathrm{C} \end{aligned}$$

and T_2 =0.52 °C.

We substitute these values in 5.4 to obtain the rate of heat flow:

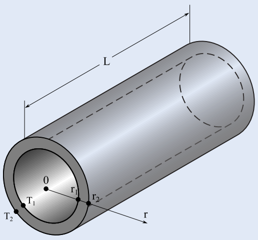
$$\begin{aligned}\frac{\mathrm{d}Q_a}{\mathrm{d}t} &= \frac{k_a A(T_1 - T_2)}{x_a}\\ &= \frac{0.08(1)(26.48 - 0.52)}{0.05}\\ &= 41.5\mathrm{W}.\end{aligned}$$

We may compare this value with the corresponding rate of heat flow of a single-pane window (keeping the same A and x_a):

$$\begin{aligned}\frac{\mathrm{d}Q_a}{\mathrm{d}t} &= \frac{k_a A(T_r - T_a)}{x_a}\\ &= \frac{0.08(1)(27 - 0)}{0.01}\\ &= 216\mathrm{W}.\end{aligned}$$

A double-pane window loses only 19% of the heat that a single-pane window would lose for these same conditions

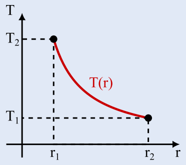
Heat transfer in a coaxial pipe with an internal temperature T_1 and an external temperature T_2:[a]



$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -kA\frac{\mathrm{d}T}{\mathrm{d}r} = k2\pi lr\frac{\mathrm{d}T}{\mathrm{d}r} = c, \qquad A = 2\pi rl$$

Solving the ordinary differential equation in the usual fashion we get:

$$r\frac{\mathrm{d}T}{\mathrm{d}r} = c_1 \longrightarrow \frac{\mathrm{d}T}{\mathrm{d}r} = \frac{c_1}{r}$$



$$\begin{aligned}T(r) &= c_1 \ln(r) + c_2\\ T(r_1) &= T_1, \qquad c_1\ln(r_1) + c_2 = T_1\\ T(r_2) &= T_2, \qquad c_1\ln(r_2) + c_2 = T_2\end{aligned}$$

$$c_1 \ln(r_2/r_1) = T_2 - T_1 \qquad c_1 = \frac{T_2 - T_1}{\ln\left(\frac{r_2}{r_1}\right)}$$

$$\begin{aligned} c_2 &= T_1 - c_1 \ln(r_1) \\ &= T_1 - (T_2 - T_1)\frac{\ln(r_1)}{\ln\left(\frac{r_1}{r_2}\right)} = \frac{\ln(r_2)T_1 - \cancel{\ln(r_1)T_1} - T_2\ln(r_1) + \cancel{T_1\ln(r_1)}}{\ln\left(\frac{r_1}{r_2}\right)} \\ &= \frac{\ln(r_2)T_1 - T_2\ln(r_1)}{\ln\left(\frac{r_1}{r_2}\right)} \end{aligned}$$

$$\frac{dQ}{dt} = k2\pi l r\frac{dT}{dr} \quad \text{and} \quad \frac{dT}{dr} = \frac{c_1}{r} \quad \rightarrow \quad \frac{dQ}{dt} = -2\pi k l\frac{T_2 - T_1}{\ln\left(\frac{r_1}{r_2}\right)}$$

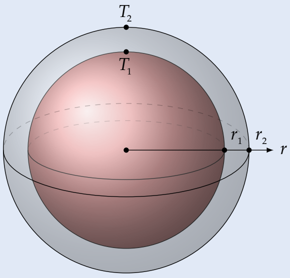
analogy to electrical resistances:

$$R = \ln\left(\frac{r_1}{r_2}\right)\frac{1}{2\pi l k}$$

---

[a] See also Cengel, Heat Transfer, 2nd Ed. Example 2-15

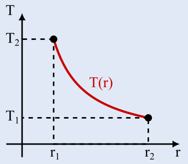
Heat transfer between two concentric spheres with temperatures T_1 and T_2:[a]



$$\frac{dQ}{dt} = -kA\frac{dT}{dr} = k4\pi r^2\frac{dT}{dr} = c, \qquad A = 4\pi r^2$$

Solving the ordinary differential equation in the usual fashion we get:

$$r^2\frac{dT}{dr} = c_1 \longrightarrow \frac{dT}{dr} = \frac{c_1}{r^2}$$



$$\begin{aligned} T(r) &= -\frac{c_1}{r} + c_2 \\ T(r_1) &= T_1, \qquad -\frac{c_1}{r} + c_2 = T_1 \\ T(r_2) &= T_2, \qquad -\frac{c_1}{r} + c_2 = T_2 \end{aligned}$$

$$c_1\left(\frac{1}{r_2}-\frac{1}{r_1}\right)=T_1-T_2 \quad\longrightarrow\quad c_1=\frac{T_1-T_2}{\left(\frac{1}{r_2}-\frac{1}{r_1}\right)}$$
$$=(T_1-T_2)\frac{r_1r_2}{r_1-r_2}=(T_2-T_1)\frac{r_1r_2}{r_2-r_1}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=k4\pi r^2\frac{\mathrm{d}T}{\mathrm{d}r} \quad\text{and}\quad \frac{\mathrm{d}T}{\mathrm{d}r}=\frac{c_1}{r^2} \quad\longrightarrow\quad \frac{\mathrm{d}Q}{\mathrm{d}t}=-4\pi k(T_2-T_1)\frac{r_1r_2}{r_2-r_1}$$

analogy to electrical resistances:

$$R=\frac{r_2-r_1}{r_1r_2}\frac{1}{4\pi k}$$

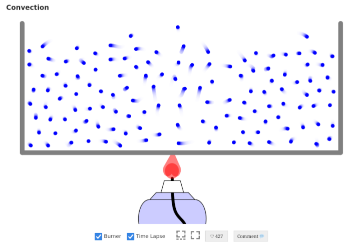
---

[a] See also Cengel, Heat Transfer, 2nd Ed. Example 2-16

5.2 Convection

Liquid or Gas, these absorb heat in a location, move and release the heat in another location.

Online visualization of natural convection in a heated pot filled with water at a microscopic level. The heated water expands, and buoyancy pulls the lighter water upwards, creating a circular movement in the pot, which also brings colder water downwards to be heated) (link in text & image)



- Natural convection: The movement is produced by a density difference associated to the temperature differences – $p=\rho RT$ (wind, sea currents, ...).
- Forced convection: Movement of the fluid imposed by a pump or a ventilator

h: convection coefficient (usually very complex to calculate!)

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=hA\Delta T \tag{5.9}$$

where for the example of a hot wall in contat with a fluid (at an arbitrary preset fluid velocity and condition; slow/fast, laminar/turbulent, etc...)

- A is the contact area between the wall and the fluid
- ΔT is the temperature difference between the wall and the main mass of the fluid.

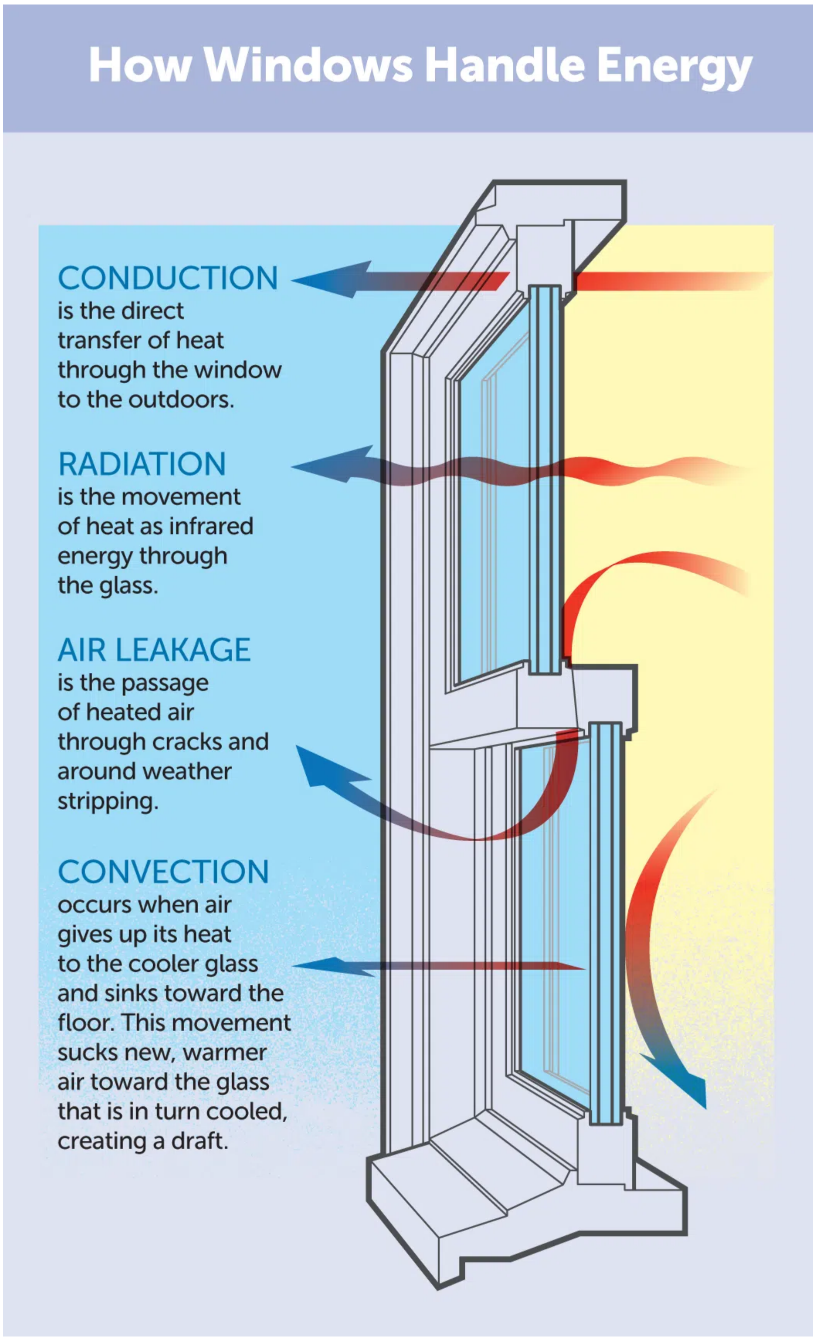
h will depend on:

- the wall shape
- whether the flow is moving horizontally or vertically
- material in contact with the wall
- density, viscosity, specific heat and conductivity of the fluid
- if there is evaporation or condensation

analogy to electrical resistances:

$$R=\frac{1}{hA}$$

Appendix: Energy transfer through a window



How Windows Handle Energy

CONDUCTION is the direct transfer of heat through the window to the outdoors.

RADIATION is the movement of heat as infrared energy through the glass.

AIR LEAKAGE is the passage of heated air through cracks and around weather stripping.

CONVECTION occurs when air gives up its heat to the cooler glass and sinks toward the floor. This movement sucks new, warmer air toward the glass that is in turn cooled, creating a draft.

Nomenclature

Variables:

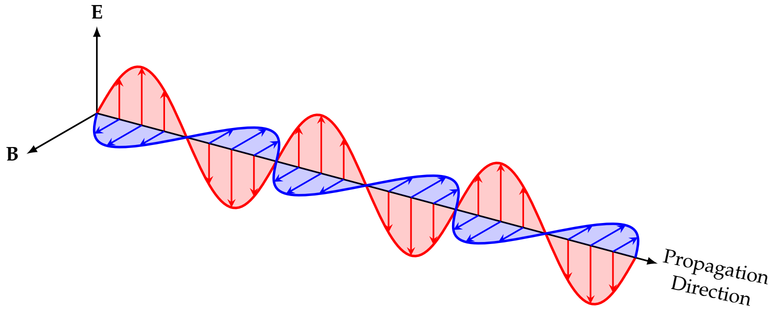
- A: Area [m^2]
- I: Current [A]
- h: Convection coefficient [W/mK]
- l: Length [m]
- k: Conductivity [W/mK]
- Q: Heat [J]
- R: Electric Resistance [Ω]
- l: Radius [m]
- V: Electric Potential [V]
- T: Temperature [K]

5.3 Radiation

Light as a Bundle of Photons

A photon:

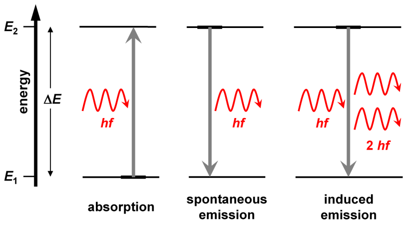
- has an energy, $E = h\nu$ (Planck's Law)
- moves at the speed of light, $v = c$
- has no mass, $m = 0$
- yet behaves as a particle with momentum $m = h/\nu$
- ...and at the same time behaves as an electromagnetic wave.



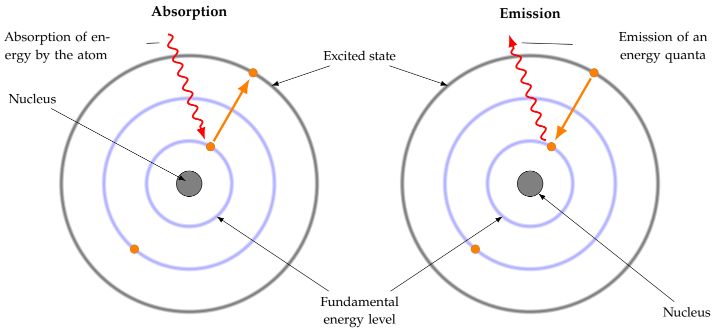
Light can be created and destroyed

Interaction with matter:

- The photon (and its energy) may be absorbed by matter.
- This only occurs if the energy of a photon exactly corresponds to the energy difference between the initial energy state and a higher available energy state of a material medium.
- The inverse process (spontaneous emission) may also happen, creating a photon of energy corresponding to the inverse energy jump (from the higher to the lower energy state).
- The induced emission process is the third and final possible radiative process.

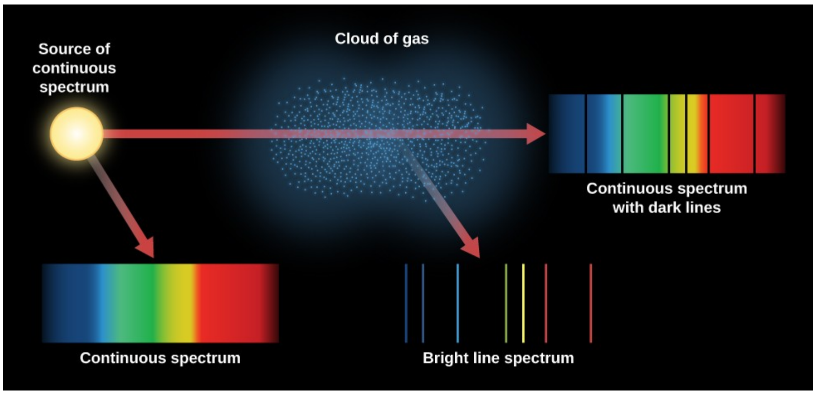


Radiation emission and absorption



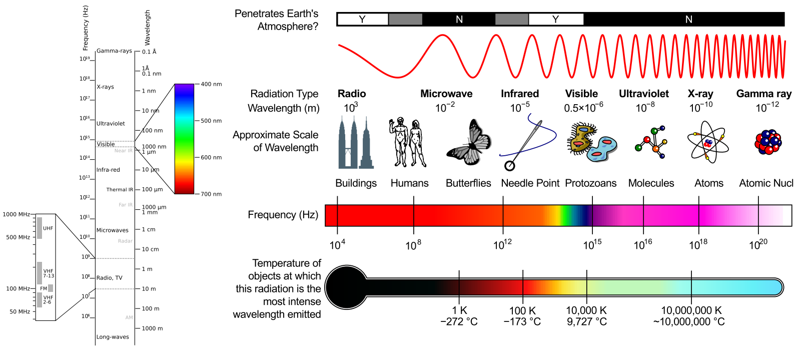
Radiation Emission and Absorption

- **Planck's Relation**: all material systems can absorb or emit electromagnetic radiation of frequency proportional to the energy gained or lost such that $\Delta E = h\nu$.
- Radiation emission/absorption can be **discrete** (collection of broadened lines) or **continuum**.



- The frequency/wavelength of the transitions is intrinsically related to the energies of the internal quantum states of the emitting/absorbing medium, and to the quantum selection rules of the allowed/forbidden transitions between these states.

Visible light is just a tiny part of all the electromagnetic spectrum



Source: wikipedia.org

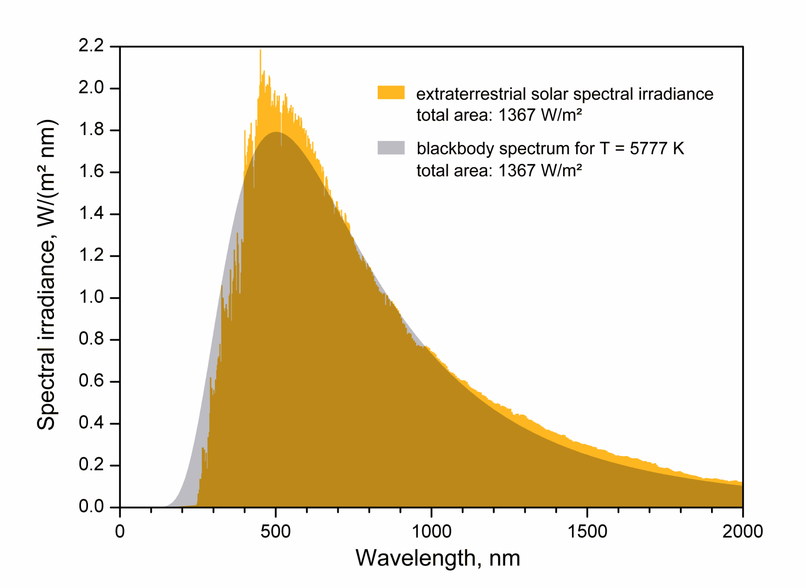
Blackbody radiation limit

The spectral emissivity of a gas/plasma has a theoretical limit given by **Planck's law**

$$B_\nu(T) = \frac{2h\nu^3}{c^2}\left[exp\left(\frac{h\nu}{k_B T}\right) - 1\right]^{-1}$$

The spectral integration yields the **Stefan–Boltzmann** Law:

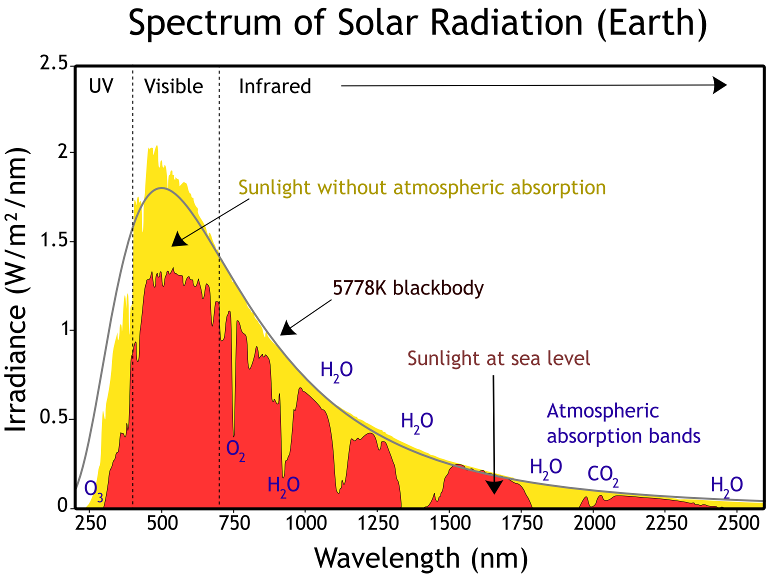
$$\int_\nu B_\nu(T) = \sigma T^4$$



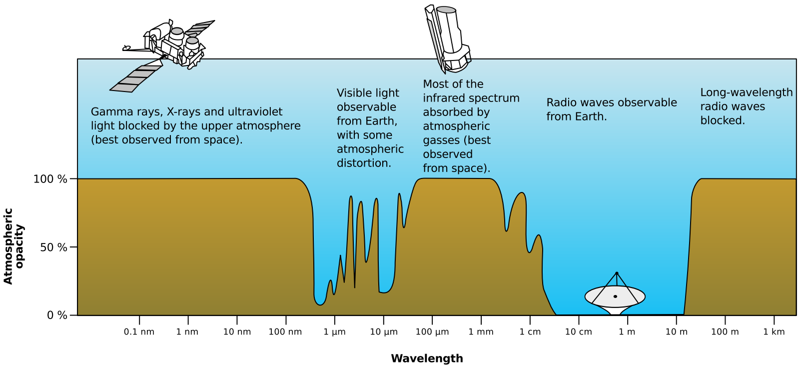
The Sun's emissivity is close to a blackbody

Radiation Emission and Absorption

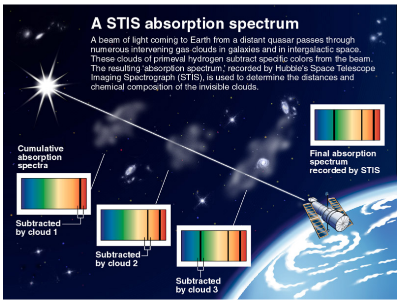
- Dense/High pressure objects emit near-blackbody continuum radiation. Combination of large number of discrete quantum transitions with line broadening effects add up to a continuum.
- Absorption by a medium who is not in radiative equilibrium (grey medium) is strongly uneven, depending on the radiation frequency.



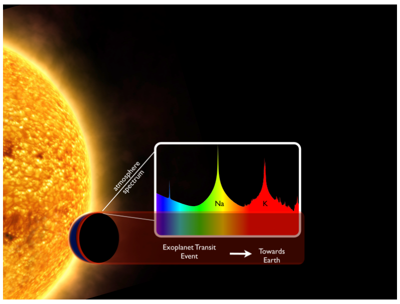
- **Earth's atmosphere** is a good example of a non-grey medium. Radiation in the **UV** and certain **IR** regions is **blocked**. **Visible** radiation and **radio waves** are not.



Remote Sensing


A STIS absorption spectrum

A beam of light coming to Earth from a distant quasar passes through numerous intervening gas clouds in galaxies and in intergalactic space. These clouds of primeval hydrogen subtract specific colors from the beam. The resulting 'absorption spectrum,' recorded by Hubble's Space Telescope Imaging Spectrograph (STIS), is used to determine the distances and chemical composition of the invisible clouds.



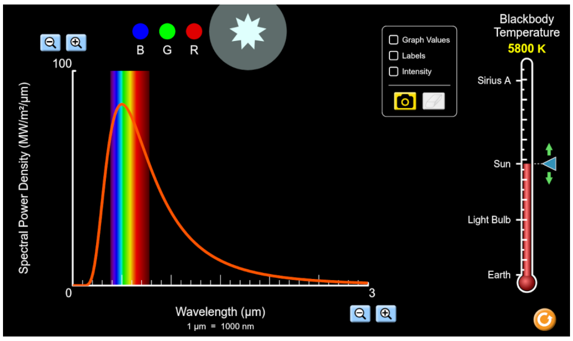
Observation of the **absorption of a near-blackbody source** (Star) trough interstellar gases or planetary atmospheres is a very popular and exciting topic in current day astronomy. Allows **detection of atmospheric components**.

All dense objects emit blackbody radiation at their characteristic Temperature T

Much of a person's energy is radiated away in the form of infrared energy. Some materials are transparent to infrared light, while opaque to visible light (note the plastic bag). Other materials are transparent to visible light, while opaque or reflective to the infrared (note the man's glasses). Image: NASA/IPAC.

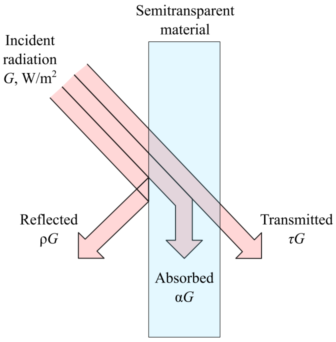
Online Simulator of Planck's Blackbody Law

Planck Blackbody spectrum simulator (link in text & image)



Useful relations

- **Wien's Law**: $(\lambda T)_{\text{max power}}$ =2897.8 μm × K
- **Emissivity**: ratio of the radiation emitted by an object and the radiation emitted by a blackbody with the same Area A and Temperature T, $\varepsilon = E/E_{\text{black}}, 0 \le \varepsilon \le 1$
- **Absorptivity**: fraction of the incident radiative flux (irradiation) absorbed by a surface, $\alpha = G_{\text{abs}}/G, 0 \le \alpha \le 1$
- **Reflectivity**: fraction of the incident radiative flux (irradiation) reflected by a surface, $\rho = G_{\text{ref}}/G, 0 \le \rho \le 1$
- **Transmissivity**: fraction of the incident radiative flux (irradiation) transmitted through a semi-transparent object, $\tau = G_{\text{tr}}/G, 0 \le \tau \le 1$



5.3.1 Applications

Earth-Sun radiative balance

Problem:

The temperature of Earth's surface is maintained by radiation from the Sun. Approximating the Sun and Earth as black bodies, show that:

$$\frac{T_{\text{Earth}}}{T_{\text{Sun}}} = \sqrt{\frac{R_{\text{Sun}}}{2D}} \tag{5.10}$$

where R_{Sun} is the radius of the Sun and D the Earth-Sun separation.

Solution:

The Sun emits a power equal to its surface area $4\pi R_{\text{Sun}}^2$ multiplied by σT_{Sun}^4. This power is known as its luminosity L (in watts):

$$L = 4\pi R_{\text{Sun}}^2 \sigma T_{\text{Sun}}^4 \tag{5.11}$$

At a distance D from the Sun, this power is uniformly distributed over a sphere with surface area $4\pi D^2$, and the Earth is only able to "catch" this power over its projected area πR_{Earth}^2. Thus the power incident on Earth is

$$\text{power incident} = L\left(\frac{\pi R_{\text{Earth}}^2}{4\pi D^2}\right). \tag{5.12}$$

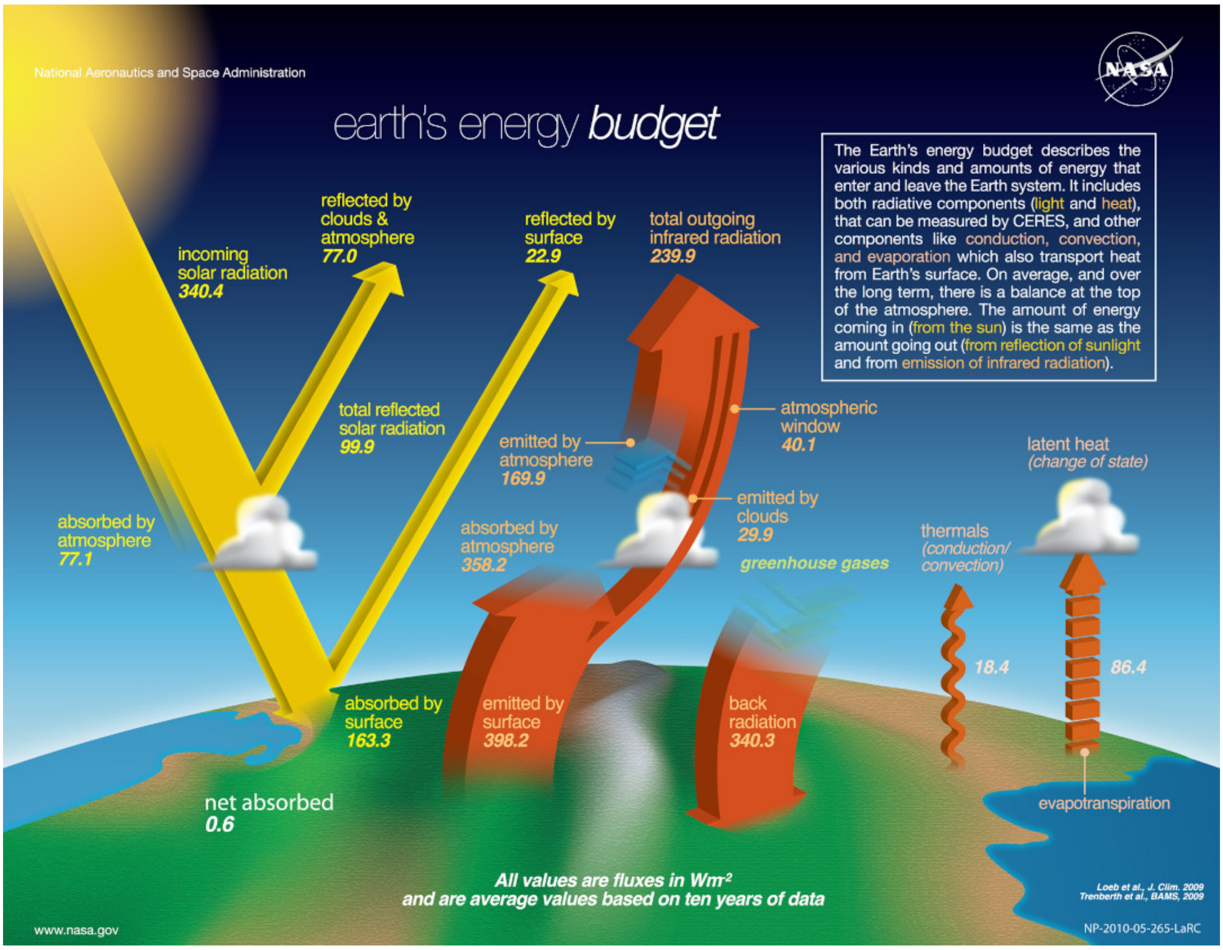
The power emitted by the Earth, assuming blackbody radiation at an uniform temperature T_{Earth}, is simply $\sigma T_{\text{Earth}}^4$, multiplied by the Earth's surface area $4\pi R_{\text{Earth}}^2$, so that

$$\text{power emitted} = 4\pi R_{\text{Earth}}^2 \sigma T_{\text{Earth}}^4. \tag{5.13}$$

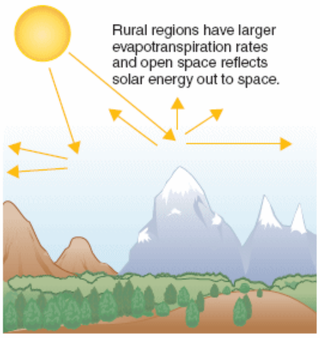
Since Earth is in thermodynamic equilibrium, power emitted = power incident and one may equate the two above expressions to yield the desired result.

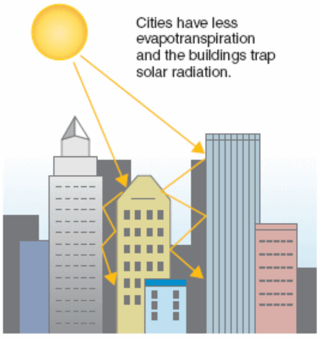
Doing the numerical application with R_{Sun}=7×10^8 m, R_{Earth}=6371 m, D=1.5×10^{11} m, and T_{Sun} =5800 K yields T_{Earth} =280 K, which is just slightly below the real value of 288 K. If we account that Earth reflects part of the solar radiation (Albedo/reflectance of 0.306), and that part of the Earth energy is retained through the greenhouse effect (ε = 0.61), we obtain the real value.

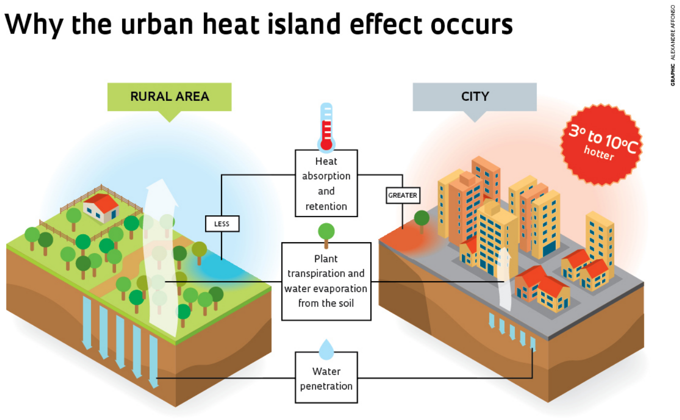
Greenhouse effect and Earth's energy balance



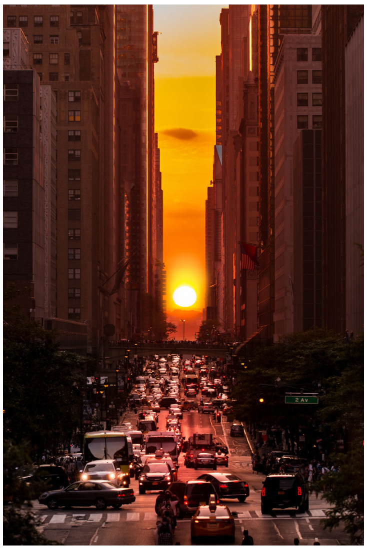
Urban Heat Island Effect

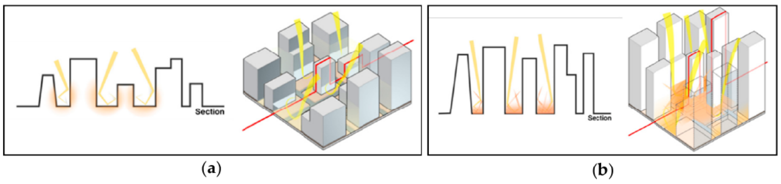






Urban Heat Island Effect

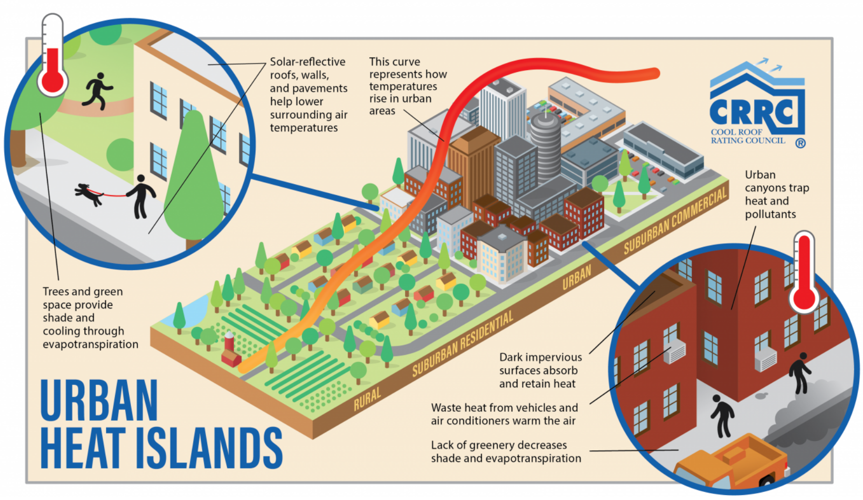




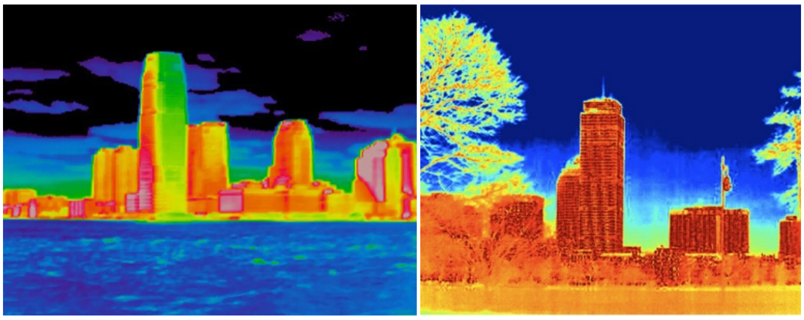
(a) (b)

Figure 6. Illustrations of (**a**) weak solar radiation trapping effects within an urban canyon with low albedo values and a high SVF; (**b**) strong solar radiation trapping effects within an urban canyon with high albedo values and a low SVF.

Urban Heat Island Effect

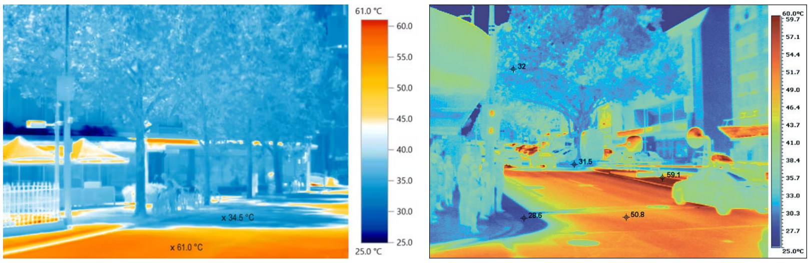


Infrared City Views



The effect of the Sun's illumination of the buildings façades is evident in the early morning

Infrared City Views



Thermal images taken in a January 2017 heatwave show the impact of urban heat islands in Melbourne. Taken by an Elizabeth Street heat camera opposite Queen Victoria Market. Photograph: City of Melbourne.

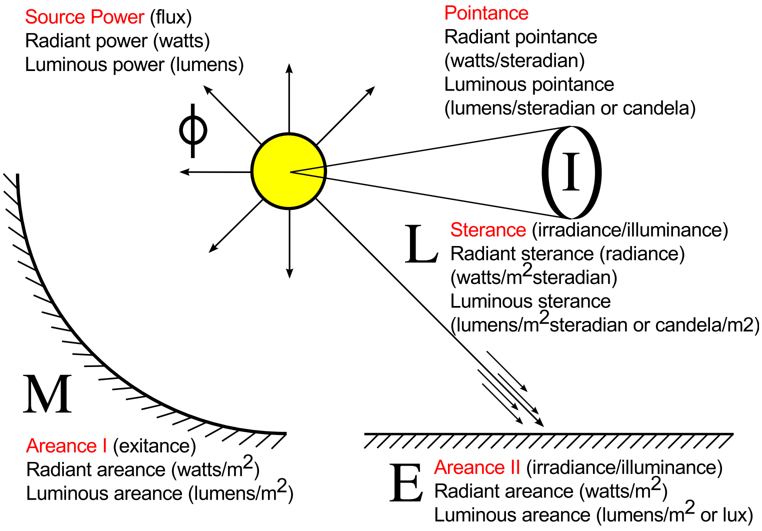
`https://www.theguardian.com/cities/2018/aug/15/what-heat-proof-city-look-like`

5.3.2 Radiative Transfer Units

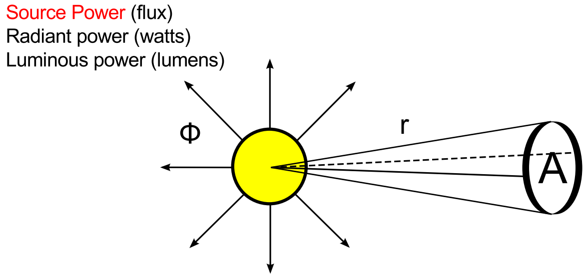
Radiometric and Photometric Units

- **Radiometry** is the study of optical radiation – light, ultraviolet radiation, and infrared radiation. **Photometry**, is concerned with humans visual response to light.
- Most common unit in **radiometry** is the **watt (W)**, which measures radiant flux (power), while the most common unit in **photometry** is the **lumen (lm)**, which measures luminous flux. Radiant intensity is measured in watts/steradian (W/sr), while luminous intensity is measured in candelas (cd, or lm/sr).
- For monochromatic light of 555 nm, 1 W = 683 lumens. For light at other wavelengths, conversion depends on the human eye response to different wavelengths.
- Knowledge on the units correspondence can be useful as the **nomenclatures are sometimes mixed**.

Radiometric and Photometric Units (1/3)



Radiometric and Photometric Units (2/3)



Unit relationships:

Solid angle $\Omega = A/r^2$
Radiant power $\Phi = 4\pi I$ (watt)
Irradiance $E = \Phi/A = I\Omega/A = IA/Ar^2 = I/r^2$ (watt/m^2)

Other Useful Units (3/3)

Other Radiative Transfer Variables

- **Emission coefficient** ε_ν : Energy spontaneously emitted in one local coordinate of the gas/plasma. $dE = \varepsilon_\nu dV dt d\Omega d\nu$.
- **Emissivity** ϵ_ν : Emission coefficient in massic units, with $\varepsilon_\nu = \frac{\epsilon_\nu \rho}{4\pi}$. $dE = 1/4\pi\epsilon_\nu \rho dV dt d\Omega d\nu$.
- **Emission Cross Section** $\sigma_{emi}(\nu)$: Measure for the probability of an emission process. $\sigma_{emi}(\nu) = \varepsilon_\nu / N$
- **Absorption Coefficient** $\alpha(\nu)$: Intensity loss for a ray crossing a distance l.

Table 5.1: Radiometric and Photometric Quantities

	Radiometric Units (R.U.)		Photometric Units (P.U.)	
Quantity	Symb.	Units	Symb.	Units
Wavelength	λ	nanometer (nm)	λ	nanometer(nm)
Radiant (R.U.) & Luminous (P.U.) energy	Q	watt-seconds (W s)	Q_v	lumen-seconds (lm s)
Radiant (R.U.) & Luminous (P.U.) energy density	U	watt-seconds/m^3 ($\mathrm{W\,s/m}^3$)	U_v	lumen-seconds/m^3 ($\mathrm{lm\,s/m}^3$)
Irradiance (R.U.) & Illuminance (P.U.)	E	watts/cm^2 ($\mathrm{W/cm}^2$) or watts/m^2 ($\mathrm{W/m}^2$)	E_v	lux (lx; $\mathrm{lm/m}^2$) or footcandle (fc; $\mathrm{lm/ft}^2$)
Radiance (R.U.) & Luminance (P.U.)	L	watts/m^2/steradian ($\mathrm{W/(m^2\,sr)}$)	L_i	lumens/m^2/steradian ($\mathrm{lm/(m^2\,sr)}$)
Radiant (R.U.) & Luminous (P.U.) intensity	I	watts/steradian (W/sr)	I_v	candela (cd; lm/sr)

- **Opacity** $\kappa(\nu)$: Absorption coefficient in mass units, $\kappa(\nu) = \alpha(\nu)/\rho$.
- **Absorption Cross Section** $\sigma_{abs}(\nu)$: Measure for the probability of an absorption process. $\sigma_{abs}(\nu) = \alpha(\nu)/N$
- **Optical Depth** τ_ν : Defines if a medium is optically thin ($\tau_\nu < 1$), or optically thick ($\tau_\nu > 1$). $d\tau_\nu = \alpha(\nu)dl$.

Chapter Summary

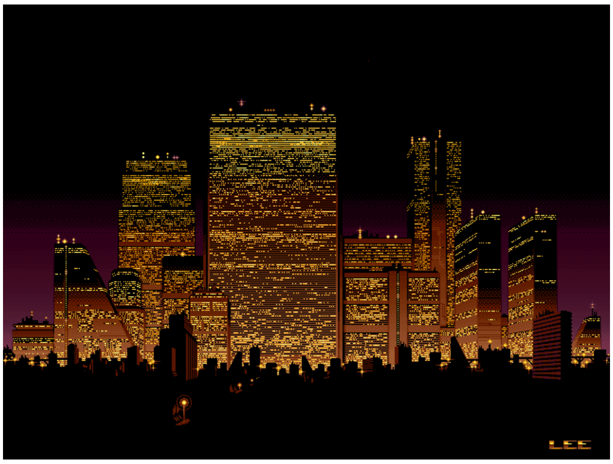
- Conduction Heat Transfer
  - Fourier Law (1D): $\mathrm{d}Q/\mathrm{d}t = -kA \times \mathrm{d}T/\mathrm{d}x$
  - Thermal conductivity for different materials
- Convective Heat Transfer
  - $\mathrm{d}Q/\mathrm{d}t = -hA \times \Delta T$
- Radiative Heat Transfer
  - Properties of a photon
  - Planck's Law: $E = h\nu$
  - Light-Matter interaction; Radiative emission and absorption
  - The electromagnetic spectrum
  - Planck's Blackbody Law: $L_\nu(T) = 2h\nu^3/c^2\,[\exp(-h\nu/k_BT) - 1]^{-1}$
    - ⁎ Emissivity, Absortivity, Reflectivity, Transmissivity.
    - ⁎ Wien's Law, $\lambda_{max}T = 2897.8\,\mu\mathrm{m\,K}$
    - ⁎ Stephan-Boltzmann's Law: $E = \varepsilon\sigma T^4$

Recommended readings

- Blundell, "*Concepts in Thermal Physics*" [5], for Chapters 23 and 37.4 discussing radiative transfer and Global Warming due to Greenhouse gases like CO_2.
- Cengel, "*Heat Transfer*" [6], Chapters 1, 2, 3, and 11, providing theoretical support on heat transfer phenomena (conduction, convection and radiation).

Thermodynamics and Culture: Relevant Works

In Chapter 5 we have discussed the mechanisms of heat transfer, and we have discussed the phenomena of "Urban Heat Islands" where it has been pointed out that the design of modern cities with tall skyscrapers, although very efficient from an urban planning point of view, nevertheless fosters challenges linked to the excessive heating of city centers, which have a shape essentially akin to a giant heat dissipator (see figure 5.2)



The aesthetics of urban environments with tall skyscrapers are the inspiration of countless works in the cyperpunk genre, however we will go a little further back in time to a movie from the silent era:

Fritz Lang, "***Metropolis***", 1927,

Metropolis is a German Science Fiction movie premiered in 1927, and directed by the Austrian film director Fritz Lang. It was, at the time, the most expensive ovie ever filmed in Europe, and is considered in the expert movies community as one of the masterpieces of the German expressionism movement. It was also a masterpiece ahead of its time, since the movie underlying themes remain relevant in modern days.

In this futuristic urban dystopia, taking place in 2026 (100 years after the movie production), wealthy industrials govern the great city of metropolis from towering skyscrapers, while workers constantly toil on the city underground to operate the machines who serve the city.

Freder, the wealthy son of the city supervisor, and Maria, a matriarch figure to the working class try to overcome the divisions that separate the different social classes of the city and act as mediators which may bring the higher and working classes to put aside their divisions and being capable of working hand in hand. The message of the movie is handled in the final intertitle: "The mediator between the head and the hands must be the heart".

THERMODYNAMICS

6 Energy Analysis of Closed Systems and the 1$^{\text{st}}$ Law

We now return to our macroscopic world, ending (for now!) our travels in the strange and wonderful microscopic world.

This the whole pack rose up into the air, and came flying down upon her: she gave a little scream, half of fright and half of anger, and tried to beat them off, and found herself lying on the bank, with her head in the lap of her sister, who was gently brushing away some dead leaves that had fluttered down from the trees upon her face.

Wake up, Alice dear!

"Oh, I've had such a curious dream!" said Alice, and she told her sister, as well as she could remember them, all these strange Adventures of hers that you have just been reading about.

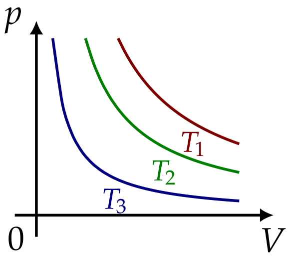
To properly anchor ourselves in this new world, let us transition to a macroscopically adapted Perfect Gas Law (reminder: see section 3.3):

$$pV = Nk_BT \qquad \rightarrow \qquad pV = nR_BT,$$

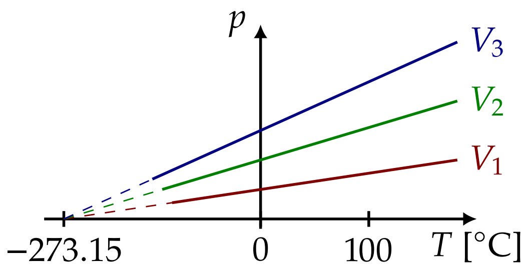
where

$$\begin{cases} N[\text{particles}] \rightarrow n[\text{mol}] & \text{with} \quad N = n \times N_A \\ k_B[\text{J/K}] \rightarrow R[\text{J/K mol}] & \text{with} \quad R = k_B \times N_A \end{cases}$$

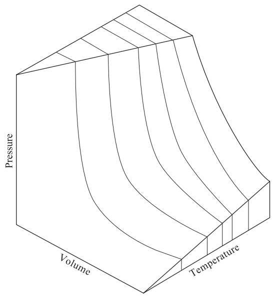
We may now represent this equation on several diagrams:



p-V diagram

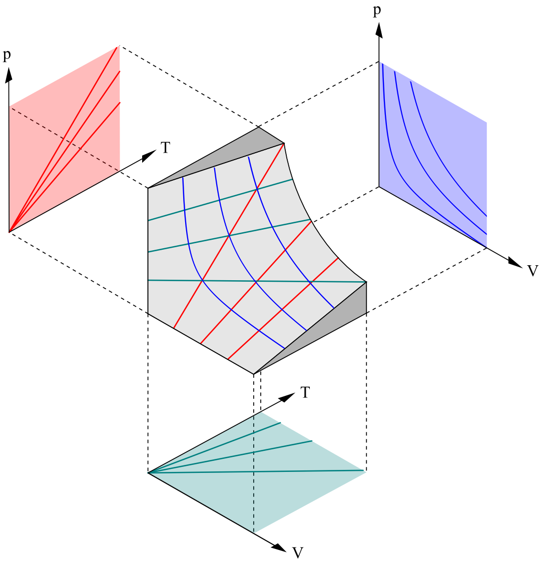


p-T diagram



p-v-T diagram

or in other terms:



6.1 Phase Changes

Let us now return to the Real Gas Equation (van der Waals equation, see Lecture 4).

The van der Waals equation is a simple mathematical model which is yet capable of reproducing the transitions experimentally observed between the vapor and liquid phases, predicting the so-called "critical zone" (the zone below a given "critical Temperature T_c", see Fig. 6.1, left side.

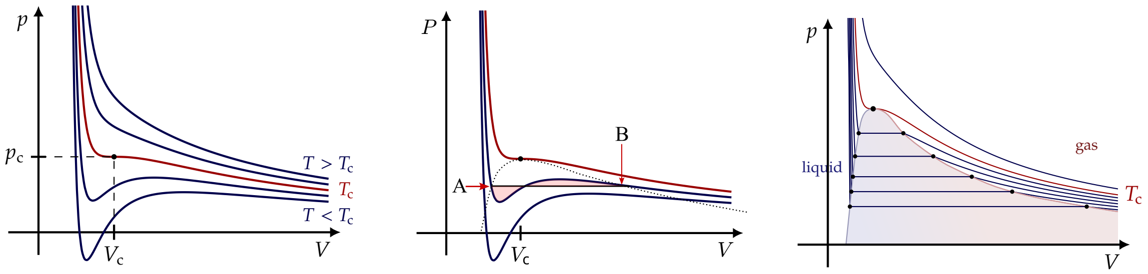


Figure 6.1: van der Waals Isotherms

In the critical zone, the system is unstable, and a thermal equilibrium cannot exist. The physical justification for this is considerably complex, requiring further notions of thermodynamics which are not addressed in this unit. The interested reader may refer to Blundell, section 26.1.

The end result is that in such a critical zone, the transition from a smaller volume (A) towards a higher volume (B) will occur horizontally, at constant T (isotermically), see Fig. 6.1, center. This corresponds to a phase change, see Fig. 6.1, right side.

The analogy to a boiling process is evident:

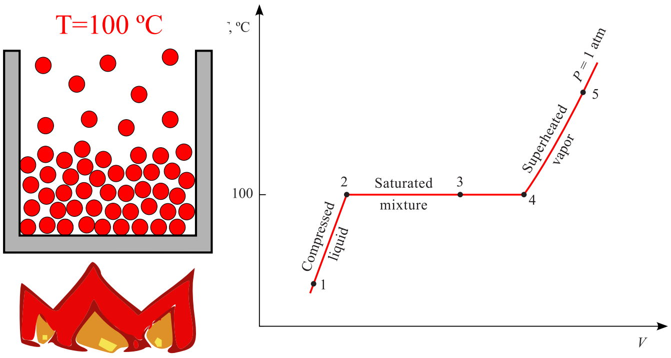


Figure 6.2: Boiling Process. Right figure adapted from *Cengel, Thermodynamics, and Engineering Approach, 5th Ed.*

When we boil a substance, we are increasingly releasing more particles of gas, which will occupy more space (the Volume increases). This process occurs at constant Temperature $T = 100\,°\mathrm{C}$ at atmospheric pressure.

Although the van de Waals equation qualitatively reproduces the liquid-vapor phase transition, for most substances, the relationships between their thermodynamic properties are too complex to be described by simple equations.

The thermodynamic properties of a substance are usually presented in the form of **tables of thermodynamic properties**
(see Appendix C in Book 2)
The students should familiarize themselves with such tables and learn how to use them to infer the thermodynamic properties of a substance at arbitrary (p, T) pairs. This is done in a separate document.

Some definitions (see also Fig. 6.2, right side):

- **Compressed/Subcooled Liquid**: A liquid which is not about to vaporize (ex: $p = 1\mathrm{atm}$, $T = 20\,°\mathrm{C}$, between ① and ② in Fig. 6.2)
- **Saturated Liquid**: A liquid which is about to vaporize (ex: $p = 1\mathrm{atm}$, $T = 100\,°\mathrm{C}$, ② in Fig. 6.2)
- **Saturated Liquid–Vapor**: A mixture of liquid and vapor phases (ex: $p = 1\mathrm{atm}$, $T = 100\,°\mathrm{C}$, ③ in Fig. 6.2)
- **Saturated Vapor**: A vapor which is about to condense (ex: $p = 1\mathrm{atm}$, $T = 100\,°\mathrm{C}$, ④ in Fig. 6.2)
- **Superheated Vapor**: A vapor which is not about to condense (ex: $p = 1\mathrm{atm}$, $T = 120\,°\mathrm{C}$, between ④ and ⑤ in Fig. 6.2)

6.2 Three-phase diagrams

If we now include the solid phase, we obtain two different kinds of $p-V$ plots, depending on whether the substance contracts upon freezing (most of the substances), or whether the substance expands instead (like the case of liquid water-ice transition). The corresponding $p-V$ diagrams are presented if Fig. 6.3.

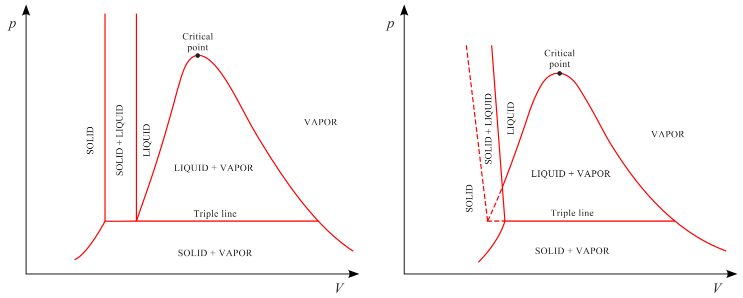


Figure 6.3: $p-V$ phase diagram for a substance that contracts upon freezing (left) and a substance that expands upon freezing (right). Adapted from *Cengel, Thermodynamics, and Engineering Approach, 5th Ed.*

We may also produce a $p-T$ diagram:

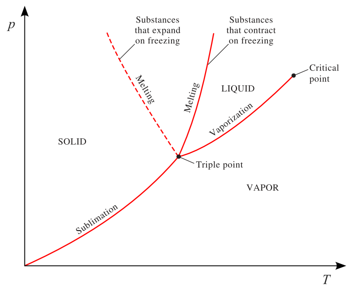


Figure 6.4: $p-T$ phase diagram for a pure substance. Adapted from *Cengel, Thermodynamics, and Engineering Approach, 5th Ed.*

... or full 3D $p-V-T$ diagrams

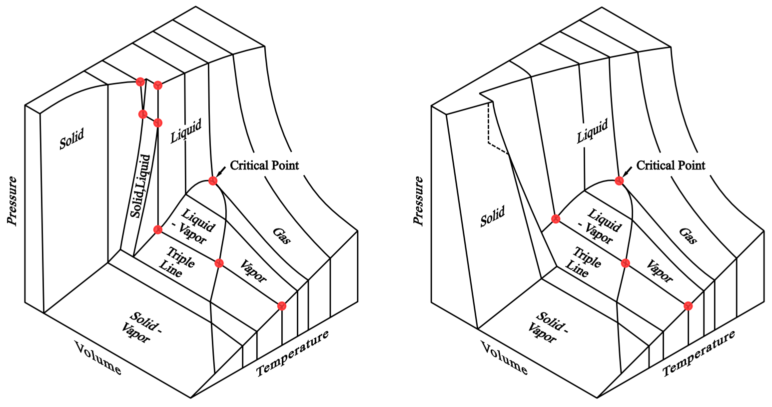


Figure 6.5: $p-V-T$ phase diagram for a substance that contracts upon freezing (left) and a substance that expands upon freezing (right).

6.3 The 1st Law of Thermodynamics

1st Law of Thermodynamics: Energy conservation principle

Historical Note: This principle was independently formulated by Julius Robert von Mayer in 1842 and James Prescott Joule in 1843. This was the cause of great drama among both researchers and their respective supporters, and a wealthy dose of "strongly-worded letters" being exchanged. Mayer is defeated in this peculiar competition, and this defeat, compounded with other misfortunes that assailed him at the same time drove him to suicide in the best tradition of the XIXth Century. But even his 1850 suicide attempt ends up in failure, as his deliberate fall from the 3rd floor of a building only results in both his legs getting broken. He latter spent several years (1851–1853) in a number of insane asylums. In a noted 1858 lecture, German chemist Justus Liebig is said to have described Mayer as "the father of the greatest discovery of the century", but also to have announced incorrectly that Mayer had died ignominiously in a mental asylum due to vilification; when Mayer heard of this and protested that such eulogies were premature, his complaints were ignored. In the meantime, Joule was crowned as the Master of the Energy Conservation Principle. This was due to a variety of factors, however, the fact that his experiments were more rigorous and better conceived than those of Mayer undoubtedly played an important role in this.

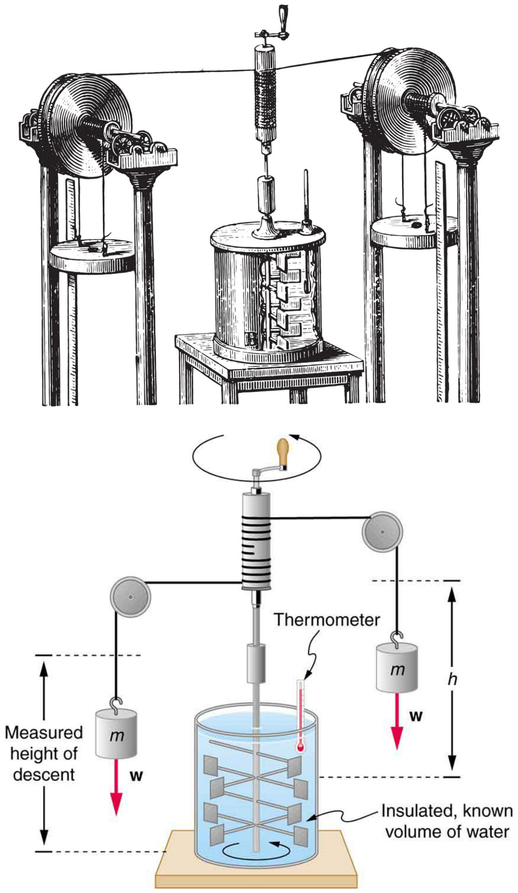


Figure 6.6: Joule Calorimeter, 1849

Fig. 6.6 shows Joule's experiment. Joule was the self-taught Son of a Brewer, and a meticulous experimentalist to boot. The success of Joules experiment was partly due to his proficiency at designing and operating extremely accurate thermometers, with whom he could measure temperature variations as small as 0.003 °C. In Joule's experiment, a mass would fall down by a certain height, turning a paddle weal inside an insulated water enclosure. This mechanical energy is dissipated into heat through friction forces, hence increasing the temperature of the water by a very small amount.

The necessary value for raising water temperature by 1 °C, as determined by Joule, was 4.157 J/g, remarkably close to the actual value of 4.186 J/g[1], with a relative discrepancy of only 0.7% !

Coming back to the definition of the 1st Law, this Law has no possible demonstration, it is a **fundamental principle** which may not be inferred from any other Law.

(Truly, we could have had expressed this Law immediately in the 1st Lecture, together with the **Zero Law**)

The rigorous expression for this Law determines that:
"The variation (increase or decrease) of the total energy of a system during a process corresponds to the difference of energy that enters the system and the energy that leaves the system"
This energy may be transferred in **three** different forms:

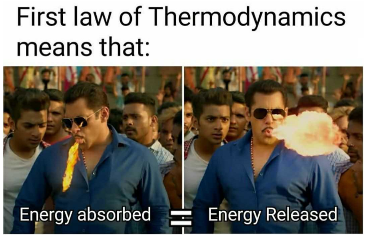
- Heat transfer Q
- Work transfer W
- Mass transfer (with its own energy) E_m

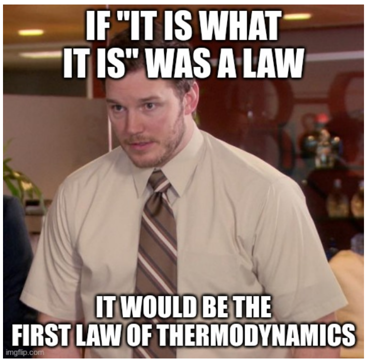
For an isolated system, we may not transfer any mass, so only the two terms Q and W apply.

Conventions used in this course:

- Heat that enters/exits the system: $+/-\ Q$
- Work that is received from/is given to the system: $+/-\ W$

While all authors agree on the convention for Q, some authors do not follow the convention W, using the opposite signals ($-/+\ W$). This is the case for example for the book *Serway: Physics for Scientists and Engineers*. The student should use extreme caution when studying through any thermodynamics book, getting acquainted with the book conventions beforehand[a].





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[1] for water at 15 °C

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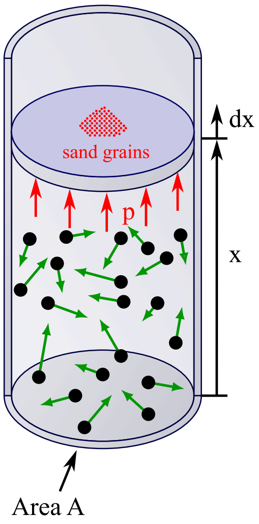
[a] Some authors such as Cengel use the subscripts *in* and *out* to refer to the heat Q and work W that enter/leave the system, in a clever way of avoiding any ambiguities

6.4 Work in Reversible processes

Let us assume a **fluid in thermal equilibrium** enclosed in a piston with a large amount of sand grains on top of the piston, exerting a certain gravitic force, counteracted by the pressure of the gas inside the piston. The piston wall are well insulated, which means that no heat is exchanged with its surroundings, and friction losses in the piston are also assumed as being negligible.

This piston is undergoing an **an infinitesimal expansion** dx as an observer removes the sand grains one by one.



We now remember that the Work W of a Force $\mathbf{F}$ exerted at a distance $\mathbf{x}$, parallel to $\mathbf{F}$ is:

$$W = F \cdot x$$

We may accordingly determine the work performed by the fluid as:

$$\mathrm{d}W = F\mathrm{d}x = pA\mathrm{d}x = p\mathrm{d}V,$$

(since $A\mathrm{d}x = \mathrm{d}V$).

We may rigorously write:

$$\boxed{\mathrm{d}W' = p\mathrm{d}V} \tag{6.1}$$

This process is reversible as we may place back the sand grains one by one until we achieve the initial state. We have further used the term $'$ in Eq. 6.1 as $\mathrm{d}W$ is not an exact differential, since it depends on the path taken.

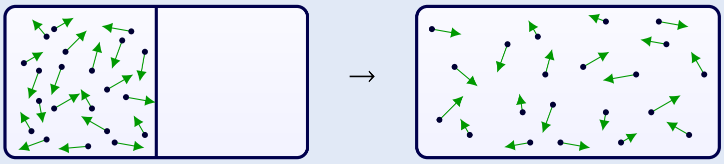
We now may start reasoning in terms of the 1^{st} Law. Here we have $\mathrm{d}W > 0$ and $\mathrm{d}U < 0$ since the system loses energy by performing work on its surroundings.

We may now define the conditions for a reversible process: PUZZ

1. The process occurs "very slowly", or in other terms the fluid will transit though a multitude of thermal equilibrium states, for which p and V are clearly defined.
2. Friction is negligible.

6.4.1 Irreversible processes

Let us now provide the example of an irreversible process, going back to the exact piston configuration of the piston previously described (well-insulated piston without friction losses). This irreversible process is called **The Joule Free Expansion**:



We consider a well insulated box (e.g. isolated from its surroundings) with a gas on one side and vacuum on the other side. We then remove the division, allowing for the gas particles to occupy the empty space. Here we have a variation of volume $\mathrm{d}V$ for the gas, yet no work is produced ($\mathrm{d}W = 0$), and no heat is exchanged with the box surroundings dince the box is well insulated (e.g. its walls are adiabatic), and accordingly $\mathrm{d}Q = 0$. This means that there is no variation of the energy of the box; $\mathrm{d}U = 0$.
This may seem a bit puzzling until we consider the microscopic energy of the particles, $\varepsilon = 1/2mv^2$. The collisions in the box walls are identical whether the particles are confined in the smaller space or move in the larger space. They just cross a larger path before hitting the wall. Accordingly $\varepsilon = const$ and $\mathrm{d}U = \mathrm{d}\sum \varepsilon = 0$

6.4.2 The many forms of Work

Work performed is a concept not limited to mechanical systems. Indeed work may assume many different forms:

- For closed systems we saw that $\mathrm{d}W$ is the mechanical work due to volume change:

$$\mathrm{d}W_{\text{mech}} = -p\mathrm{d}V \tag{6.2}$$

  where p is the Pressure against the moving surface and $\mathrm{d}W$ the change in Volume.
- For a moving charge $\mathrm{d}q$ across a potential difference ϕ:

$$\mathrm{d}U_q = +\phi\mathrm{d}q \tag{6.3}$$

- For dielectric systems, the change of electric dipole moment $\mathrm{d}P$ in the presence of an electrical field E is associated to a change of energy

$$\mathrm{d}U_{\text{el}} = -E\mathrm{d}P \tag{6.4}$$

- For magnetic systems, the change of magnetic dipole moment $\mathrm{d}M$ in the presence of a magnetic field B is associated to a change of energy

$$\mathrm{d}U_{\text{mag}} = -B\mathrm{d}M \tag{6.5}$$

- For a change of surface area $\mathrm{d}\Sigma$ with an associated interfacial energy γ (interfacial energy per unit area)

$$\mathrm{d}U_{\text{surf}} = +\gamma\mathrm{d}\Sigma \tag{6.6}$$

In general, a system may account for all these different forms of Work, with each term being the product of an intensive variable, and the differential of an extensive variable (see Lecture 1).
The change in internal energy of such a system is then written as:

$$\mathrm{d}U = \mathrm{d}Q - p\mathrm{d}V + \phi\mathrm{d}q - E\mathrm{d}P - B\mathrm{d}M + \gamma\mathrm{d}\Sigma \tag{6.7}$$

Getting back to our piston case, we now may integrate Eq. 6.1 to obtain the work done by a fluid in a reversible process between the initial Volume V_i and the final Volume V_f:

$$W_{i\to f} = \int_{V_i}^{V_f} \mathrm{d}'W = \int_{V_i}^{V_f} p\mathrm{d}V \tag{6.8}$$

We know that **each equilibrium state** of the system may be represented by only two variables (p, V), and that the system transits through a series of equilibrium states (p_i, V_i) which may be represented by one curve in the plane (p, V). (Historical Note: This representation, named the "indicator diagram", was firstly proposed by James Watt (1736–1819) in 1796.

As inferred from Fig. 6.7, $W_{i\to f}$ will depend on the path taken:

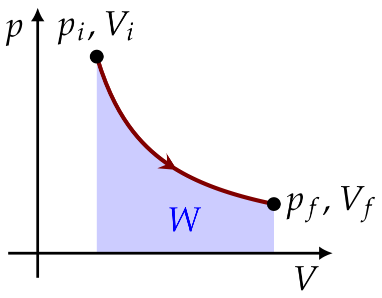
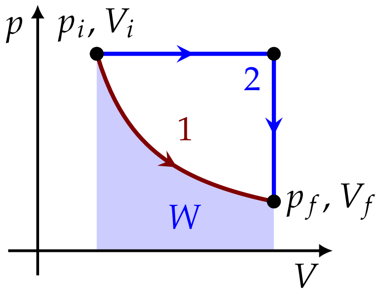


Figure 6.7: Indicator diagram ($W_{i \to f}$ is the shaded area)

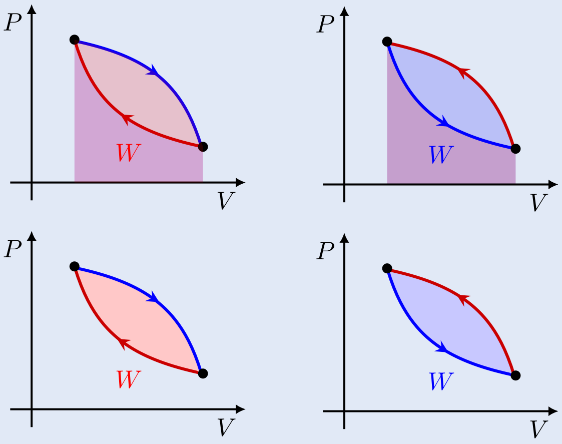


... and as such the differential is not exact, hence the ′ sign.

Nevertheless, the difference of energies ($U_f - U_i$) will not depend on the path taken, and as such **there is no state function which represents the work contained in a system**.

Example: We may travel from Shanghai to Beijing directly, or doing a detour through Nanjing. If by chance a passenger does this whole trip asleep, she/he only knows that she/he left from Shanghai (U_i) and arrived at Beijing (U_f). The information about the Work W of the trip is lost.

Work delivered and work received



In the diagram above, one needs to distinguish the direction of the process. For our initial process where Pressure p decreases and Volume V increases ($p_i, V_i \to p_f, V_f$), we are producing positive Work, see Eq. 6.8. Now we may choose to go back to the initial state by increasing Pressure and reducing Volume ($p_i, V_i \to p_f, V_f$), and here we are consuming Work ($W < 0$).

Again, we do not need to take the same path backwards. We may chose an “easier” path for coming back to (p_i, V_i), than the one taken for descending to (p_f, V_f), the work put back in the system will be lower than the one given by the system:

$$W_{i\to f} > -W_{f\to i} \tag{6.9}$$

and we will have a net work production $\sum W > 0$ by the system through a full cycle $i \longrightarrow f \longrightarrow i$. In the opposite case, we will have a net work consumption $\sum W < 0$.
Mathematically we may write:

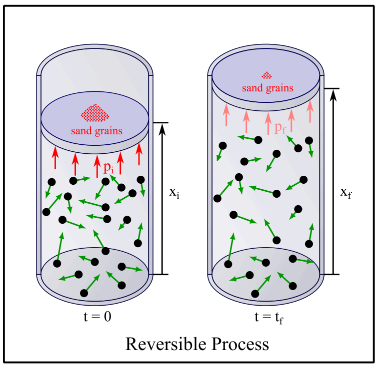
$$W = \oint pdV$$

One may notice for a pV diagram that this corresponds to a clockwise vs. anticlockwise cycle. This is a very important property for a thermodynamic system!
For a given thermodynamic cycle:

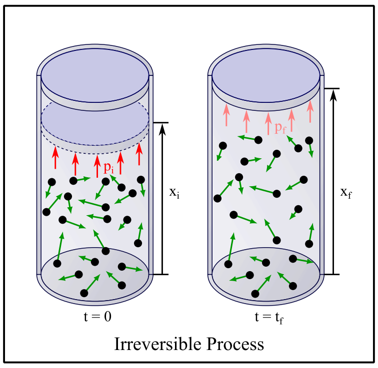
- Net Work W will be positive if the cycle proceeds in a clockwise fashion.
- Net Work W will be negative if the cycle proceeds in a anticlockwise fashion.

6.5 Energy change in a Reversible and an Irreversible expansion: Microscopic demonstration

Let us now revisit our piston undergoing an expansion. We have previously shown the difference between a reversible and irreversible process using the example of removing sand grains from the top of the piston (hence slowly reducing the gravitic force that counterbalances the pressure force of the gas) for a reversible process, and the example of removing a piston barrier between an enclosure with the same gas, and an enclosure in vacuum, for an irreversible process:



Reversible Process



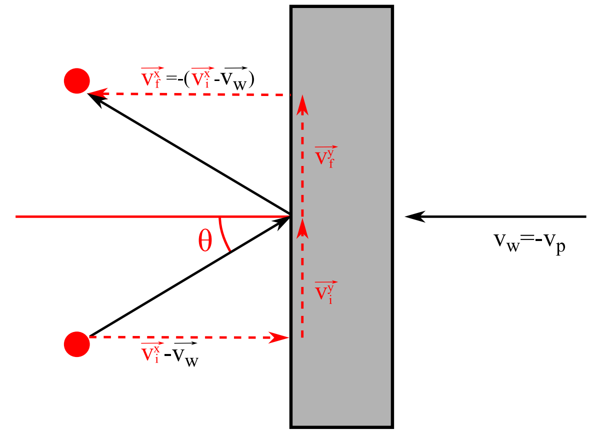
Irreversible Process

In the first case, the piston is moving (although at a glacial pace with $v = 0^+$), and in the second case the piston disappears instantaneously.

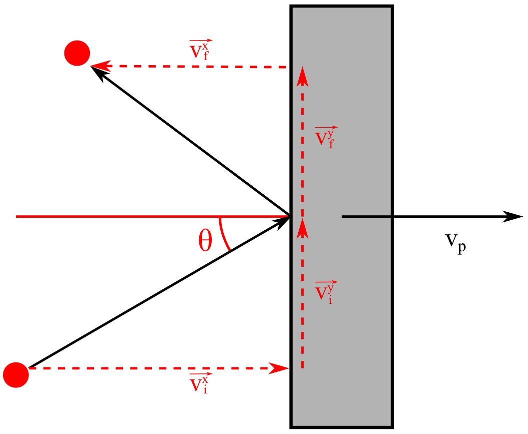
Let us now move to the microscopic world and observe a particle during its collision with the piston for the **reversible process (left)** and the **irreversible process (right)**:

Reversible process

Movement in the piston frame:



Movement in the inertial reference frame:



The velocity vectors are:

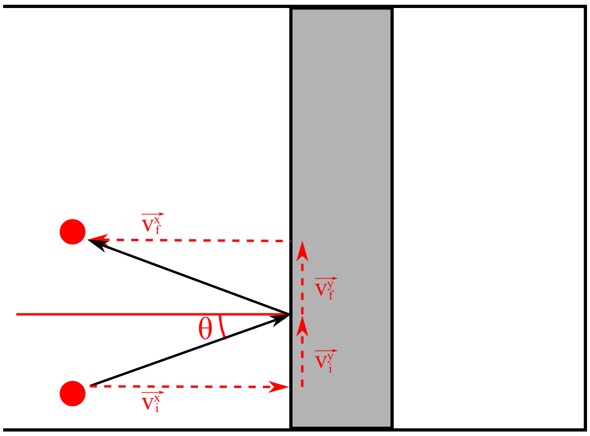
$$\underset{\text{Ⓐ}}{\left\{\begin{matrix}\vec{v}_p\\ \vec{v}^i_x\\ \vec{v}^i_y\end{matrix}\right.}\quad \underset{\text{Ⓑ}}{\left\{\begin{matrix}\vec{0}\\ \vec{v}^i_x-\vec{v}_p\\ \vec{v}^i_y\end{matrix}\right.}\quad \underset{\text{Ⓒ}}{\left\{\begin{matrix}\vec{0}\\ -\vec{v}^i_x+\vec{v}_p\\ \vec{v}^i_y\end{matrix}\right.}\quad \underset{\text{Ⓓ}}{\left\{\begin{matrix}\vec{v}_p\\ -\vec{v}^i_x+2\vec{v}_p\\ \vec{v}^i_y\end{matrix}\right.}$$

With:

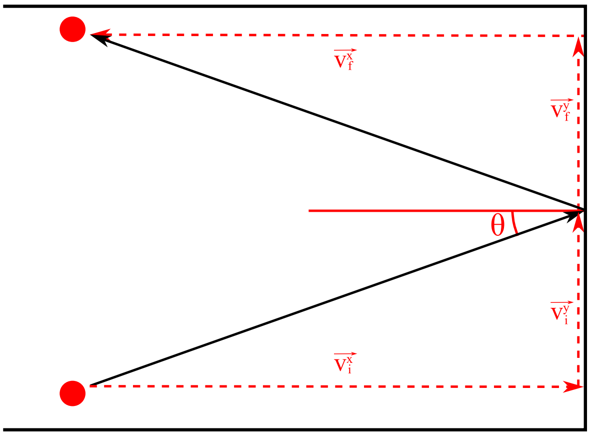
- Ⓐ : Inertial referential; before collision
- Ⓑ : Piston referential; before collision
- Ⓒ : Piston referential; after collision
- Ⓓ : Inertial referential; after collision

Irreversible process

Particle collision prior to piston removal:



The same particle if the piston has vanished before collision. The particle instead collides with the vessel wall.



The collision is elastic and in both cases:

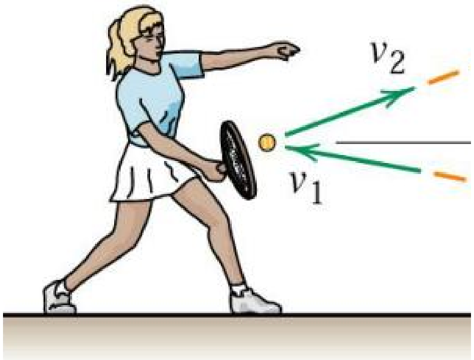
$$\left\{\begin{matrix}\vec{v}^f_y = \vec{v}^i_y\\ \vec{v}^f_x = -\vec{v}^i_x\end{matrix}\right.$$

If we now compute the particle kinetic energy we have, in the inertial referential:

- $E_i = 1/2m_i \left[\left(v_x^i\right)^2 + \left(v_y^i\right)^2 \right]$
- $E_f = 1/2m_i \left[\left(-v_x^i + 2v_p\right)^2 + \left(v_y^i\right)^2 \right]$

Since we know that $\left(-v_x^i + 2v_p\right)^2 < \left(v_x^i\right)^2$ we have $E_f < E_i$, the particle will lose kinetic energy while colliding with the piston which is moving away.

(Think about the tennis player that may imprint a velocity change to the tennis ball by modulating the velocity of the racket)



Summing for all the particles:

$$U_f = \sum_n \frac{1}{2} m_n \left(v_n^f\right)^2 < \sum_n \frac{1}{2} m_n \left(v_n^i\right)^2 = U_i$$

$$\boxed{dU < 0; \quad dW > 0}$$

(1^{st} Law)

And the corresponding kinetic energies are:

$$\begin{aligned} E_i &= 1/2m_i \left[\left(v_x^i\right)^2 + \left(v_y^i\right)^2 \right] \\ &= 1/2m_i \left[\left(-v_x^i\right)^2 + \left(v_y^i\right)^2 \right] \\ &= E_f \end{aligned}$$

Summing for all the particles:

$$U_f = \sum_n \frac{1}{2} m_n \left(v_n^f\right)^2 = \sum_n \frac{1}{2} m_n \left(v_n^i\right)^2 = U_i$$

$$\boxed{dU = 0; \quad dW = 0}$$

(1^{st} Law)

If we invoke the equipartition theorem[2]:

$$\begin{aligned} U &= N\langle K \rangle \\ &= \frac{1}{2} N k_B T \\ &= \frac{1}{2} nRT \end{aligned}$$

Temperature T will decrease for the reversible process but will stay constant for the irreversible process!

6.6 Specific Heat at constant pressure and constant volume

Reminder: We have previously defined the heat capacity of a given substance as the quantity of heat δQ necessary for raising its temperature

[2] with $\langle K \rangle$ the average particle kinetic energy

by ΔT:

$$C[\mathrm{J/K}] = m[\mathrm{Kg}] \times c[\mathrm{J/KgK}] = \frac{\Delta Q}{\Delta T},$$

where c is the specific heat of a substance.

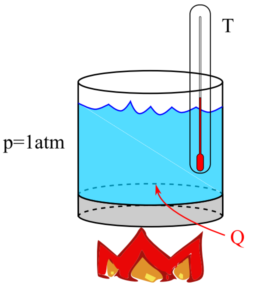
For a gas/liquid, this corresponds to the **specific heat at constant pressure**.

Using molar units we may write

$$n[\mathrm{mol}]C_p[\mathrm{J/molK}] = \frac{\Delta Q}{\Delta T},$$

or

$$\mathrm{d}Q = nC_p\mathrm{d}T \tag{6.10}$$



Boiling water on the stove is a constant pressure process

Let us now determine the **specific heat at constant volume**[3].

Since the Volume V is constant; $\mathrm{d}V = 0$ we have $W = 0$ ($\int p\mathrm{d}V = 0$).

$$\mathrm{d}U = \mathrm{d}Q - \cancel{\mathrm{d}W} = nC_v\mathrm{d}T$$

which simplifies to

$$\mathrm{d}U = nC_v\mathrm{d}T \tag{6.11}$$

Considering the 1^{st} Law:

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}Q - \mathrm{d}W \\ &= \mathrm{d}Q - p\mathrm{d}V\end{aligned}$$

Substituting the term $\mathrm{d}U$ by Eq. 6.10, and the term $\mathrm{d}Q$ by Eq. 6.12,

$$nC_v\mathrm{d}T = nC_p\mathrm{d}T - p\mathrm{d}V \tag{6.12}$$

We will now differentiate the ideal gas law]using the differentiation by parts rule for the pV term, $(uv)' = u'v + uv'$:

[

$$\begin{aligned}pV &= nRT \;\longrightarrow \\ V\mathrm{d}p + p\mathrm{d}V &= nR\mathrm{d}T\end{aligned}$$

and through rearranging we obtain

$$\begin{aligned}pV &= nRT \;\longrightarrow \\ p\mathrm{d}V &= nR\mathrm{d}T - V\mathrm{d}p\end{aligned}$$

Now lets remember that we are working in the scope of a reversible process, and that there isn't any heat transfer to the system. It stems from the 1^{st} Law that

$$\mathrm{d}U = \cancel{\mathrm{d}Q} - \mathrm{d}W$$

We may also remember that for an ideal gas, and considering the equipartition theorem, the gas energy will only depend from its Termperature T, $\langle E\rangle = N/2k_BT$.

We accordingly write

$$\begin{aligned}\mathrm{d}W &= -f(T) \\ \mathrm{d}W &= nR\mathrm{d}T - V\mathrm{d}p\end{aligned}$$

[3] in the assumption of an ideal gas

dW only depends from T, hence $-V\mathrm{d}p = 0$, and therefore

$$\mathrm{d}W = p\mathrm{d}V = nR\mathrm{d}T$$

We now may substitute the above relation in Eq. 6.11:

$$\cancel{n}C_v\cancel{dT} = \cancel{n}C_p\cancel{dT} - \cancel{n}R\cancel{dT}$$

$$\boxed{C_p = C_v + R} \tag{6.13}$$

We now have a very simple relationship correlating the specific heats at constant pressure and constant volume, for the specific case of an ideal gas.

6.6.1 Enthalpy

(Text extracted from *Schröder, "An introduction to Thermal Physics", Oxford, 2021*)
Constant-pressure processes occur quite often, both in the natural world and in the laboratory. Keeping track of the compression-expansion work done during these processes gets to be a pain after a while, but there is a convenient trick that makes it a bit easier. Instead of always talking about the *energy* content of a system, we can agree to always add in the work needed to make room for it (under a constant pressure, usually 1 atm). This work is pV , the pressure of the environment times the total volume of the system (that is, the total space you would need to clear out to make room for it). Adding pV onto the energy gives a quantity called the enthalpy, denoted H:

$$H = U + pV. \tag{6.14}$$

This is the total energy you would have to come up with, to create the system out of nothing and put it into this environment (see Fig. below).. Or, put another way, if you could somehow annihilate the system, the energy you could extract is not just U, but also the work (pV) done by the atmosphere as it collapses to fill the vacuum left behind.

To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to pV , to push the atmosphere out of the way to make room. The total energy required is the enthalpy, $H = U + pV$.

Nomenclature

Variables:

- A: Area [m^2]
- E: Energy of a system [J]
- F: Force [N]
- E_m: Mechanical Energy [J]
- H: Enthalpy $H = U + pV$ [J]
- K: Kinetic energy [J]
- m: Mass [Kg]
- M: Molar Mass [g/mol]
- N: Number of particles [-]
- n: Number of moles $n = N/N_a$ [mol]
- p: Pressure [Pa]
- Q: Heat [J]
- T: Temperature [K]
- t: Time [s]
- v: Velocity [m/s]
- V: Volume [m^3]
- W: Work [J]

- x: Length [m]

- C: Heat Capacity [J/K]
- c: Specific Heat of a substance [J/KgK]
- C_p: Molar Specific Heat at Constant Pressure [J/molK]
- C_v: Molar Specific Heat at Constant Volume [J/molK]

Constants:

- $k_B = 1.3806488 \times 10^{-23}$ [J/K]: Boltzmann Constant
- $N_A = 6.02214076 \times 10^{23}$ [mol^{-1}]: Avogadro Number/Constant
- $R = 8.31447$ [J/molK]: Universal Gas Constant

Acronyms, subscripts and superscripts

- i: initial
- f: final
- p: piston
- w: wall
- x: x coordinate [m]
- y: y coordinate [m]

Chapter Summary

- State diagrams $p-V$, $p-T$ and $p-V-T$ for ideal and real gases (van der Waals).
- State diagrams for substances (solid, liquid, gas).
- 1^{st} Law of Thermodynamics: $dE = dQ - dW$; $dE/dt = \dot{Q} - \dot{W}$.
- Isothermal Expansion, Joule Free Expansion.
  - Work performed by a fluid in a reversible process: $W = \int p dV$
- Heat Capacities at Constant Volume C_v and Constant Pressure C_p.
  - $dQ = nC_p dT$
  - $dU = nC_v dT$
  - $C_p = C_v + R$

Recommended readings

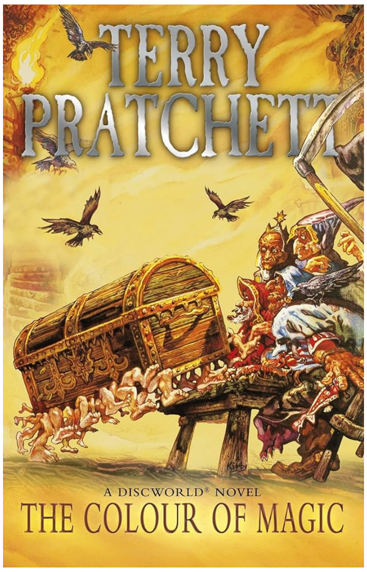
- Blundell, "*Concepts in Thermal Physics*" [5], Chapter 11.
- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [7], for Chapters 2.3, 3.2, 3.3, 3.4, 3.9.

Thermodynamics and Culture: Relevant Works

Chapter 6 introduces a key concept of Thermodynamics: the Energy Conservation Law (1^{st} Law). A relevant literary work is

Terry Pratchett, "*The Colour of Magic*", 1983,

a fantasy romance, the first of the Discworld series. The book satirizes fantastic adventures book tropes in the same way that the book "*The Hitchhiker's Guide to the Galaxy*" satirizes science-fiction book tropes.



We usually say that Magic is impossible in the real worls since it does not abide by the Laws of Thermodynamics (things appear out of nothing; we separate heat and cold; there is no conservation of energy, etc. . .). Terry Pratchett reconciles Magic and Thermodynamics by stating the **Law of Conservation of Reality**: "*the effort required for an action using a spell must be equal to the force required to perform the action using more conventional means*".

Some examples:

- For instance, when a wizard wishes to levitate to the top of the Tower of Art, he must remove a rock from the tower's crumbling top to do so.
- Making an illusion of a glass of wine (or anything else) is easy- it's just manipulating light- but actually creating a glass of wine takes much more power. (energy!).

How about that! Magic and Thermodynamics can be compatible!

6.A Appendix: The Birth of the 1st Law

6.A.1 State-of-the-art prior to Mayer and Joule

Prior to *Mayer* and *Joule*, the caloric theory, which held that heat could neither be created or destroyed had dominated thinking in the science of heat since introduced by *Antoine Lavoisier* in 1783 [1].

This theory had already been questioned, even prior to Mayer and Joule, most notably following the observations of Benjamin Thompson, Count Rumford, regarding frictional heat generated by boring cannon at the arsenal in Munich, Bavaria, circa 1797. Rumford immersed a cannon barrel in water and arranged for a specially blunted boring tool. He showed that the water could be boiled within roughly two and a half hours and that the supply of frictional heat was seemingly inexhaustible [2].

6.A.2 The 1st Law of Thermodynamics: Original publications by Mayer and Joule

The First Law of Thermodynamics was independently formulated by *Julius Robert von Mayer* in 1842 and *James Prescott Joule* in 1843 in a series of articles and reports that firstly described the concept of equivalence of Heat and Mechanical Energy.

- The 1842 article from *Julius Robert von Mayer*, originally published on the German journal "*Annalen der Chemie*" (Ref. [3]), and later translated to English in 1862, in the British journal "*Philosophical Magazine*" (Ref. [4]). Here Mayer put forward the idea that heat and work are equivalent.
- The 1843 article from *James Prescott Joule*, initially rejected by the "*Royal Society*" and subsequently published in the British journal "*Philosophical Magazine*" (Ref. [5])[4].

[4] By 1840–1841 *Joule* had already attained a crude understanding on the relation between current, electric resistance and heat generation [6], owing to its prior experiments which led to the discovery of the so-called "*Joule effect*" in electricity [7].

6.A.3 Quantitative Determination of the Mechanical Equivalent of Heat

- In his booklet "*Die Organische Bewegung im Zusammenhang mit dem Stoffwechsel*" (The Organic Movement in Connection with the Metabolism, Ref. [8]) Mayer proposes a numerical value of the mechanical equivalent of heat: at first as 365 kgf m/kcal (3.579 kJ/kcal), later as 425 kgf m/kcal (4.168 kJ/kcal).
- The first attempts by Joule at measuring the mechanical equivalent of heat were met with a large scatter of the predicted values (from 587 ft lbf/Btu to 1040 ft lbf/Btu, corresponding to 3.161–5.600 kJ/kcal, see Ref. [5]) making it impossible to establish the proportionality between mechanical work and heat production [6]. Within the course of a few years, he was able to significantly improve his famous paddle-wheel experiment, refining its value to 819 ft lbf/Btu, corresponding to 4.404 kJ/kcal in 1845 [9], before achieving a final, more accurate value of 772.692 ft lbf/Btu, corresponding to 4.150 kJ/kcal in 1850 [10], very close to the real value

(within 0.6%). Joule also provided an estimate of the value for the mechanical equivalent of heat of 1034 ft lbf/Btu from Thompson's publication [2]. This has been criticised on the grounds that Thompson's experiments lacked systematic quantitative measurements.

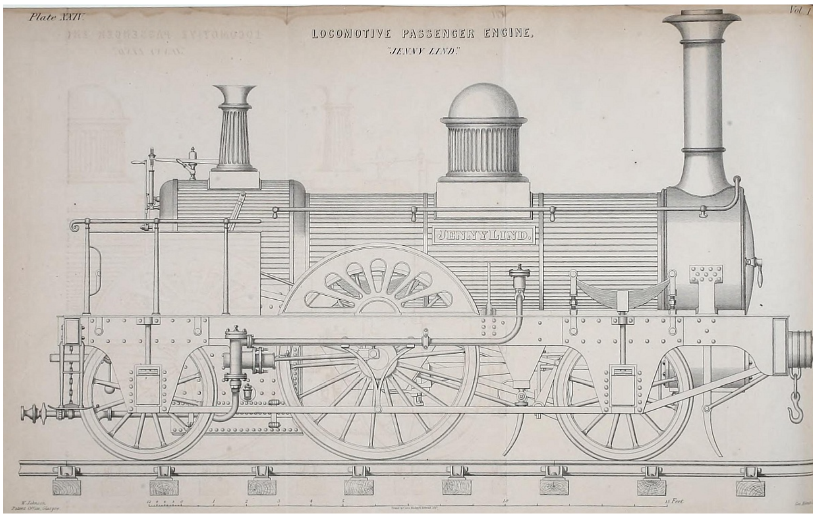
- The modern values are 4.184 kJ/kcal (426.6 kgf m/kcal) for the thermochemical calorie and 4.1868 kJ/kcal (426.9 kgf m/kcal) for the international steam table calorie.

6.A.4 State-of-the-art for Steam Engines in 1850

Thermodynamics is a rather unique discipline in the sense that its working principles were experimentally discovered and developed to a great refinement before even most of the theoretical framework was available.

So what was the state-of-the-art for steam engines at the time that something as fundamental for Thermodynamics as the **1st Law** was discovered? Answer: The *Jenny Lind* locomotive.

The *Jenny Lind* (named after one of the first worldwide famous music stars, the Swedish Opera singer *Jenny Lind*) was built in 1847 and was the first mass-produced locomotive. With a tractive effort of 28.36 kN (or 2.9 Ton). This locomotive had a great degree of sophistication, specially taking into account that very little was known of the theoretical basis of Thermodynamics at the time[5].



[5] Not quite true actually. As we will see in the extra lecture about the history of thermodynamics, a few concepts of this discipline were already quite mature, although the foundations were still lacking!

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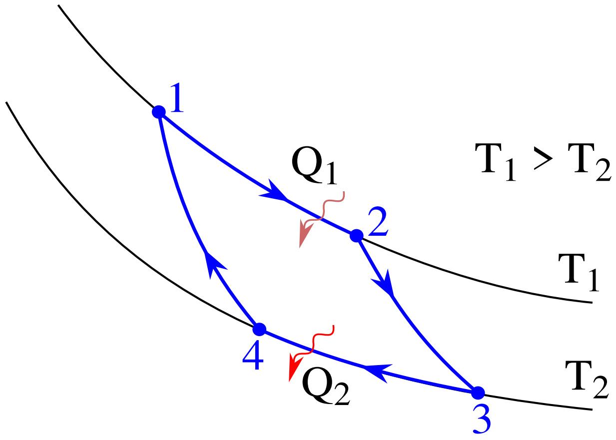


9 Fundamental Thermodynamic Processes and Machines

9.1 Examples of Thermodynamic Processes

9.1.1 Isobaric Process (constant pressure)

$p = const$. This process is **reversible**.

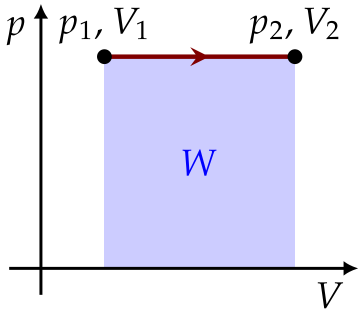
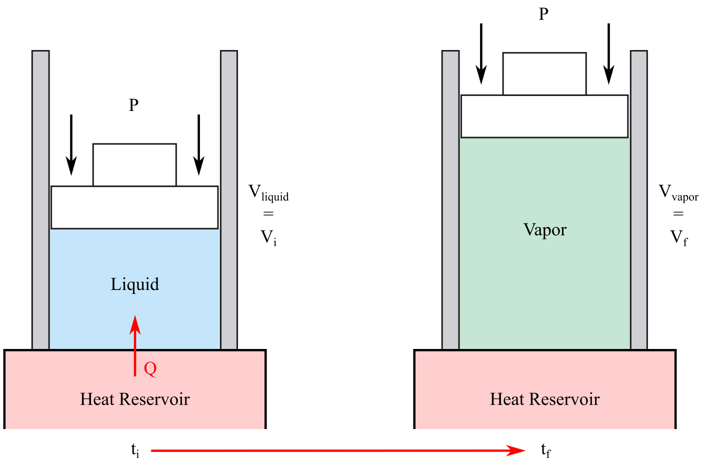


Figure 9.1: Isobaric process; pV diagram

$$W_{i\to f} = p\int_{V_i}^{V_f} \mathrm{d}V = p(V_f - V_i)$$

Example: Vaporization of water at constant pressure $p = const$.



For the process $i \longrightarrow f$, we heat the water and move the piston upwards. We may write for m grams of water:

$$\Delta U = Q - W = m\lambda_{vap} - p(V_{vap} - V_{liq}),$$

with λ_{vapor} the latent heat of vaporization for 1 g of water.

9.1.2 Isochoric Process (constant volume)

$V = const$. This process is **reversible**.

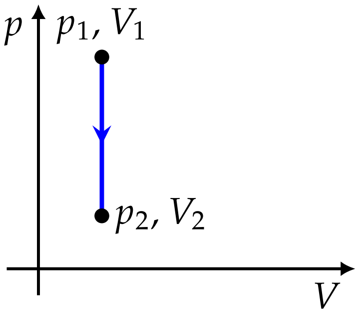
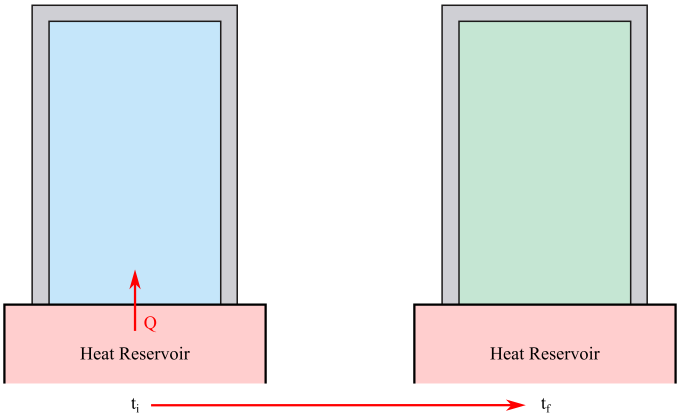


Figure 9.2: Isochoric process; pV diagram

$$W_{i\to f} = \int_{V_i}^{V_i} p\mathrm{d}V = p(V) \times \cancelto{0}{(V_i - V_i)} = 0$$

Example: Heating of a gas in a closed volume ($V = const.$)



9.1.3 Adiabatic Process (without heat transfer)

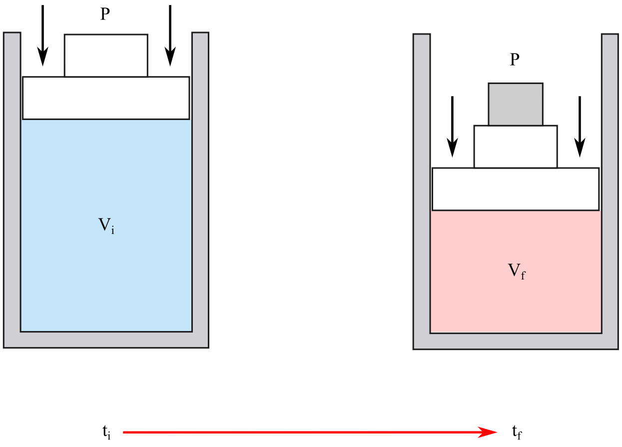
Without heat transfer.

$$Q = 0 \quad \Rightarrow \quad \Delta U = \overset{0}{\cancel{Q}} - W \quad \longrightarrow \quad U_f - U_i = -W_{i\to f}$$

The process may be reversible or irreversible! If the process is reversible:

$$W_{i\to f} = \int_{V_i}^{V_f} p\mathrm{d}V$$

Example: Adiabatic compression



- For the process $i \longrightarrow f$: Adiabatic compression

  $W_{i\to f} < 0 \quad \longrightarrow \quad \Delta U > 0$ and $\underline{\text{usually}}^*$ $T_f > T_i$: **the gas heats**

- For the process $i \longleftarrow f$: Adiabatic expansion

  $W_{f\to i} > 0 \quad \longrightarrow \quad \Delta U > 0$ and $\underline{\text{usually}}^*$ $T_f > T_i$: **the gas cools**

*: Light gases like H_2 and He have the opposite behavior. This is dangerous in the case of H_2 because when you expand the gas from a bottle it heats instead: H_2 + heat + air = BOOM!

9.1.4 Isothermal Process (constant temperature)

$T = const.$

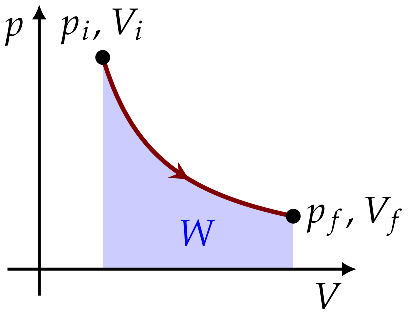
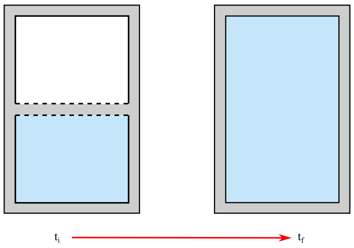


Figure 9.3: Isothermal process; pV diagram

For an ideal gas $U = U(T)$, therefore $\Delta U = 0 \;\longrightarrow\; \mathrm{d}'Q = \mathrm{d}'W$

Any energy that enters as heat is converted to work.

Note: The adiabatic expansion is different from the Joule free expansion ($W = 0$; $Q = 0$; $\Delta U = 0$).



9.2 Reversible Processes for an Ideal Gas

We will now restrict ourselves to the case of an ideal gas[1], ($pV = nRT$). We will also consider all processes into consideration to be reversible.

[1] Not a very harsh restriction... We know that the ideal gas law stands for all the usual temperature and pressure ranges of most thermodynamic machines

9.2.1 Isothermal process

$$T = const. \;\Rightarrow\; nRT = const.$$

$$\boxed{pV = const.} \tag{9.1}$$

9.2.2 Adiabatic process

$$\mathrm{d}Q = 0;\; \mathrm{d}U = \mathrm{d}'Q - \mathrm{d}'W \;\Rightarrow\; \mathrm{d}U = -p\mathrm{d}V$$

Since $\mathrm{d}U = nC_v\mathrm{d}T$ (see Lecture 6), we have:

$$-p\mathrm{d}V = nC_v\mathrm{d}T$$

We now differentiate[2] $pV = nRT$

$$\begin{aligned} V\mathrm{d}p + p\mathrm{d}V &= nR\mathrm{d}T \\ V\mathrm{d}p &= -p\mathrm{d}V + nR\mathrm{d}T \\ &= nC_v\mathrm{d}T + nR\mathrm{d}T \\ &= n(C_v + R)\mathrm{d}T \\ &= nC_p\mathrm{d}T \\ &= nC_v\mathrm{d}T\frac{C_p}{C_v} \\ &= \underbrace{nC_v\mathrm{d}T}_{-p\mathrm{d}V}\,\gamma \\ V\mathrm{d}p &= -p\mathrm{d}V\gamma \end{aligned}$$

with $\gamma = C_p/C_v$.

We may rearrange the above expression to:

$$\boxed{\frac{\mathrm{d}p}{p} = -\gamma\frac{\mathrm{d}V}{V}} \tag{9.2}$$

For an ideal gas, γ will be independent from Temperature in our range of application; roughly $T = [100 - 2000\,\mathrm{K}]$ (see Lecture 3, section 3.1.1, boxed).

We recall the equipartition theorem:

$$E = \frac{N}{2}k_BT \Rightarrow \frac{\mathrm{d}E}{\mathrm{d}T} = C_v = \frac{N}{2}k_B \left(\text{or } C_v = \frac{N}{2}R \text{ in molar units}\right)$$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{\frac{N+2}{2}R}{\frac{N}{2}R} = \frac{N+2}{N}$$

$$\boxed{\gamma = \frac{N+2}{N}} \tag{9.3}$$

- For a **monoatomic gas** with $N = 3$ degrees of freedom (x, y, z):

$$\boxed{\gamma = \frac{5}{3}} \tag{9.4}$$

- For a **diatomic gas** with 2 additional degrees of freedom (unfrozen at about $T = 2 - 90\,\mathrm{K}$), and assuming that vibrations remain frozen up until about $T = 2000\,\mathrm{K}$, we have $N = 5$ and:

$$\boxed{\gamma = \frac{7}{5}} \tag{9.5}$$

If we integrate Eq. 9.2, assuming γ is constant:

$$\int_p^{p_0}\frac{\mathrm{d}p}{p} = -\gamma\int_V^{V_0}\frac{\mathrm{d}V}{V} \Rightarrow \ln\left(\frac{p}{p_0}\right) = -\gamma\ln\left(\frac{V}{V_0}\right) = \ln\left(\frac{V}{V_0}\right)^{-\gamma} = \ln\left(\frac{V_0}{V}\right)^{\gamma}$$

$$\Rightarrow \frac{p}{p_0} = \left(\frac{V_0}{V}\right)^{\gamma} \Rightarrow \boxed{pV^{\gamma} = p_0V_0^{\gamma} = \text{const.}} \tag{9.6}$$

[2] as usual, using the product rule $(uv)' = u'v + uv'$

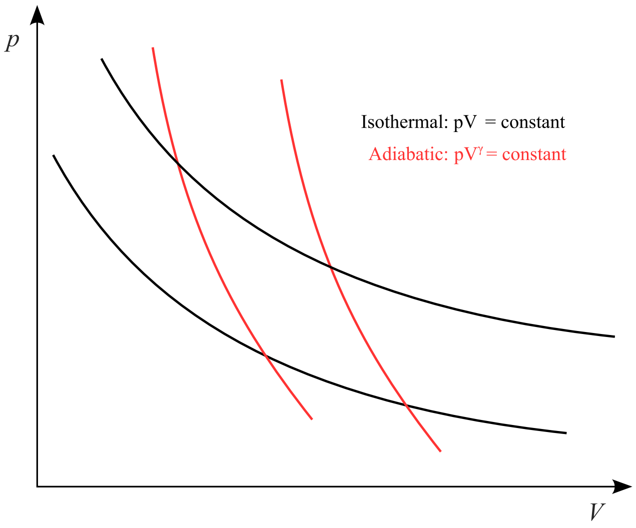


Figure 9.4: Isotherms and Adiabats

Alternatively we may write:

$$
\begin{aligned}
& pV^{\gamma} = p_0 V_0^{\gamma};\; pV = nRT;\; pVV^{\gamma-1} = nRTV^{\gamma-1} \\
& \Rightarrow nRTV^{\gamma-1} = nRT_0 V_0^{\gamma-1} \\
& \Rightarrow \boxed{TV^{\gamma-1} = \text{const.}} \qquad (9.7)
\end{aligned}
$$

Isotherm and adiabat plots at sample temperatures are presented in appendix for an atomic and a molecular gas.

9.3 Work performed trough Reversible Processes for an Ideal Gas

9.3.1 Isothermal process

$$W_{i\to f} = \int_{V_i}^{V_f} p\mathrm{d}V = \int_{V_i}^{V_f} \frac{nRT}{V}\mathrm{d}V = nRT\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = nRT\left[\ln(V_f) - \ln(V_i)\right]$$

For an isothermal, reversible process:

$$\boxed{W_{i\to f} = nRT\ln\left(\frac{V_f}{V_i}\right)} \qquad (9.8)$$

9.3.2 Adiabatic process

We consider $pV^{\gamma} = c_1 = \text{const.}$

$$W_{i\to f} = \int_{V_i}^{V_f} p\mathrm{d}V = \int_{V_i}^{V_f} \frac{c_1}{V^{\gamma}}\mathrm{d}V = c_1\left[\frac{V^{-(\gamma-1)}}{1-\gamma}\right]_{V_i}^{V_f} = \frac{c_1}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right),$$

since $c_1 = p_i V_i^\gamma = p_f V_f^\gamma$:

$$W_{i\to f} = \frac{c_1 V_f^{1-\gamma} - c_1 V_i^{1-\gamma}}{1-\gamma} = \frac{p_f V_f^\gamma V_f^{1-\gamma} - p_i V_i^\gamma V_i^{1-\gamma}}{1-\gamma} = \frac{p_f V_f - p_i V_i}{1-\gamma}.$$

For an adiabatic, reversible process:

$$\boxed{W_{i\to f} = \frac{-\left(p_f V_f - p_i V_i\right)}{\gamma - 1}} \tag{9.9}$$

9.4 Limitations of the 1st Law

According to the 1st Law, as long as energy is conserved, any process is possible. This includes:

- A pot with water, with a flame beneath, transferring its energy to the flame, heating it and cooling the water (to the point that water may even freeze!).
- A marble standing on a surface may have the surface shed some of its heat (the surface cools), and have this heat transformed in work, putting the marble in movement. This is the inverse process of a marble braking to standstill due to friction.

In a general way, the 1st Law allows us to go back on time:

- A glass that falls and shatters into pieces may reintegrate itself and come back to the shelf from where it fell.
- The body of a person deceased one month ago may reconstitute itself and the person may come back to life.
- etc...

Yet, as we already intuitively know, this cannot happen in real life and as such, only a small subset of the cases allowed by the 1st Law actually happen!

(in other terms, most of the processes in our Universe are irreversible processes, such as friction breaking a marble, a shattering glass, or Death.)

We need additional Laws to restrict the physically possible cases!

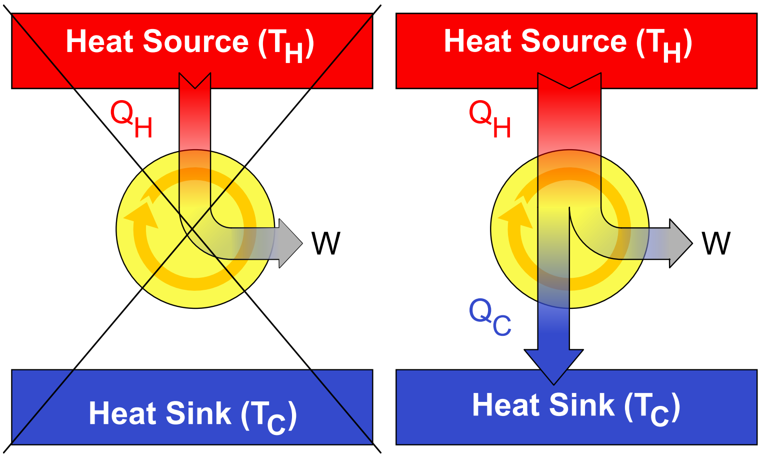
Two different statements were postulated to enforce additional restrictions to the ones derived from the 1st Law:

9.4.1 The Kelvin-Planck Statement

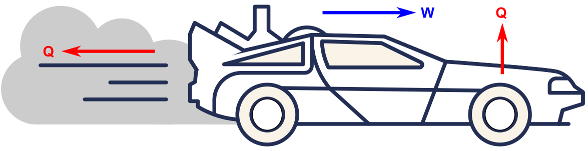
The Kelvin–Planck statement Ⓚ postulates that:

> "*It is impossible to perform a process whose sole effect is removing heat from a thermal reservoir and producing an equivalent quantity of work*"

In its graphical form:



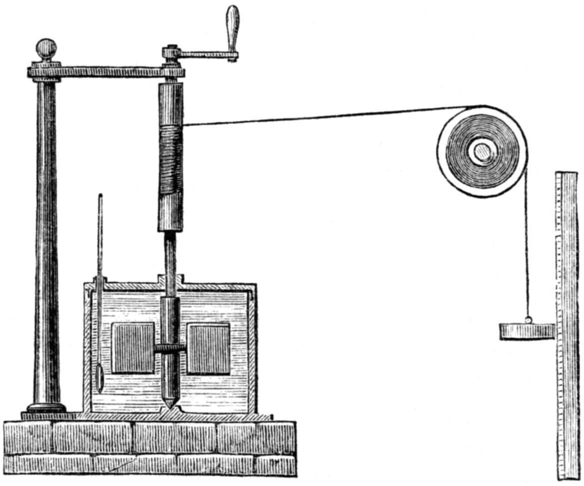
An example of this statement is a car. A car engine is known to dissipate heat besides producing work (plus the heat from the exhaust gases).



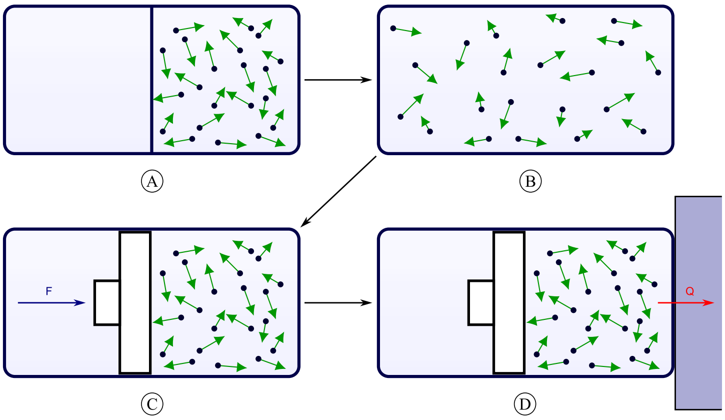
(A more detailed explanation on why we cannot fully convert heat to work is presented in *Cengel, Thermodynamics, and Engineering Approach, 5th Ed, pp. 285: "Can we save* Q_{out}*?".*)

Consequences:

- Friction losses from mechanical work are irreversible (the inverse of Joule's experiment does not occur).



- The Joule free expansion is an irreversible process.



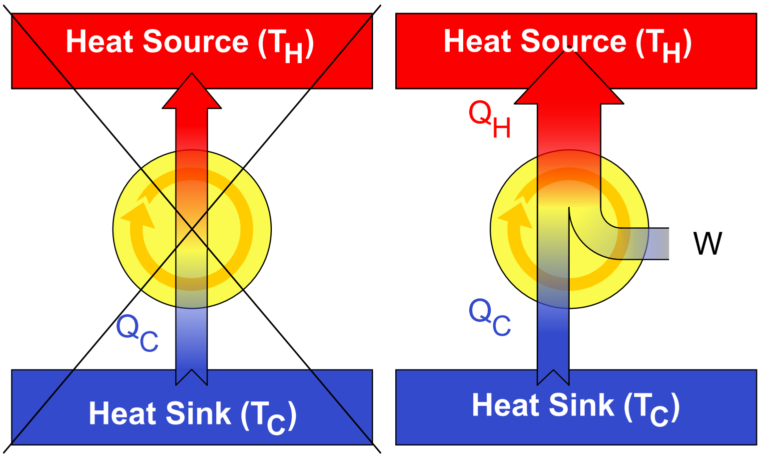
After undergoing a Joule free expansion (process Ⓐ → Ⓑ), returning to the initial Ⓐ state implies performing work on the gas (process Ⓒ) to push it back to the original spatial arrangement, and removing any excess heat if process Ⓒ was carried out faster than an isothermal compression (process Ⓓ).

The Kelvin-Planck statement forbids a so-called "**miracle engine**".

9.4.2 The Clausius Statement

The Clausius statement Ⓒ postulates that:

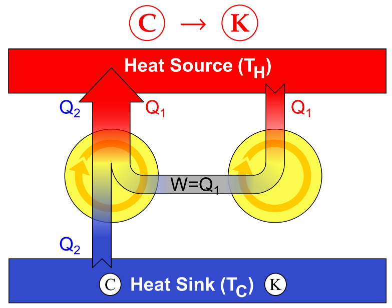
> "*It is impossible to perform a process whose sole effect is transferring heat from a colder body towards a hoter body*"



The Clausius statement forbids a so-called "**miracle refrigerator**", which cools continually without any work input (like plugging the refrigerator to the electric current).

9.4.3 Equivalence of both statements

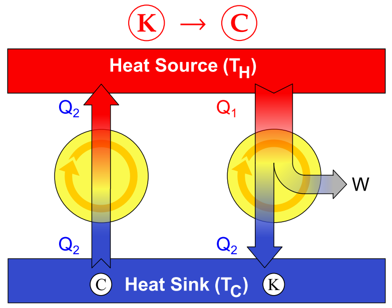
We may demonstrate that both statements are equivalent. To do so we may demonstrate that a violation of one statement implies the violation of the other one. Let us consider the two cases:



Assuming Ⓚ is false:

- We remove heat from the heat source at T_H and we convert this heat in work
- We use this work to power a refrigerator between T_C and T_H which moves heat Q_2 to the source T_1

The only effect is to transfer heat from $T_C < T_H$ to T_H.
(miracle refrigerator)
we determine Ⓒ to be false.



Assuming Ⓒ is false:

- We remove heat Q_2 from the heat sink at T_C to the heat source T_H
- We use an engine between T_H and T_C who gives back exactly Q_2 to the heat source (which is in this case the heat sink)

The only effect is to convert Q_1-Q_2 into work.
(miracle engine)
we determine Ⓚ to be false.

9.5 Heat Engines and Refrigerators

9.5.1 Heat Engine

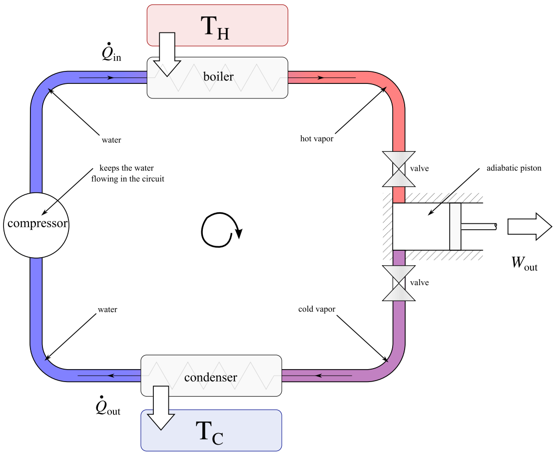
A Heat Engine is a machine that produces work from heat, operating in a cyclical fashion.

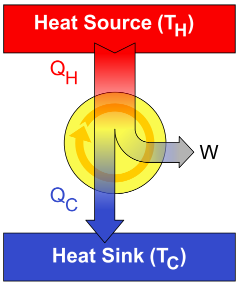
From the Kelvin–Planck statement, we know that this is impossible to achieve with only a heat source. We need at least two thermal reservoirs at different temperatures, or in other terms we need a heat source at temperature T_H and a heat sink at temperature T_C (T_H<T_C).

- Q_H: Heat supplied **to** the system **by** the heat source on each cycle
- Q_C: Heat supplied **by** the system **to** the heat sink on each cycle

1st Law: In a cycle: **W** = $Q_H - Q_C$.

$Q_C > 0$ (since we need the heat sink so as not to violate the Kelvin–Planck statement Ⓚ). Accordingly **W** < Q_H.





Q_C is rejected heat that is not put to any use (it is either dissipated into the atmosphere or taken away by the condenser cooling water. We may note that this rejected heat may still be useful in an industrial process. Think about the many processes that need heat to function! Many times, thermal power plants (fueled by coal, oil or gas) have adjacent factories that make use of such rejected heat in many diverse processes. This is called **Co-generation**.

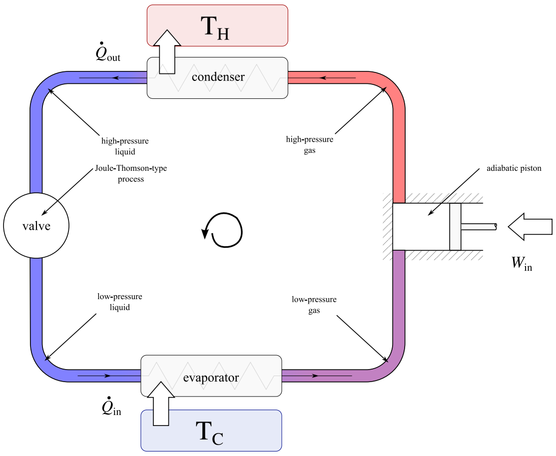
We may now define the efficiency of a heat engine as:

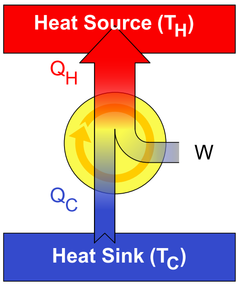
$$\boxed{\eta = \frac{\mathbf{W}}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}} \tag{9.10}$$

9.5.2 Refrigerator

A refrigerator is essentially a heat engine working in the reverse direction (anticlockwise).

$Q_H = \mathbf{W} + Q_C$ since we need to add work to the system ($\mathbf{W} > 0$ so as not to violate the Clausius statement Ⓒ).





A refrigerator will use a working fluid with a high latent heat of vaporization (so that it may transfer large quantities of heat). It is also important that the working fluid be capable of vaporizing at low pressure and condensing at high pressure so that it may vaporize at $T_C < T_H$ at which it condenses.

The efficiency (also called "Coefficient Of Performance" – COP) of a refrigerator is the ratio of the heat Q_C extracted from the cold source and the input work **W**:

$$\boxed{\varepsilon = \frac{Q_C}{\mathbf{W}}} \tag{9.11}$$

Note that the efficiency of a Heat Engine is mandatorily $0 \leq \eta \leq 1$, however the efficiency/COP ε of a refrigerator may be larger than 1 (and it usually is).

9.5.3 Heat Pumps

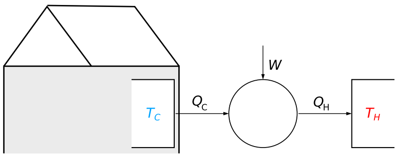
If we look more carefully at the working principle of a refrigerator, we may notice that it represents a quite versatile heat transfer machine, since it is used to remove heat from a given source, and to move it to another sink. We may therefore be interested either in removing heat from a system and flush it to the outside, or instead, in putting heat into a system by taking it from the outside. This is the principle of a heat pump, which is commonly used for heating houses.

Using a heat pump for cooling implies placing the evaporator inside the house, whereas using it for heating implies placing the condenser inside the house. Schematically we have:

Cooling mode:

Efficiency: $\boxed{\varepsilon = \frac{Q_C}{\mathbf{W}}}$

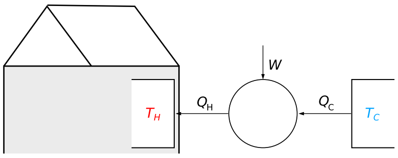
$Q_C = Q_{out}$



Heating mode:

Efficiency: $\boxed{\varepsilon = \frac{Q_H}{\mathbf{W}}}$

$Q_H = Q_{in}$



We note that the circuit of a heat pump might be cleverly designed so as to allow for the pump to work reversibly, or in other terms, by simply switching the direction of the fluid. A more detailed description of a reversible heat pump is presented as supplementary material.

9.6 The Carnot Cycle

This an idealized cycle originally proposed by the French Engineer *Sadi Carnot* (1796–1832) in 1824.

Carnot was concerned with the design of good steam engines, realising that French designs had fallen behind the dominance of British designs after the Napoleonic wars. Carnot was willing to help France achieve a more efficient utilization of steam through more advanced engine designs.

The genius of Carnot's approach was his consideration of a highly idealized process, delving into its physical essence, unlike British engineers who had up to then resorted to a more specific an practical approach, arguing about actual running conditions of steam engines, as well as the merits of low and high-pressure engines, with single or multiple pistons.

The key idea of Carnot was to consider a fully reversible cycle which would incur as little waste/losses as possible. This included:

- Heat absorption Q_H from the Hot Source to be carried out without heat losses. This means that there may not be any heat conduction involved (reminder: $\dot{Q} = kA(T_H - T_C)/L = 0$). This only means to achieve this constraint is to have $\Delta T = 0$, and the heat of the source needs to be absorbed with the engine maintaining the same temperature than the source (**Isothermic Process**). This may only be achieved conceptually, since in practice this means that the process will take an infinite time $t \longrightarrow \infty$ to conclude. You have to raise very slowly the temperature of your heat source to ensure that no temperature gradient with your engine occurs.
- Heat release Q_C to the Cold Sink has to be carried out isothermically for the same reasons.
- For the parts of the cycle where there is a transition between the Hot Temperature T_H and the Cold Temperature T_C, no heat exchange should equally occur. The only possible way to achieve this under the required conditions ($T \neq const.$ and $\dot{Q} = 0$) is to consider a **Reversible Adiabatic Process**[3] where there is no heat exchange (typically a compression or expansion sufficiently fast that there is no time for such a process. Theoretically speaking, it would have to be an infinitely fast process $t \longrightarrow 0$ to achieve these idealized conditions).

This Carnot cycle is presented in detail in Fig. 9.5.

Carnot's Theorem:
*"No machine which operates between a given Hot Source and a given Cold Sink has an efficiency higher than a **Carnot Engine**. All the **Carnot Engines** that operate between the same sources have the same efficiency."*

9.6.1 Efficiency of a Carnot Machine

Let us consider all the 4 steps (not in order) of the Carnot cycle:

[3] why can't we consider an adiabatic process also for the heat exchange part of the process? Answer: because an adiabatic process by definition implies that there cannot be any heat exchange!

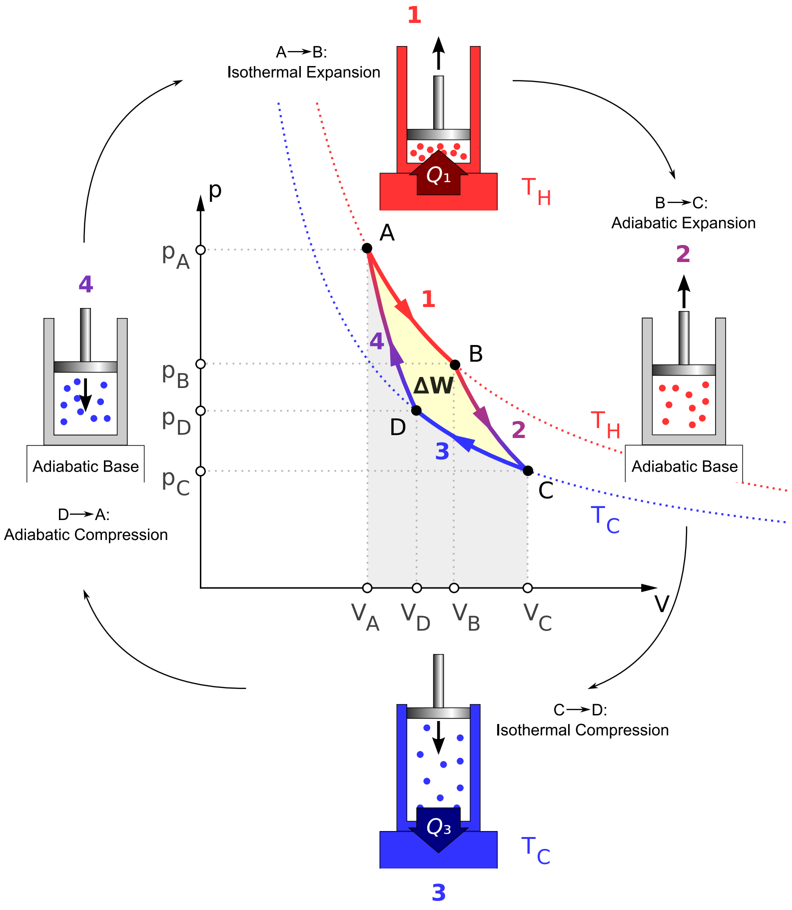


Figure 9.5: Carnot Cycle

- $A \longrightarrow B$: **Isothermal Process, Ideal Gas**
  $T = const. \longrightarrow U = U(T) \longrightarrow \Delta U = 0 \longrightarrow W = Q$

$$Q_H = nRT_H \ln\left(\frac{V_b}{V_a}\right) \tag{9.12}$$

- $C \longrightarrow D$: **Isothermal Process, Ideal Gas**
  $T = const. \longrightarrow U = U(T) \longrightarrow \Delta U = 0 \longrightarrow W = Q$

$$Q_C = nRT_C \ln\left(\frac{V_c}{V_d}\right) \tag{9.13}$$

- $B \longrightarrow C$: **Adiabatic Process, Ideal Gas**
  $V^{\gamma-1}T = const.$

$$V_b^{\gamma-1}T_H = V_c^{\gamma-1}T_C \tag{9.14}$$

- $D \longrightarrow A$: **Adiabatic Process, Ideal Gas**
  $V^{\gamma-1}T = const.$

$$V_a^{\gamma-1}T_H = V_d^{\gamma-1}T_C \tag{9.15}$$

Adjoining Eqs. 9.14 and 9.15 we have:

$$\left(\frac{V_b}{V_a}\right)^{\gamma-1} = \left(\frac{V_c}{V_d}\right)^{\gamma-1} \Leftrightarrow \left(\frac{V_b}{V_a}\right) = \left(\frac{V_c}{V_d}\right) \tag{9.16}$$

The ratio from Eqs. 9.12 and 9.13 is:

$$\frac{Q_H}{Q_C} = \frac{T_H \ln\left(\frac{V_b}{V_a}\right)}{T_C \ln\left(\frac{V_c}{V_d}\right)}$$

Adjoining Eq. 9.16 we may simplify the above expression to:

$$\frac{Q_H}{Q_C} = \frac{T_H \cancel{\ln\left(\frac{V_b}{V_a}\right)}}{T_C \cancel{\ln\left(\frac{V_c}{V_d}\right)}} = \frac{T_H}{T_C}$$

since $\eta = 1 - \frac{Q_C}{Q_H}$ we have:

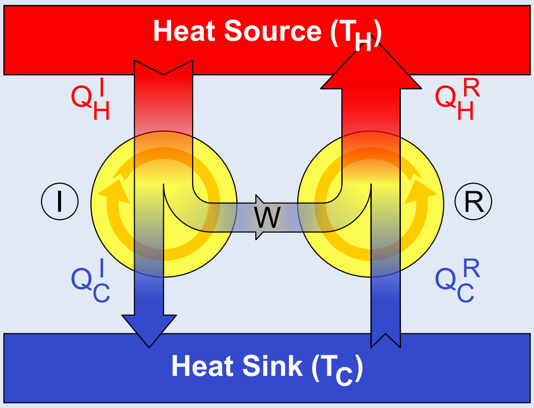
$$\boxed{\eta_{carnot} = 1 - \frac{T_C}{T_H}} \tag{9.17}$$

This expression has two corollaries:

- $\eta < 100\%$ respecting the Kelvin–Planck statement
- $T_H > 0$ by definition and $T_C > 0$ stems from the previous corollary. It is impossible to reach absolute zero

Demonstration of Carnot's Theorem:
Considering a reversible Carnot engine Ⓡ and an hypothetic engine Ⓘ with an efficiency $\eta_I > \eta_R$. The two engines produce the same quantity of work W.

Since the Carnot engine Ⓡ is reversible, we will use the work W produced by I to place Ⓡ working as a refrigerator.



We have[a]:

$$\left.\begin{aligned} W^I_{out} = W^R_{in} &= W \\ \eta_I = \frac{W^I_{out}}{Q^I_H} > \frac{W^R_{out}}{Q^R_H} &= \eta_R \end{aligned}\right\} \text{then } Q^I_H < Q^R_H \tag{9.18}$$

$W^R_{out} \Leftrightarrow = W^R_{in}$ the Carnot machine is reversible

From Eq. 9.18 if we have $Q_H^I < Q_H^R$ then $Q_C^I = Q_H^I - W < Q_H^R - W = Q_C^R$.
Then it follows that $Q_C^R > Q_C^I$.

For this combined machine, for each cycle we would simply have a "miraculous refrigerator" which would transfer heat $Q = Q_C^R - Q_C^I > 0$ from the heat sink at T_C to the heat source at T_H without any Work W input from the outside (since the work W in this case is given from the left "sub-machine" to the right "sub-machine".

A machine with efficiency $\eta > \eta_{carnot}$ cannot exist as it violates the Clausius statement Ⓒ.

---

[a] if $A/B > A/C$ then $B < C$

Nomenclature

Variables:

- A: Area [m^2]
- L: Length [m]
- k: Conductivity [W/mK]
- m: Mass [Kg]
- n: Number of moles $n = N/N_a$ [mol]
- N: Number of particles [-]
- N: degrees of freedom of a gas [-]
- p: Pressure [Pa]
- Q: Heat [J]
- t: Time [s]
- T: Temperature [K]
- U: Energy of a system [J]
- V: Volume [m^3]
- W: Work [J]

- C: Heat Capacity [J/K]
- c: Specific Heat of a substance [J/KgK]
- λ: Latent Heat [J/Kg]
- C_p: Molar Specific Heat at Constant Pressure [J/molK]
- C_v: Molar Specific Heat at Constant Volume [J/molK]
- γ: Specific Heats ratio $\gamma = C_p/C_v$ [-]

- η: Efficiency of an Engine $\eta = W/Q_{in}$ [-]
- ε (COP): Efficiency of a Refrigerator/Heat Pump $\varepsilon = Q_{in,out}/W$ [-]

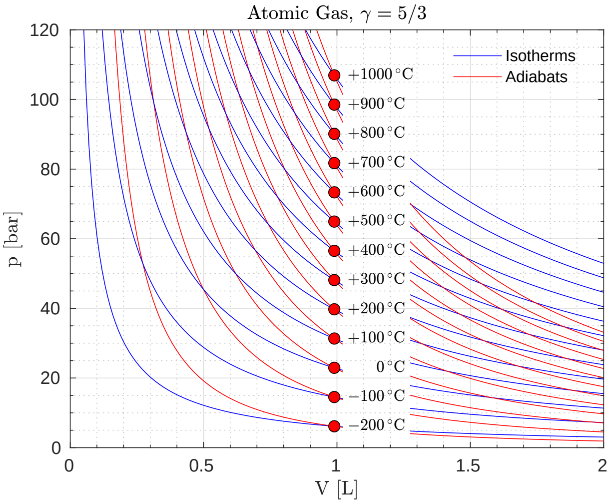
Constants:

- $N_A = 6.02214076 \times 10^{23}$ [mol^{-1}]: Avogadro Number/Constant
- $R = 8.31447$ [J/molK]: Universal Gas Constant

Acronyms, subscripts and superscripts

- C: cold
- H: hot
- i: initial
- f: final
- in: from the outside towards the system
- out: from the system towards the outside
- liq: liquid
- vap: vapor

Appendix: Sample Isotherms and Adiabats



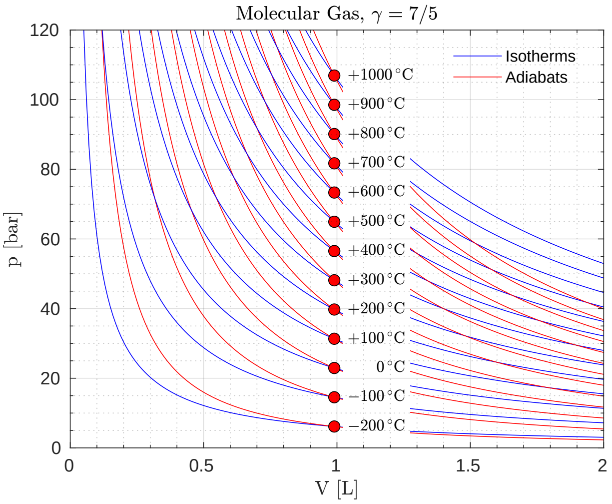


Figure 9.6: Sample isotherms and adiabats for an atomic gas (top) and a molecular gas (bottom)

Chapter Summary

- Isobaric (p =const.); Isochoric (V =const.); Isothermal (T =const.); Adiabatic ($Q = 0$) processes;
- Reversible processes for an Ideal Gas; pV =const. for Isothermal; pV^{γ} =const, $TV^{\gamma-1}$ =const. for Adiabatic;
- Work performed for reversible Isothermal and Adiabatic processes in an Ideal Gas;
- Limitations of the 1st Law;
    - Clausius and Kelvin-Planck statements;
- Heat engine and refrigerator cycles;
    - Efficiencies of heat engines, refrigerators and heat pumps;
- Carnot cycle;
    - Efficiency of a Carnot cycle;
    - Demonstration of Carnot's theorem;
- Efficiency of a Carnot Engine: $\eta = W/Q_{hot} = (Q_{hot} - Q_{cold})/Q_{hot} = 1 - Q_{cold}/Q_{hot} = 1 - T_{cold}/T_{hot}$
- $\mathrm{COP}_{\mathrm{cold}}$ of a Carnot Refrigerator: $\varepsilon = Q_{cold}/W = Q_{cold}/(Q_{hot} - Q_{cold}) = 1/(Q_{hot}/Q_{cold} - 1) = 1/(T_{hot}/T_{cold} - 1)$
- $\mathrm{COP}_{\mathrm{hot}}$ of a Carnot Heat Pump: $\varepsilon = Q_{hot}/W = Q_{hot}/(Q_{hot} - Q_{cold}) = 1/(1 - Q_{cold}/Q_{hot}) = 1/(1 - T_{cold}/T_{hot})$
- $\mathrm{COP}_{\mathrm{hot}} = \mathrm{COP}_{\mathrm{cold}} + 1$

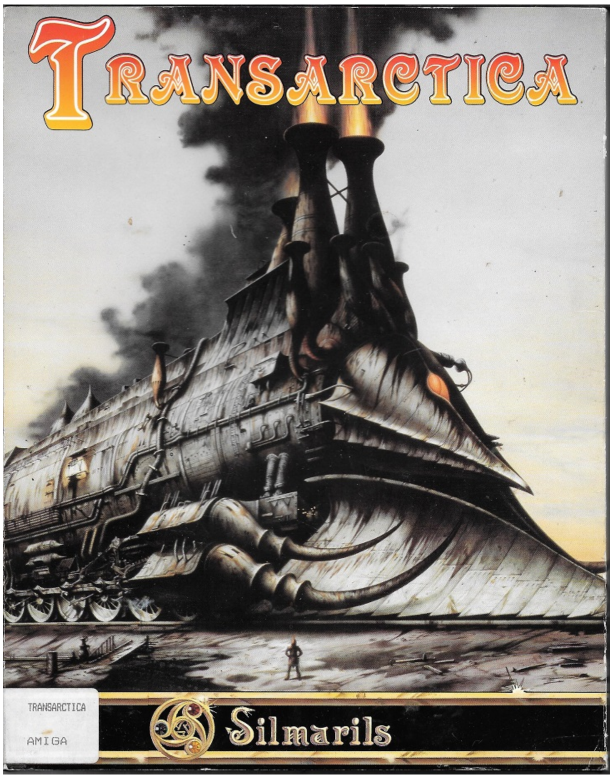
Recommended readings

- Blundell, "*Concepts in Thermal Physics*" [5], Chapters 12, 13.
- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [7], Chapter 5.

Thermodynamics and Culture: Relevant Works

Chapter 9 finally introduces the steam engine, a key invention that powered the Industrial Revolution and enabled new self-powered vehicles such as trains. Our selected literary work will accordingly focus on trains:

Georges–Jean Arnaud, "*The Ice Company*", 1980–2005,



La Compagnie des glaces ("*The Ice Company*") is a series of 97 post-apocalyptic science fiction novels by the French writer Georges-Jean Arnaud, published between 1980 and 2005. It is the longest science fiction work ever published by a single author.

Its setting is the Earth of the far future, Centuries if not millennia later, the planet is entirely covered by ice by −50 °C, under a thick, opaque dust layer caused by an accidental explosion of the Moon. Giant wolf packs roam the frozen wastes, and the mammoth has re-emerged from the elephant stock. The Red Men, genetically transformed humanoids, also survive and thrive under such low temperatures. Mankind ekes out a living in a few handfuls of domed cities governed dictatorially by railroad companies which effectively rule the world, and connected by a network of massive armored trains. Their motto: "No life beyond the rails".

In this dystopian setting, a bunch of ragtag adventurers are going to set up in search of the Sun, beyond the companies grasp.

10 A History of Steam

10.1 A History of Steam

A History of Steam

The Power of Steam is has been known for as far back as the antiquity, more than 2,000 years ago...

Hero/Heron of Alexandria (AD 10–85)

- One of the Greatest Engineers in the history of Mankind. Like Archimedes.
- Lived in Alexandria (in today's Egypt).
- His treatises (**Pneumatica**, **Automata**) described in great detail mechanical inventions by himself and predecessors.
- They are the *Magnum Opus* of Greek Mechanical Science.

Figure 10.1: 17th Century German depiction of Heron

Pneumatica and Automata Treatises

- Hero describes in great detail how to build several mechanical and steam-operated contraptions.
- Many copies of his works lost in the turmoil of the fall of the Western Roman Empire.
- Other copies kept safe in abbeys, or translated by Arabs and reintroduced in Europe during the Renaissance.
- The invention of the printing press later led to the dissemination of many copies.

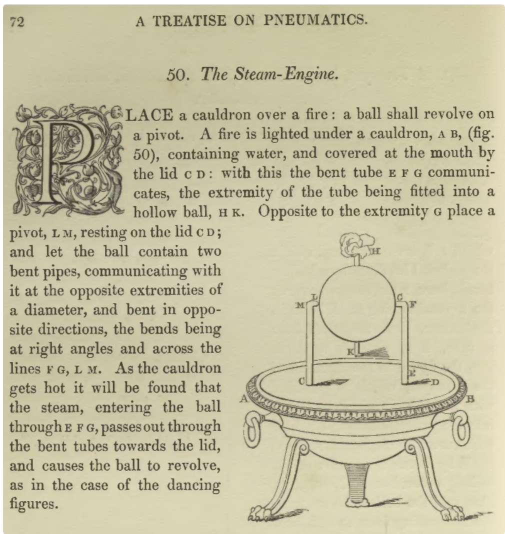
GLI
ARTIFITIOSI
ET CVRIOSI MOTI
SPIRITALI DI HERRONE.
TRADOTTI DA M. GIO. BATTISTA
ALEOTTI D'ARGENTA.
Aggiontoui dal medeſimo Quattro Theoremi
non men belli, & curioſi de' gli altri.
Et il modo con che ſi fà artificioſamente ſalir vn Canale d'Acqua viua, ò morta, in cima d'ogn'alta Torre.

Al Sereniſs.mo Signore D. Alfonso II.
Duca di Ferrara ſuo Signore.

IN FERRARA. MDLXXXIX.
Per Vittorio Baldini, Stampator Ducale.

Figure 10.2: *Pneumatica*, translation to Italian by Bernardino Baldi in 1589

Hero's Book Provides Precise Instructions on How to Build His Machines



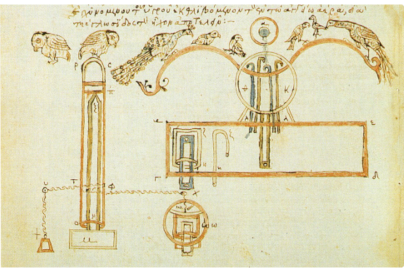
72 A TREATISE ON PNEUMATICS.

50. *The Steam-Engine.*

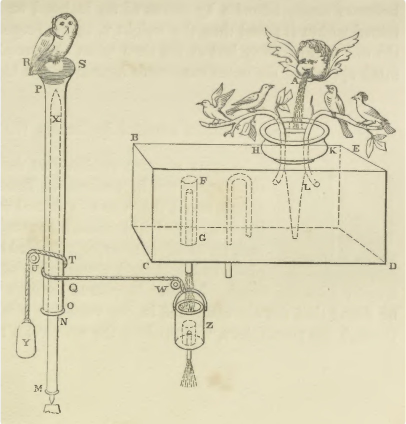
PLACE a cauldron over a fire: a ball shall revolve on a pivot. A fire is lighted under a cauldron, A B, (fig. 50), containing water, and covered at the mouth by the lid C D: with this the bent tube E F G communicates, the extremity of the tube being fitted into a hollow ball, H K. Opposite to the extremity G place a pivot, L M, resting on the lid C D; and let the ball contain two bent pipes, communicating with it at the opposite extremities of a diameter, and bent in opposite directions, the bends being at right angles and across the lines F G, L M. As the cauldron gets hot it will be found that the steam, entering the ball through E F G, passes out through the bent tubes towards the lid, and causes the ball to revolve, as in the case of the dancing figures.

Automaton n°50: Aeolipile with translated instructions

Each Translation Would Propose its Own Schematics Interpreting the Text



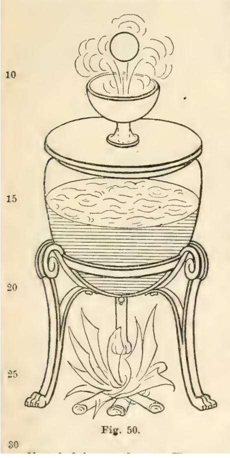
Automaton n°13: 13th Century Illustration



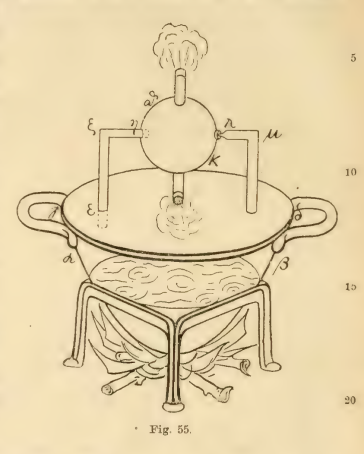
Automaton n°13: 1851 Illustration

- Drawings from the 19th Century are a significant improvement compared to 13th Century drawings.
- One of the key contributions of the Renaissance was the introduction of geometrically based **Perspective**.
- This would prove very important for improving the quality of technical drawings and better communicating ideas.

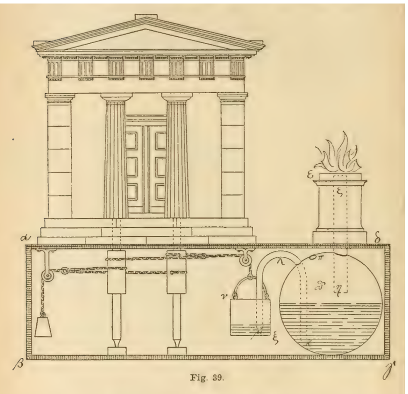
Some Examples of Hero's Steam Engines



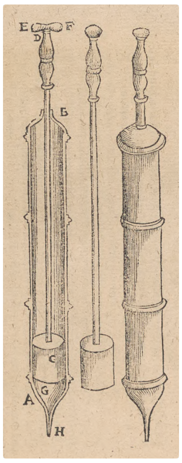
Automaton n°45: Jet stream supporting a sphere



Automaton n°50: Aeolipile

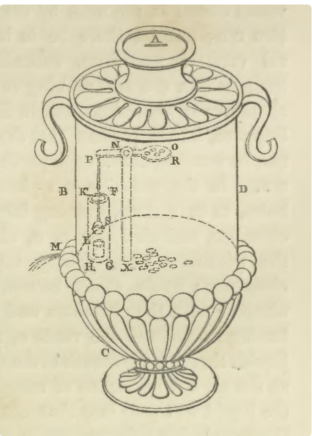


Automaton n°37: Temple doors opened by fire on an altar

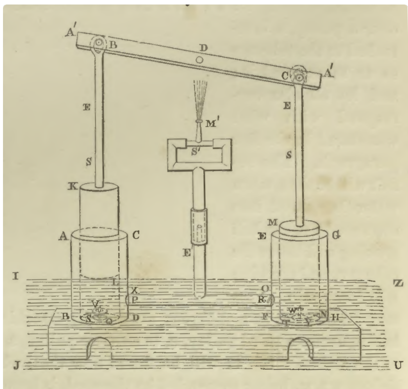


Automaton n°57: Syringe

...and Other Examples of Hero's Genius



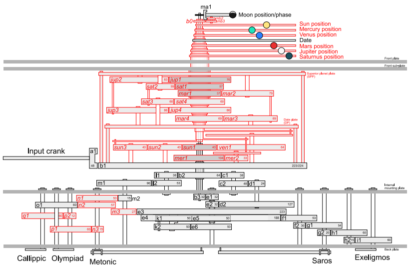
Automaton n°21: The 1st vending machine in the world (!)



Automaton n°27: The 1st fire engine in the world
(only reinvented in the 16th Century)

The Antikythera Mechanism

- **Hand-powered Orrery** (model of the Solar System). A pinnacle of Greek Engineering.
- Mechanism discovered in 1901 on a shipwreck off the coast of the **Antikythera Island**. Built around **200 BC** (Estimated).
- Mechanism examined with modern technology reveals an **astounding level of complexity and craftsmanship** which would not be be rivalled until the astronomical clocks of Richard of Wallingford in the 14th Century.



Why Didn't the Industrial Revolution Occur in Ancient Rome?

Several theories/hypothesis:

- Class-structure explanation:
  - Affluent and literate upper classes occupied with philosophy and physical theory, but little concerned with manufacturing/building, which were left to the lower class artisans and workers.
  - Ready availability of slave labor, making steam engines economically unappealing beyond being novelties/toys.
- Technological explanation:
  - Lack of enabling discoveries (many being achieved in the 17th Century like the concept of vacuum and atmospheric pressure, or Boyle's Law). Old inaccurate theories (Aristotelian belief that motion requires friction or resistance, *Horror Vacui*, etc...).
  - Lack of technological solutions: threaded joints, primitive metallurgy, no precision manufacturing (critical for pistons).
- Epistemological explanation:
  - Ideas needed a lot of time to develop and mature and build up to the rapid pace seen in modern times.
  - Invention of the press and scientific method allowed the faster diffusion of ideas.

Modern Examples of Inventions Ahead of Their Time

The **Concorde** and the **Space Shuttle** once heralded a new era in **Flight** and **Space Exploration**. Yet today, Airplanes or Spacecrafts of this kind can only be found in Museums!

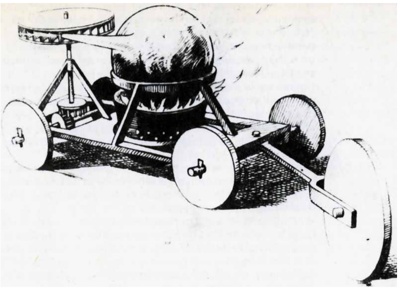
Why Didn't the Industrial Revolution Occur in China?

- Chinese Science and Technology is a key part of the Universal history of Science.
- Amongst many other things, we may outline the *Four Great Inventions*
    - **The Compass:** Traced back to the Warring States period (476–221 BC), when Chinese people utilized a device known as "south-governor"(sïnán 司南) to point in the right direction. First undisputed magnetized needles in Chinese literature appear in 1086.
    - **Gunpowder:** Invented in the 9th Century by Chinese alchemists searching for an elixir of immortality. First described in a formula contained in the Taishang Shengzu Jindan Mijue (太上祖金丹秘) in AD 808.
    - **Papermaking:** Traced back to AD 105. Cai Lun, official in the imperial court during the Han dynasty (202 BC – AD 220), created a sheet of paper using mulberry and other bast fibres
    - **Printing:** Semi-mythical record in the Book of the Southern Qi, in the 480s of Gong Xuanyi – Gong the Sage (玄宣) who was the first printer. The first mention of printing is in an AD 593 imperial decree by the Sui Emperor Wen-ti, who mandates the printing of Buddhist pictures and scriptures. Printing becomes widespread during the Tang dynasty (AD 618 – 906).
- Many inventions did not take hold
    - Example of **Printing**: Printing presses in the Chinese alphabet required much more characters than European ones using the Latin alphabet, making printing less attractive, and precluding the exchange of ideas and the increase of the population literacy.
- Political, Cultural and Economic Factors
    - The **Xuande Emperor** outlawed the building of ocean-going ships in **1432**, at a time when China was the world leader in this domain. **Portuguese Jorge Álvares** is the 1st European to reach China by Sea first in **1513**.
    - Large available workforce mades steam engines economically unattractive.

- Lack of application of the Scientific Method
    - Namely the lack of tradition in making technical drawings.
- Yet, Chinese Science and Technology was one of the enabling factors of the European Industrial Revolution
    - Inventions and Innovations arriving in the Renaissance, in the wake of **Marco Polo** and Arab traders.
    - The **compass** and **gunpowder** would be critical discoveries enabling the **Age of Exploration** (1st globalization event).
    - Later many scientific and cultural exchanges by the hand of the Jesuits in the 16th–17th Centuries.

...but the First Self-Propelled Vehicle in History might have been made in China!

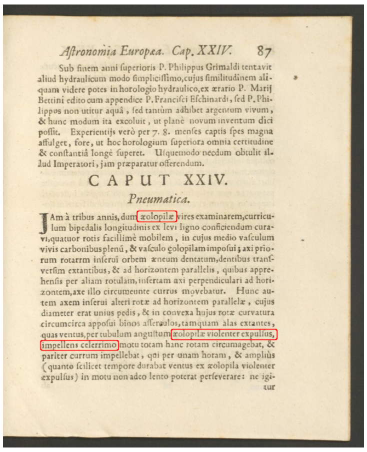
- **Ferdinand Verbiest** (**1623 – 1688**)
- Flemish Jesuit missionary in China during the **Qing dynasty**. Known as **Nan Huairen** (南仁) in Chinese.
    - Accomplished mathematician and astronomer.
    - Proved that European astronomy was more accurate than Chinese astronomy.
    - Corrected the **Chinese calendar**.
    - Asked to rebuild and re-equip the **Beijing Ancient Observatory**.
- Only Westerner in Chinese history to ever receive the honour of a posthumous name by the Emperor.



The steam "car" designed by Verbiest in 1672 from an 18th Century print

The car was a toy made for the Kangxi Emperor – a steam-propelled trolley which was, quite possibly, the first working steam-powered vehicle ("auto-mobile"). It is not verified by other known sources if Verbiest's model was ever built at the time and no authentic drawing of it exists.

Figure 10.3: Ferdinand Verbiest



Aſtronomia Europæa. Cap. XXIV. 87

Sub finem anni ſuperioris P. Philippus Grimaldi tentavit aliud hydraulicum modo ſimpliciſſimo, cujus ſimilitudinem aliquam videre potes in horologio hydraulico, ex ærario P. Marij Bettini edito cum appendice P. Franciſci Eſchinardi, ſed P. Philippus non utitur aquâ, ſed tantùm adhibet argentum vivum, & hunc modum ita excoluit, ut planè novum inventum dici poſſit. Experientijs verò per 7. 8. menſes captis ſpes magna affulget, fore, ut hoc horologium ſuperiora omnia certitudine & conſtantiâ longè ſuperet. Uſquemodo necdum obtulit illud Imperatori, jam præparatur offerendum.

CAPUT XXIV.

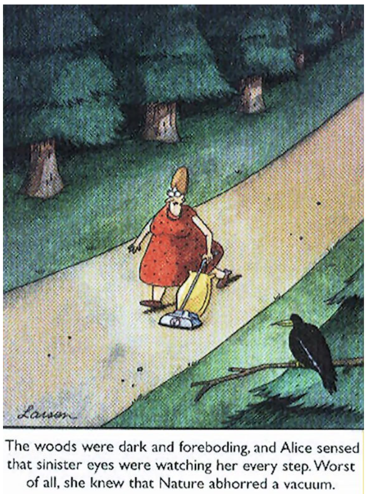
Pneumatica.

JAm à tribus annis, dum æolopilæ vires examinarem, curriculum bipedalis longitudinis ex levi ligno conficiendum curavi, quatuor rotis facillimè mobilem, in cujus medio vaſculum vivis carbonibus plenũ, & vaſculo æolopilam impoſui; axi priorum rotarrm inſerui orbem æneum dentatum, dentibus tranſverſim extantibus, & ad horizontem parallelis, quibus apprehenſis per aliam rotulam, inſertam axi perpendiculari ad horizontem, axe illo circumeunte currus movebatur. Hunc autem axem inſerui alteri rotæ ad horizontem parallelæ, cujus diameter erat unius pedis, & in convexa hujus rotæ curvatura circumcirca appoſui binos aſſerculos, tamquam alas extantes, quas ventus, per tubulum anguſtum æolopilæ violenter expulſus, impellens celerrimo motu totam hanc rotam circumagebat, & pariter currum impellebat, qui per unam horam, & ampliùs (quanto ſcilicet tempore durabat ventus ex æolopila violenter expulſus) in motu non adeo lento poterat perſeverare: ne igitur

Figure 10.4: Ferdinand Verbiest, *Astronomia Europaea*, 1687

Why Did the Industrial Revolution Occur in Europe?

- Continuous innovation after the fall of the Western Roman empire during Medieval Ages (The "*Dark Ages*" concept is a myth dispelled by Historians).
- Multitude of small, warring states. Military and economical competition fosters innovation. Continuous wars in Europe from the Fall of Rome up to 1945.
- Religious Wars and the circulation of printed pamphlets increased literacy in the general population, leading to increased exchanges of ideas.
- This led to the invention of the Scientific Method that brought down obsolete theories (**Aristotelian** Theories) and fostered new ones (**Copernician, Galilean, and Newtonian** revolutions).
- Advances in Physics led to progress in Calculus (logarithms, differentials, integrals).



10.1.1 The Road to Practical, Science-based Steam Engines

Vacuum and Atmospheric Pressure

- **Aristotle** believed that no void could occur naturally (*Horror Vacui*)
  - Vaccum was inconceivable. No point in trying to create it!
- In the 17th Century **Descartes** defined the philosophically modern notion of empty space as a quantified extension of volume.
- **Torricelli's** mercury barometer of 1643 and Pascal's experiments both demonstrated a partial vacuum.

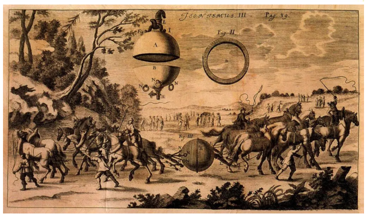


Figure 10.5: Magdeburg experiment, 1654

First Conceptual Steam Engine

- **Denis Papin**, **1690**, publishes design.
- Set architecture of all engines through modern day – Piston moves up and down through cylinder.
- Papin nearly invented the internal combustion engine (propelled by gunpowder) but couldn't get the valves right to vent air.
- Papin's cylinder is propelled by atmospheric pressure, not steam pressure – Work done when steam is condensed and resulting vacuum draws piston down. Work on **downstroke**.
- Papin did not have the mechanical skill to actually build his engine successfully – Couldn't machine the cylinder and piston pressure-tight.

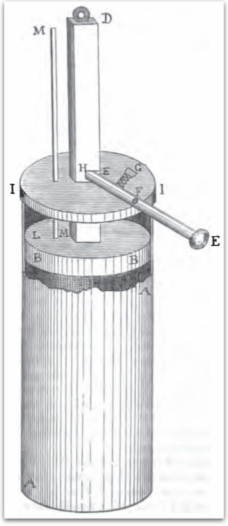


Figure 10.6: Papin's first design, now in Louvre. No patent, no working model.

Great Britain – Where the Steam Engine was Born

- **16th–17th Century pre-industrial energy crisis**.
- World maritime trade, housing construction, mining industry, brought a sharp rise in **deforestation** and wood scarcity.
- **Mineral Coal** for heating was an alternative. Plentiful in Great Britain.
- But also, rainy weather. **Mine flooding** a critical issue.

Steve Hanks, “*Waiting in the Rain*”, Watercolours 2014

First Commercial Use of Steam

“A new Invention for Raiseing of Water and occasioning Motion to all Sorts of Mill Work by the Impellent Force of Fire which will be of great vse and Advantage for Drayning Mines, serveing Towns with Water, and for the Working of all Sorts of Mills where they have not the benefitt of Water nor constant Windes.”

Thomas Savery, patent application filed in **1698** (good salesman, but he was wrong – this can only pump water)

- Essentially a steam-driven vacuum pump, good only for pumping liquids.
- Max pumping height: ~10 m. (atmospheric pressure)
- Efficiency below 0.1% (compare to horses..)
- **Why did anyone buy it? What for?**
- Found immediate use in Scottish and English mines, to pump out water. Fuel was essentially free. 2000 times less efficient than people or animals, but they can’t eat coal.

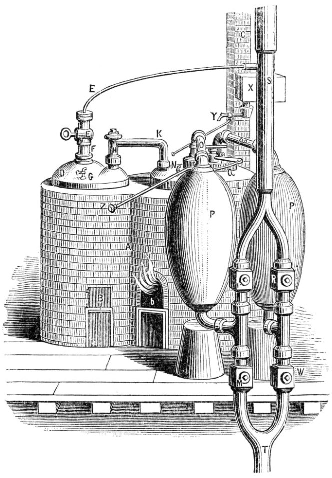


Figure 10.7: The 1698 Savery Engine

First True Steam Engine

- **Thomas Newcomen**, **1712**, blacksmith.
- Copy of 1690 Papin’s engine, piston falling as steam cooled, drawn down by generated low pressure.
- First reciprocating engine: force transmitted by motion of piston.
- Can pump water to arbitrary height.
- Force only on downstroke of piston.
- Very low efficiency: ~ 0.5%.
- Intermittent force transmission.
- In early versions, manually operated valves by the “*plug man*”.

Newcomen’s design is state of the art for 60+ years

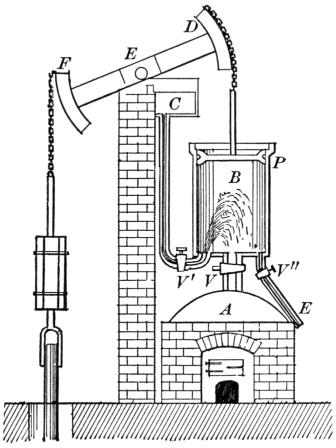
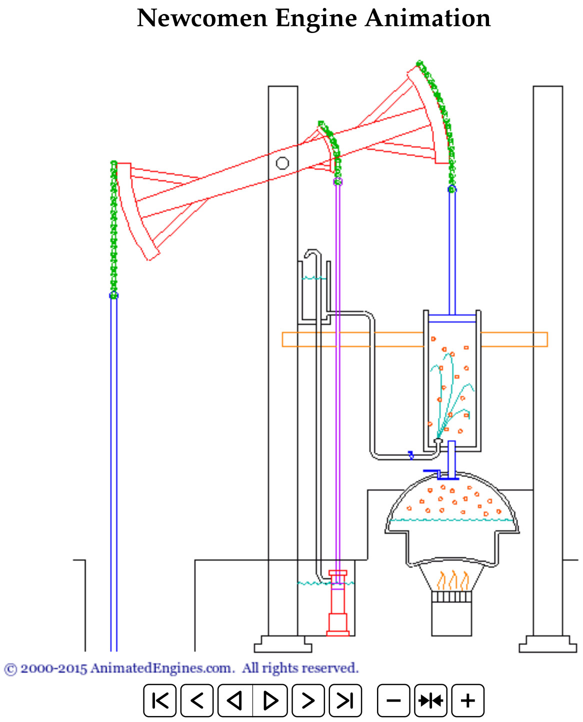


Figure 10.8: Newcomen engine



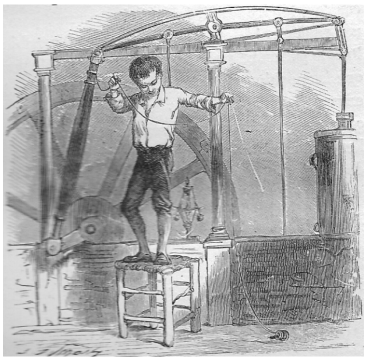


Figure 10.9: Legend that in 1713 a cock boy named Humphrey Potter, whose duty it was to open and shut the valves of an engine he attended, made the engine self-acting by causing the beam itself to open and close the valves by suitable cords and catches (known as the "potter cord").

James Watt Steam Engine

- **James Watt** patents a new design in **1769**, first engines produced in **1774**.
- Introduction of a separate condenser leads to higher efficiencies than in Newcomen's engine:
- There is less wasted heat by removing the need to heat and cool the entire cylinder.
- Watt's improved engine design allows for steam engines to start being introduced to factories (previously relying on hydraulic power) and not just being confined to mines.

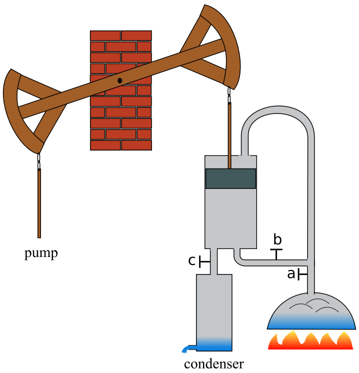


Figure 10.10: Watt engine schematic

James Watt Steam Engine, ctd.

- Higher efficiency: **2%**
- Force only on piston downstroke.
- Intermittent force transmission.
- No rotational motion.

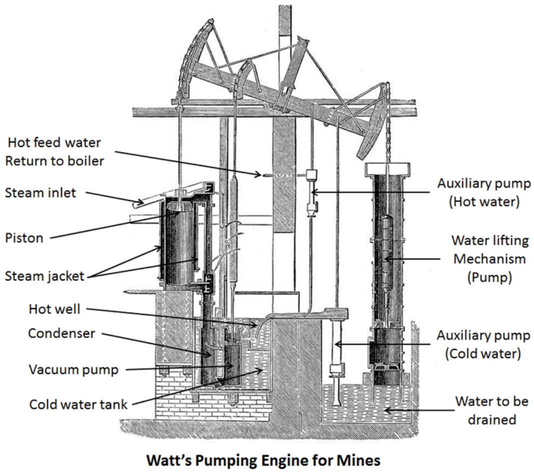
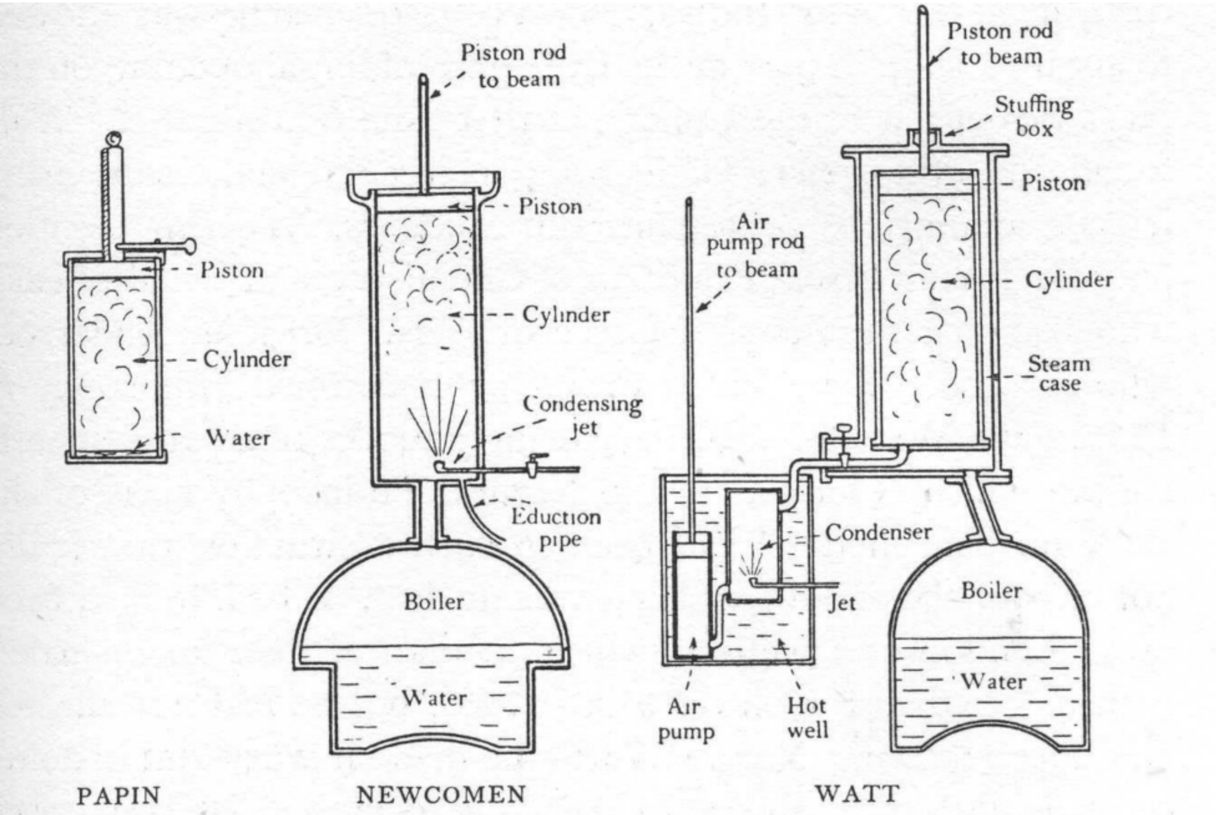


Figure 10.11: Watt engine

One Century of Innovations



Improved James Watt Steam Engine

- **James Watt** improved **1783** design. Albion Mill, London.
- Keeps separate condenser.
- Higher efficiency: ca. **3%**.
- Force on both up- and downstroke.
- Continuous force transmission.
- Rotational motion (**Sun and Planet gearing**).
- **Engine speed regulator** – No need for fancy electronic controls.

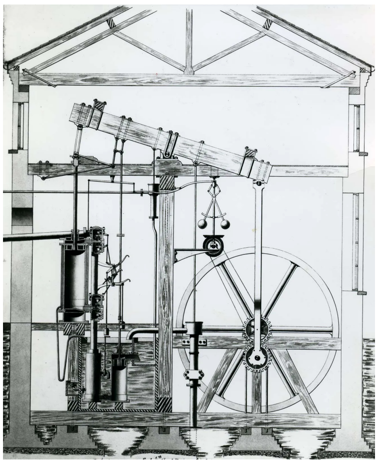


Figure 10.14: James Watt's rotative steam engine with sun-and-planet gear, original drawing, 1788. In the Science Museum, London.

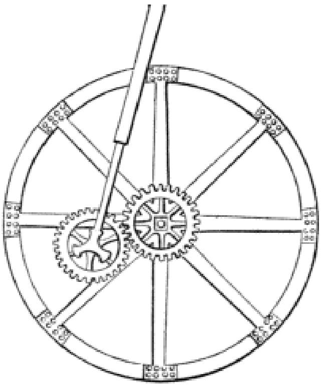


Figure 10.12: Sun and Planet Gear: Converts linear-motion into rotation, mimics a water wheel

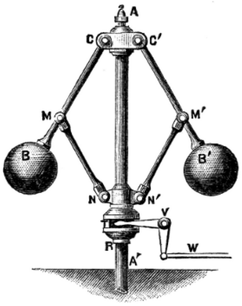


Figure 10.13: The Governor: No need for electronics controls – a mechanical system also works!

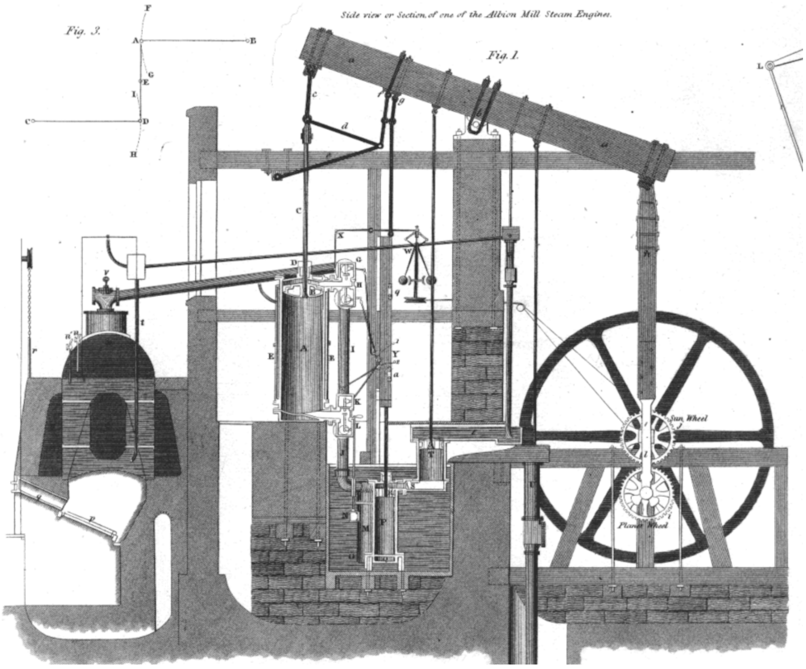
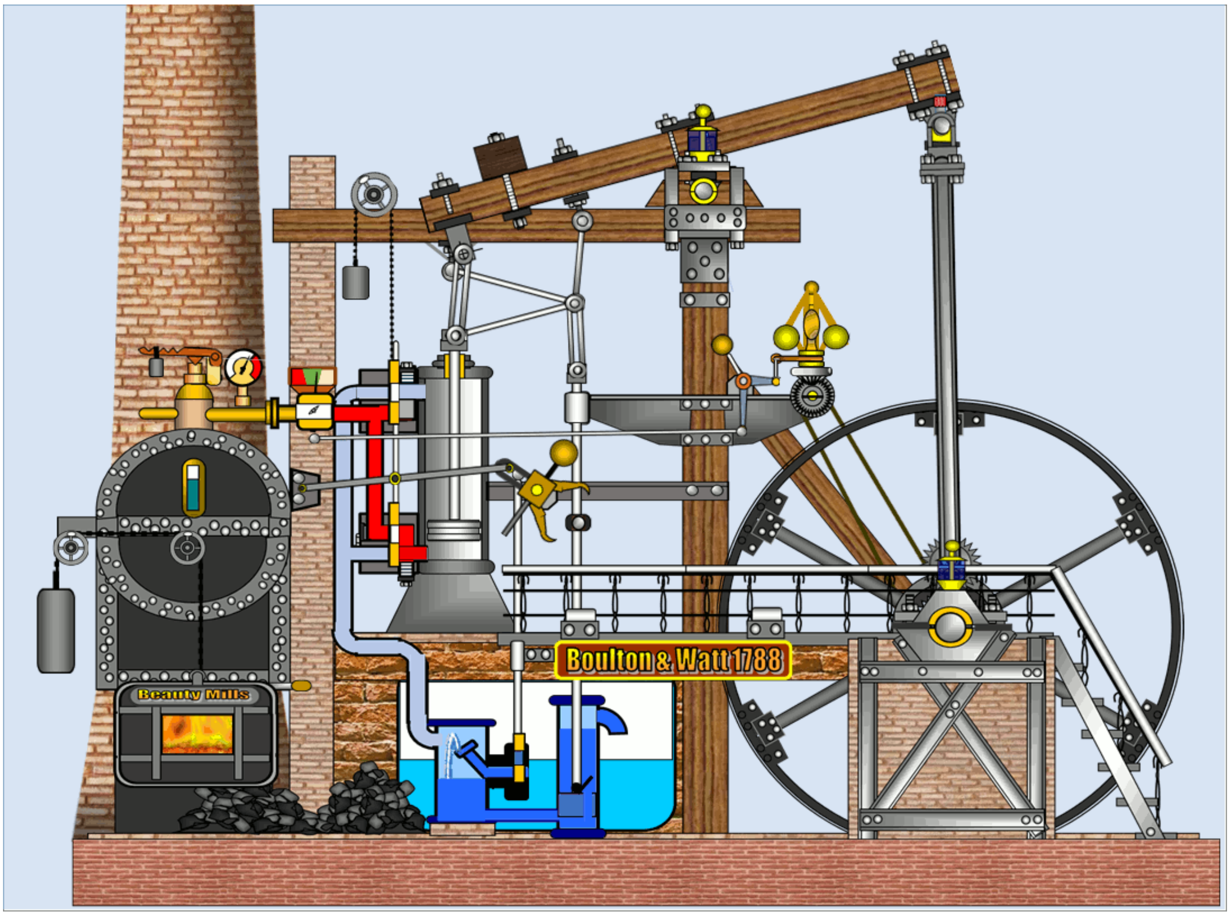


Figure 10.15: Side view of James Watt Albion Mill Steam Engine

Watt Engine Animation



credit: `https://www.k-wz.de/dampfmaschine/`

Double Action Steam Engine

- No vacuum-induced downstroke.
- Piston pushed by steam on both up- and down-stroke.
- Slide valve alternates input & exhaust.
- Steam vented at high temperature.

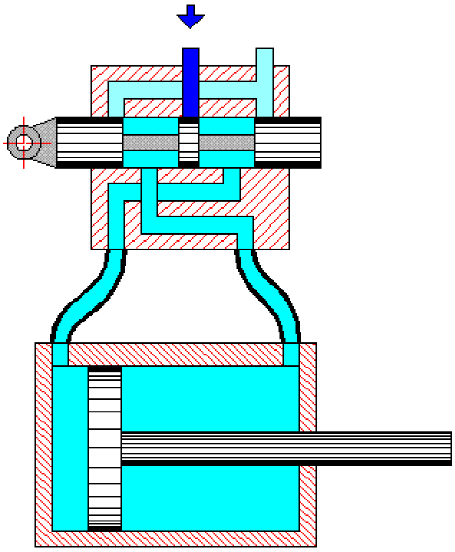


Figure 10.16: Double action piston animation

- **Benefits**
  - **Faster cycle**: No need to wait for condensation. Can get more power, higher rate of doing mechanical work.
  - **Lighter and smaller**: No need to carry a condenser around.
- **Drawbacks**
  - **Inefficiency**: Venting hot steam means you are wasting energy.
  - **High water usage**: Since we lose steam, we have to keep replacing the water.
- **Applications**
  - **Ground transportation**: Enabled the invention of the locomotive.

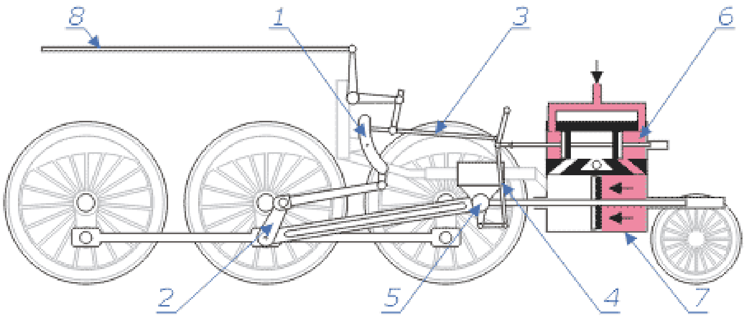


Figure 10.17: Double action piston locomotive

Triple Expansion Steam Engine

- **Benefits**
  - Offsets the drawbacks of the Double Action Engine: Evacuated Steam may be used to power additional pistons, albeit with decreasing energy.
  - More efficient – Conserves Fuel and Water.
- **Drawbacks**
  - Larger and heavier engines (specially if high-power).
- **Applications**
  - Steamships

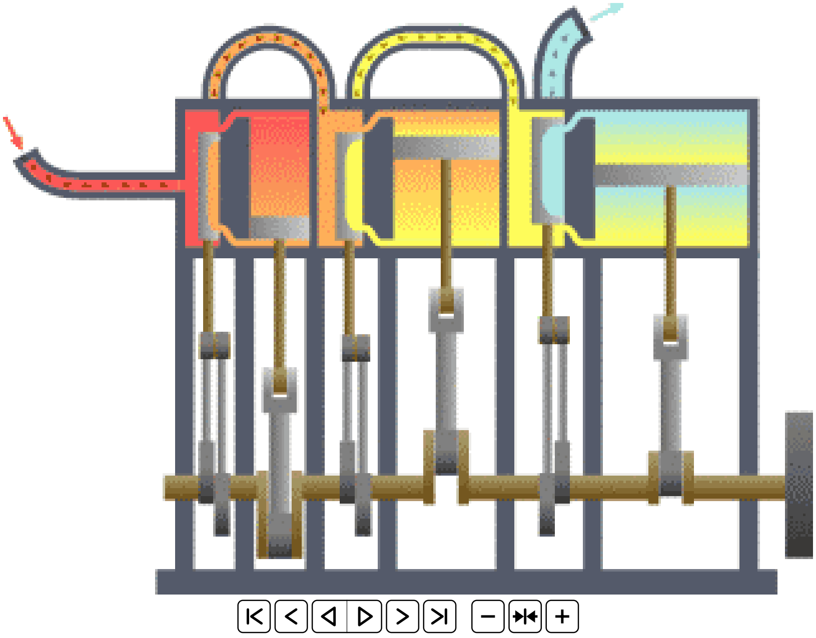


Figure 10.18: Triple expansion steam engine

Assessing and Improving the Efficiency of Steam Engines

- **Indicator Diagrams**.
- First invented and patented by **Watt**.
- Practical way to draw a real pV cycle and tracking engine inefficiencies.
- Continuous improvement of Steam Engines at a time where the **Fundamentals of Thermodynamics** were unknown!

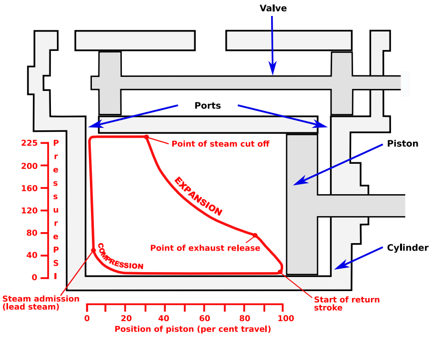
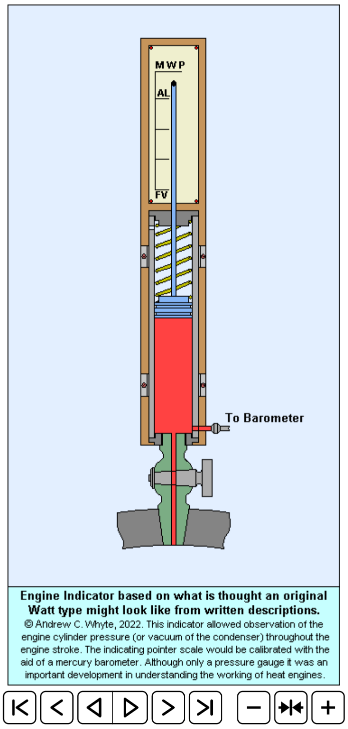
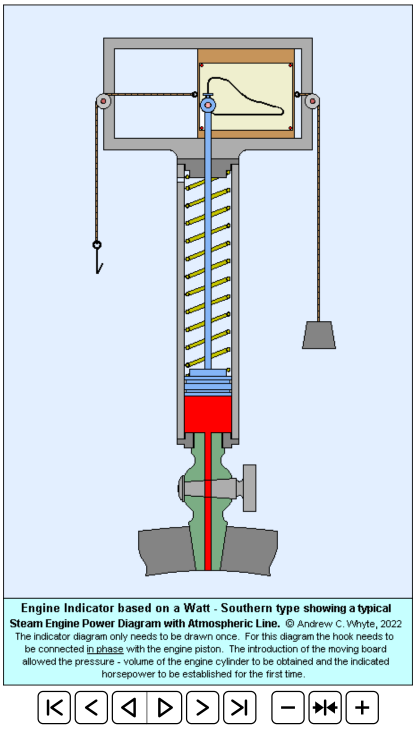


Figure 10.19: Indicator diagrams told engineers how much work a cylinder put out on each stroke

Indicator Diagrams



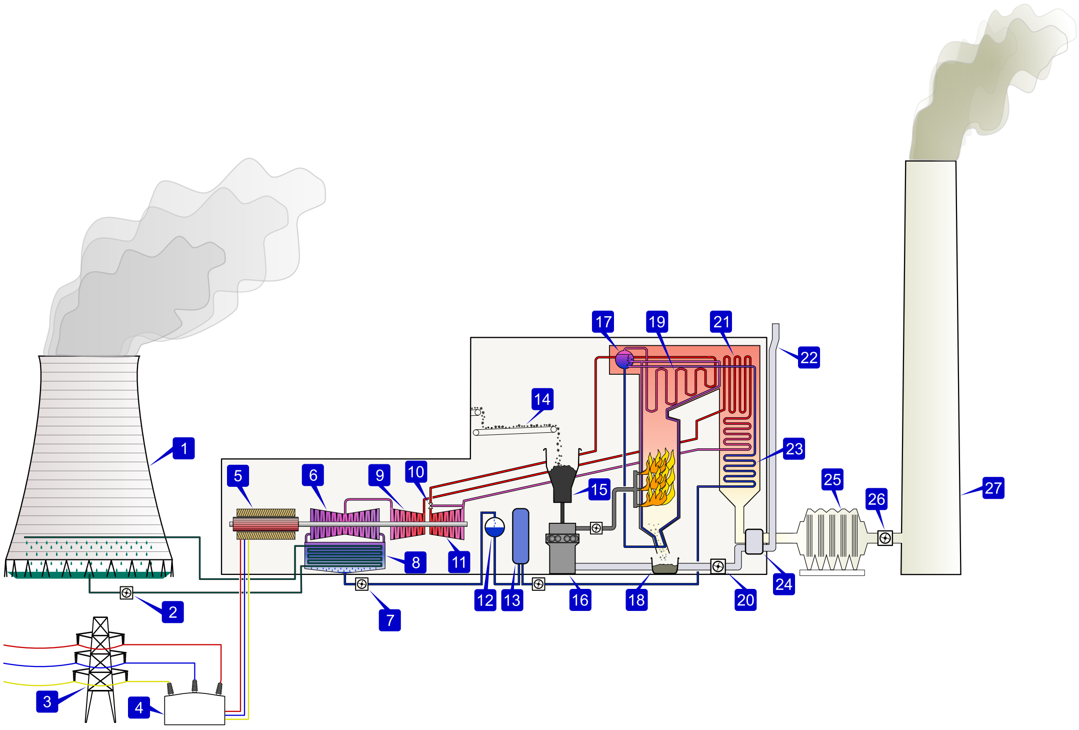
Engine Indicator based on what is thought an original Watt type might look like from written descriptions.
© Andrew C. Whyte, 2022. This indicator allowed observation of the engine cylinder pressure (or vacuum of the condenser) throughout the engine stroke. The indicating pointer scale would be calibrated with the aid of a mercury barometer. Although only a pressure gauge it was an important development in understanding the working of heat engines.



Engine Indicator based on a Watt - Southern type showing a typical Steam Engine Power Diagram with Atmospheric Line. © Andrew C. Whyte, 2022
The indicator diagram only needs to be drawn once. For this diagram the hook needs to be connected in phase with the engine piston. The introduction of the moving board allowed the pressure - volume of the engine cylinder to be obtained and the indicated horsepower to be established for the first time.

credit: `https://acwhyte.droppages.com/`

Today's Modern Steam Engines...



10.2 Discovering Steam Power in China, 1840s – 1860s

This section borrows heavily from the excellent article: **Hsien-Chun Wang, *“Discovering Steam Power in China, 1840s–1860s”*, Technology and Culture, Vol. 51, No. 1, Jan. 2010, pp. 31–54, DOI: `https://doi.org/10.1353/tech.0.0388`**, which is provided as supplementary material

Steam Engines Introduced to China

- The first steamship visited the only port where foreigners were allowed to live and trade: The city of **Guangzhou** in southern China, in **1828**.
- Steamships would prove instrumental in the British battles with the Chinese Naval fleet during the **1st Opium War**.
- At the end of the war in **1842**, Qing officials understood the mechanism of steamships.

Figure 10.20: The East India Company steamship Nemesis (right background) destroying war junks during the Second Battle of Chuenpi, 7 January 1841.

The Issue With Deficient Drawings

- **Chinese** designers supplemented their drawings (tu) with scale models (yang), because they were well aware of the limits of drawings for communicating instructions.
- Unlike their **European** counterparts, who exploited the power of drawings in visual communication, Chinese artisans put their trust in models.

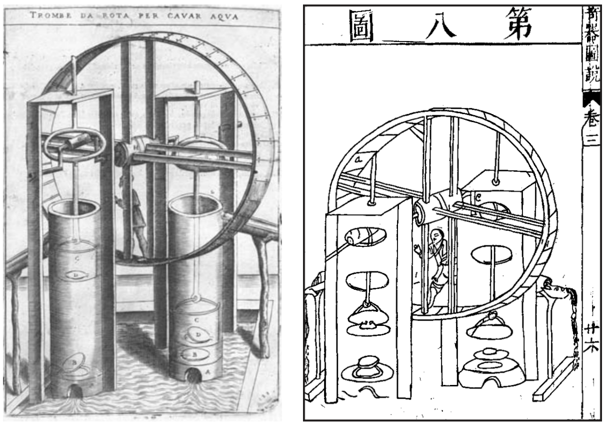


Figure 10.21: 1607 drawing of a human-powered water pump (left), and 1627 Chinese translation (right). The pump piston mechanisms were not fully understood by the translator, making the drawing incomprehensible.

First Successes

- **Ding Gongchen**: 1st Chinese to correctly describe the steam mechanism in writing.
- His book, **Yanpao Tushuo Jiyao** (Illustrative treatise on gunnery), 1st printed in 1841, included an essay discussing his experiments with the steam engine.
- Ding asked artisans to build a small locomotive, and a small steam boat. Unfortunately the craftsmen in Guangzhou, possessing no tools that build machines, could not build big ships.

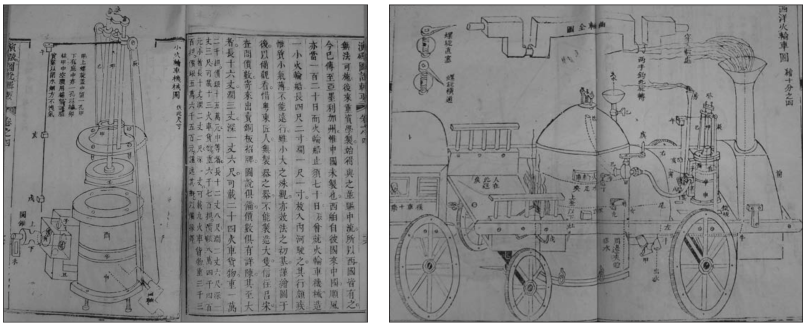


Figure 10.22: Ding Gongchen steam cylinder (left) and steam locomotive (right).

- **Hua and Xu** build **1st Chinese steamboat** in **1863**.
    - Wooden-hulled with a screw-propeller system.
    - Boat cruised for about 1 li (576 meters) before running out of steam.
    - Faulty engine did not include boiler tubes.
- Hua and Xu had not quite mastered the technology. Still were able to harness steam technology by using indigenous skills.
- This stresses the importance of machine tools and technical drawing in modern engineering skills.

The Dissemination of the Steam Engine

- The **Treaty of Nanking** in **1842** ended the First Opium War. The Qing government agreed to open five ports, allowing foreign merchants to trade and reside there.
- Dockyards for servicing and building steamships started to emerge in the treaty ports.
- **Late 1840s**, a foreign dockyard was established in **Shanghai**, and the number of dockyards soon rose to **six** in the **1850s** and **nine** in the **1860s**.
- By **1860**, three docks were operating on **Hong Kong** Island and four in the port of **Hangpu, near Guangzhou**.

- British dockyard firm **Boyd & Company** in **Shanghai** in **1862**.
    - Installed steam engines and machine tools such as lathes, planers, boring mills, rolling mills, a steam hammer, and a furnace.
    - Hailed as one of the best-equipped dockyards in the Far East.
    - By **1865**, had built seventeen seventy-horsepower small steamboats.
    - In **1870**, the firm built a 1,300-ton steamship, including its steam engine and boiler.

  - in **1880**, Boyd & Company employed 1,000 to 1,400 Chinese workers, who had the ability to execute the blueprints they were assigned.
- A U.S. dockyard, **Farnham & Company**, established in **1864**, employed more than 2,000 Chinese during the 1880s.
- In other treaty ports such as **Xiamen**, **Fuzhou**, **Tianjin**, and **Yantai** (known to foreigners as Chefoo), foreign-owned dockyards and machine shops were also active.
- **All these dockyards brought Western engineering skills to China.**

- **Qing government** grants permission to establish the **1st Chinese shipyard** in **Fuzhou** in **1866**.
- **1st Chinese Steamer** built in **1869**.
- **China's First Engineering School**, training both Workers and Engineers.

...and the Rest is History!

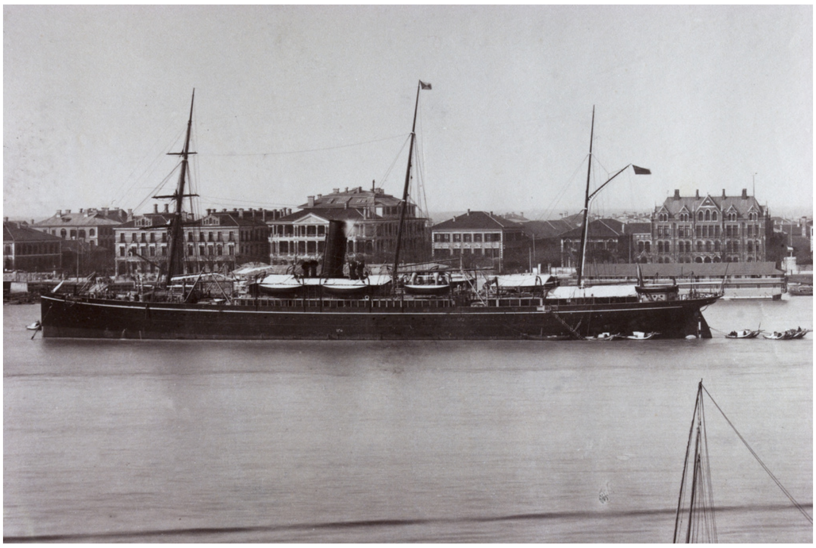


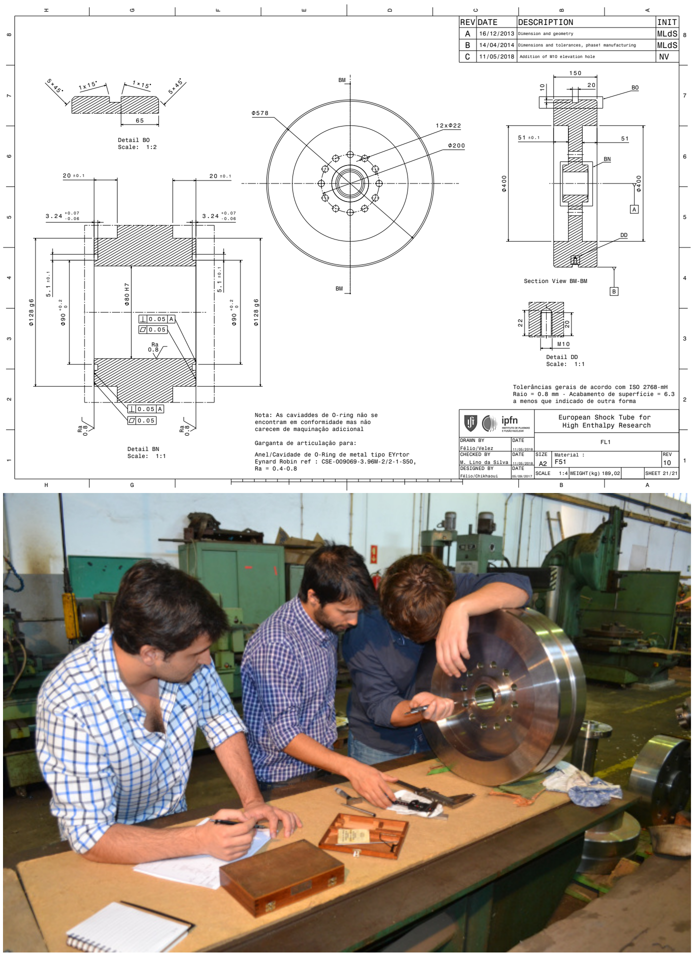
Figure 10.23: Detail from a panoramic view of the Huangpu River and Bund, Shanghai.The Shanghai Club is behind the funnel of the ship. Above the ship's stern is the Russell Building. This large black steamship is flying the P&O houseflag. It is either the PENINSULAR of 1888 or the ORIENTAL of 1889. At 5000 tons gross, these were the largest ships visiting Shanghai in the early 1890s. Visits in the period 1890–91 were ORIENTAL (January 1890), PENINSULAR (February 1890), ORIENTAL (August 1890), ORIENTAL (March 1891), PENINSULAR (August 1891) and PENINSULAR (December 1891).

Figure 10.24: Steamships in Shanghai, c.a. 1900.

Concluding Remarks

- **Rise of Thermodynamics** in the **1850s**. Machine building no longer a matter of trial and error. **Mathematical skills** required.
- Need for **technical drawings** and **machine tools**.
- Need for **training** large numbers of engineers and **financial resources** to maintain large industry.

Modern Day Examples



REV	DATE	DESCRIPTION	INIT
A	16/12/2013	Dimension and geometry	MLdS
B	14/04/2014	Dimensions and tolerances, phase1 manufacturing	MLdS
C	11/05/2018	Addition of M10 elevation hole	NV

Tolerâncias gerais de acordo com ISO 2768-mH
Raio = 0.8 mm - Acabamento de superfície = 6.3
a menos que indicado de outra forma

Nota: As caviaddes de O-ring não se
encontram em conformidade mas não
carecem de maquinação adicional

Garganta de articulação para:

Anel/Cavidade de O-Ring de metal tipo EYrtor
Eynard Robin ref : CSE-009069-3.96M-2/2-1-S50,
Ra = 0.4-0.8

European Shock Tube for
High Enthalpy Research

FL1

DRAWN BY: Félio/Velez — DATE: 11/05/2018
CHECKED BY: M. Lino da Silva — DATE: 11/05/2018
DESIGNED BY: Félio/Chikhaoui — DATE: 05/09/2017
SIZE: A2
Material : F51
REV: 10
SCALE: 1:4
WEIGHT(kg) 189,02
SHEET 21/21

Figure 10.25: Parts drawing and manufacturing for author's own facility.

11 Irreversibilities and the 2^{nd} Law

11.1 The Clausius Inequality

For a Carnot cycle we have seen that:

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

We may accordingly write:

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \quad \Leftrightarrow \quad \frac{Q_C}{T_C} = \frac{Q_H}{T_H} \tag{11.1}$$

Using the convention of the 1^{st} Law:

$$\mathbf{W} = Q_H - Q_C = Q_{in} - Q_{out}$$

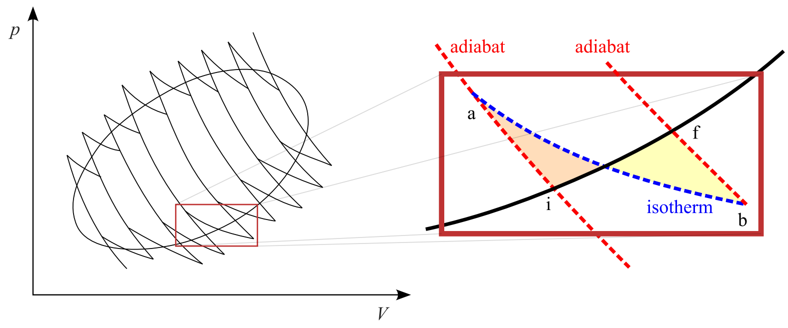
Q_H has a negative sign (it is energy that leaves the system) and we accordingly substitute Q_H by $-Q_H$ in Eq. 11.1:

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H} \quad \Leftrightarrow \quad \boxed{\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0},$$

which is valid for any reversible process.

Let us now consider an arbitrary reversible cycle γ.

We may represent this cycle as as sum of infinitesimal Carnot cycles:



The left (orange) and right (yellow) areas are identical (to do so, we pick the appropriate isotherms and adiabats that allow this equality among the infinite number of curves available). We then have: $W_{i\to f} = W_{i\to a\to b\to f}$.

We may therefore define a succession of Carnot cycles which correspond to the exchanged heat Q and the delivered work W in an arbitrary reversible process γ.

Each Carnot cycle i absorbs a quantity of heat $\mathrm{d}Q_H^i$ at Temperature T_H^i, and gives back a quantity of heat $\mathrm{d}Q_C^i$ at Temperature T_C^i:

$$\frac{\mathrm{d}Q_H^i}{\mathrm{d}Q_C^i} = \frac{-T_H^i}{T_C^i} \quad \Leftrightarrow \quad \frac{\mathrm{d}Q_H^i}{T_H^i} + \frac{\mathrm{d}Q_C^i}{T_C^i} = 0$$

(using the sign convention of the 1st Law)

If we now sum all the cycles i we have: $(\natural + \natural + \natural + \cdots)$

$$\boxed{\oint_\gamma \frac{\delta Q}{T} = 0 \quad \text{(for a reversible process)}} \tag{11.2}$$

For the case of an irreversible process γ we may consider:

$$\begin{aligned} \eta_{irrev.} = 1 - \frac{\mathrm{d}Q_C^i}{\mathrm{d}Q_H^i} &< \eta_{carnot} = 1 - \frac{T_C^i}{T_H^i} \\ \Rightarrow \frac{\mathrm{d}Q_C^i}{\mathrm{d}Q_H^i} &> \frac{T_C^i}{T_H^i} \\ \Rightarrow \frac{\mathrm{d}Q_C^i}{T_C^i} &> \frac{\mathrm{d}Q_H^i}{T_H^i} \end{aligned}$$

If we again consider the sign conventions of the 1st Law ($\mathrm{d}Q_C^i \to -\mathrm{d}Q_C^i$) we may write:

$$\frac{\mathrm{d}Q_H^i}{T_H^i} + \frac{\mathrm{d}Q_C^i}{T_C^i} < 0$$

$$\boxed{\oint_\gamma \frac{\delta Q}{T} < 0 \quad \text{(for an irreversible process)}} \tag{11.3}$$

These two relations are denominated the **Clausius Theorem**.

11.2 Entropy

From Eq. 11.1 we concluded that the cyclic integral of $\frac{\delta Q_H^i}{T_H^i}$ is 0.

We may revisit our previous Chapters, and in particular Chapter 6, and re-analyze other cyclic integrals $\oint$. We have for example the definition of Work W where

$$W = \oint p\mathrm{d}V \neq 0$$

(which is fine! since otherwise no closed cycle would produce work and there wouldn't be any possible engines). The same reasoning applies to the cyclic integral of heat Q.

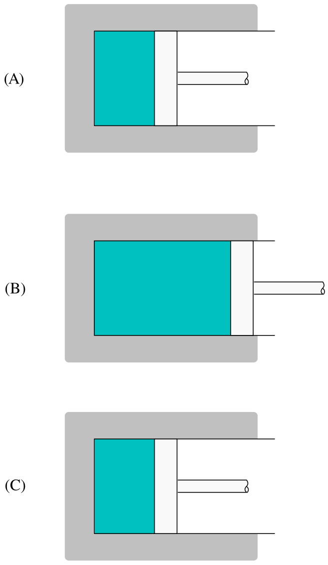


Figure 11.1: Full cycle of a piston stroke

We have next the case of the cyclic integral for the volume occupied by a gas in a piston-cylinder ensemble. At the cycle end, the piston reverts to the initial position, hence we have:

$$\oint \mathrm{d}V = 0$$

or in other terms, the cyclic integral for the Volume V or any other **State Variable** (p, T) is always 0 since at cycle end we always reset the system properties to their initial states. Yet a **Process Variable** (Q, W) will not have a null cyclic integral.

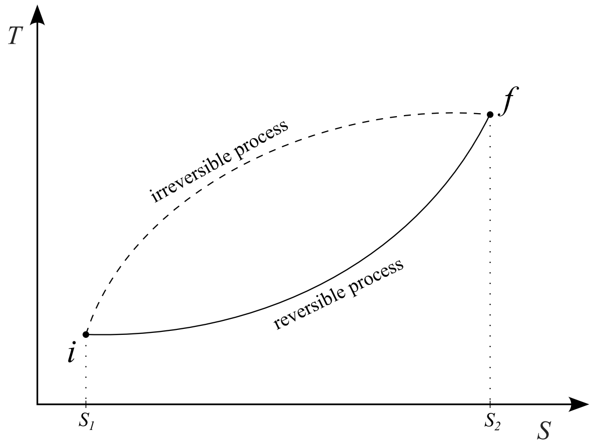
Clausius understood in 1865 that his inequality in fact introduced a **New Thermodynamic State Variable** which he dubbed as **Entropy** S:

$$\boxed{\mathrm{d}S = \left(\frac{\delta Q}{T}\right)_{\text{internally reversible}} [\mathrm{J/K}]} \tag{11.4}$$

Entropy S (in J/K units) is an extensive property of a system, dubbed "total entropy". The entropy per unit mass s (in J/(kg K) units) is an intensive property.

The variation of the entropy of a system during a process may be determined through the integral for Eq. 11.4 between the initial and final states:

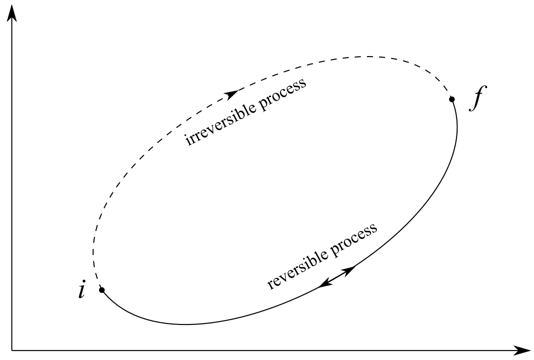
$$\Delta S = S_f - S_i = \int_i^f \left(\frac{\delta Q}{T}\right)_{\text{int. rev.}} \quad [\mathrm{J/K}]$$



(we note that the entropy variation is independent on whether the process is reversible or irreversible, as it should since S is a state variable).

We notice that we are yet unable to determine the entropy of a state, we may only determine the difference in entropy between two states. This is enough for the Engineer who only cares for the variation of the properties of a system.

11.2.1 Irreversible Processes



We will now consider a circular process which encompasses an irreversible part $i \longrightarrow f$ and a reversible part $f \leftrightarrow i$.

Considering the Clausius inequality we have:

$$\oint \frac{\mathrm{d}Q}{T} \leq 0$$

We now expand the inequality over the two processes[1]:

$$\int_i^f \frac{\mathrm{d}Q_{irrev/rev}}{T} + \int_f^i \frac{\mathrm{d}Q_{rev}}{T} \leq 0$$

$$\Leftrightarrow \int_i^f \frac{\mathrm{d}Q}{T} \qquad - \int_i^f \frac{\mathrm{d}Q_{rev}}{T} \leq 0 \quad \Rightarrow \quad \int_i^f \frac{\mathrm{d}Q}{T} \leq \int_f^i \frac{\mathrm{d}Q_{rev}}{T}$$

This inequality is valid independently in how close i and f states are, and in the limit $i \longrightarrow f$ we may write:

$$\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

If we now consider a thermally insulated system ($\mathrm{d}Q = 0$), the inequality becomes:

$$\boxed{\mathrm{d}S \geq 0}$$

Which is another interpretation of the 2nd Law of Thermodynamics.

This relationship implies that any process in a thermally insulated system either maintains the same entropy (for a reversible process), or leads to an increase in entropy (for an irreversible process), up until the entropy of an isolated system eventually reaches a maximum.

We may apply this concept (and the 1st Law) to the Universe in its entirety (which of course we may consider as a thermally isolated system).

- 1st Law: U_{Universe} : constant
- 2nd Law: S_{Universe} always increases.

---

[1] for a reversible process: $\int_A^B f(x)dx = -\int_B^A f(x)dx$, and we omit the $irrev/rev$ subscript starting on the 2nd line

11.2.2 1st Law Revisited

The 1st Law ($\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$) may be rewritten for reversible processes, considering that $\mathrm{d}W = -p\mathrm{d}V$ and $\mathrm{d}Q = T\mathrm{d}S$:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \tag{11.5}$$

We may now remark that all variables from Eq. 11.5 are state functions and hence do not depend on the path of the process. This means that the relationship is also valid for irreversible processes:

$$\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V} \qquad \text{reversible and irreversible} \tag{11.6}$$

How can that be? Don't we have for irreversible processes[2] $\mathrm{d}W > -p\mathrm{d}V$ and $\mathrm{d}Q < T\mathrm{d}S$? The explanation is as follows: The system produces less work, and as such requires less Heat Q to be given back to compensate the lost energy (and enforcing the 1st Law).

Summary of relationships:

- $\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$: always true.
- $\mathrm{d}Q = T\mathrm{d}S$: only true for reversible processes.
- $\mathrm{d}W = -p\mathrm{d}V$: only true for reversible processes.
- For irreversible processes $\mathrm{d}Q < T\mathrm{d}S$ and $\mathrm{d}W > -p\mathrm{d}V$
- $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$: always true.

11.3 Entropy Variation for Reference Thermodynamic Processes

11.3.1 Adiabatic, Reversible process

$$\mathrm{d}'Q_r = 0 \qquad \Rightarrow \qquad \Delta S = \frac{\mathrm{d}'Q_r}{T} = 0$$

11.3.2 Phase change

p and T remain constant during phase change: ⟶ this is an isothermal, reversible process[3].

$$\Delta S = \frac{1}{T}\int_i^f \mathrm{d}'Q_r = \frac{\Delta' Q_r}{T}$$

For a mass unit m, $\Delta Q_r = m\lambda$, with λ, the latent heat for the phase change (in J/K).

---

[2] If friction (irreversible process) is present, then for example the force exerted by the gas during an expansion will be: $F_{eff} = F_{rev} - F_{friction}$ with $F_{rev} = pA$, and $\mathrm{d}W > -p\mathrm{d}V$ with $\mathrm{d}V > 0$. For compressing a gas we need to add extra force to overcome friction: $F_{eff} = F_{rev} + F_{friction}$, and $\mathrm{d}W > -p\mathrm{d}V$ with $\mathrm{d}V < 0$.

[3] $\Delta S = S_f - S_i$

11.3.3 Ideal Gas

$(p_i, V_i, T_i) \longrightarrow (p_f, V_f, T_f)$

$$\left.\begin{array}{rl} \mathrm{d}'Q_r &= \mathrm{d}U + p\mathrm{d}V \\ \mathrm{d}S &= \frac{\mathrm{d}'Q_r}{T} \end{array}\right\} \quad \mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\mathrm{d}V$$

We consider one mole ($N = 1$) of an ideal gas,

$$\mathrm{d}U = C_v(T)\mathrm{d}T$$
$$pV = RT$$
$$(p\mathrm{d}V + V\mathrm{d}p = R\mathrm{d}T)$$

Let us now examine all the possible pairs of variables p, V, and T.

We will consider molar entropy s (in J/(K mol))

1. **s = s(V,T)**

$$\mathrm{d}s = \underbrace{\frac{C_v(T)}{T}}_{\mathrm{d}U/T}\mathrm{d}T + \underbrace{\frac{R}{V}}_{P/T}\mathrm{d}V$$

$$s_f - s_i = \int_{T_i}^{T_f} \frac{C_v(T)}{T}\mathrm{d}T + R\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V}$$

Assuming[4]. $C_v(T) \simeq const.$ between T_i and T_f

$$\Delta s = C_v \ln(T_f/T_i) + R\ln(V_f/V_i).$$

$$\boxed{s(V,T) = C_v \ln(T) + R\ln(V) + const.} \quad S(V,T) = ns(V,T) \tag{11.7}$$

2. **s = s(p,T)**

We depart again from:

$$\mathrm{d}s = \underbrace{\frac{C_v(T)}{T}}_{\mathrm{d}U/T}\mathrm{d}T + \frac{p}{T}\mathrm{d}V$$

Since $p\mathrm{d}V = R\mathrm{d}T - V\mathrm{d}p$:

$$\mathrm{d}s = \frac{C_v + R}{T}\mathrm{d}T - \frac{v\mathrm{d}p}{T}$$

Then since $C_p = C_v + R$ and $\frac{V}{T} = \frac{R}{p}$

$$\mathrm{d}s = \frac{C_p}{T}\mathrm{d}T - R\frac{\mathrm{d}p}{p}$$

$$s_f - s_i = \int_{T_i}^{T_f} \frac{C_p}{T}\mathrm{d}T - R\int_{p_i}^{p_f} \frac{\mathrm{d}p}{p}$$

if we assume $C_p(T) = const.$ between T_i and T_f

[4] very reasonable approximation in "usual" temperature ranges, see Chapter 3 and the discussion about degrees of freedom (Section 3.1.1), $N = 3$ or 5 for atoms, molecules in the 100-1500 K range

$$\Delta s = C_p \ln\left(\frac{T_f}{T_i}\right) - R \ln\left(\frac{p_f}{p_i}\right)$$

$$\boxed{s(p,T) = C_p \ln(T) - R\ln(p) + const.} \quad S(p,T) = ns(p,T) \tag{11.8}$$

3. **s = s(V,p)**

   We depart from:

$$\begin{aligned} s &= C_v \ln(T) + R\ln(V) + const. \\ &= C_v \ln\left(\frac{pV}{R}\right) + R\ln(V) + const. \\ &= C_v \ln(p) + C_v \ln(V) - \underbrace{C_v \ln(R)}_{const.} + R\ln(V) + const. \\ &= C_v \ln(p) + \underbrace{(C_v + R)}_{C_p} \ln(V) + const. \\ &= C_v[\ln(p) + \underbrace{(C_p/C_v)}_{\gamma} \ln(V)] + const. \\ &= C_v\,[\ln(p) + \ln(V^\gamma)] + const. = C_v\,[\ln pV^\gamma] + const. \end{aligned}$$

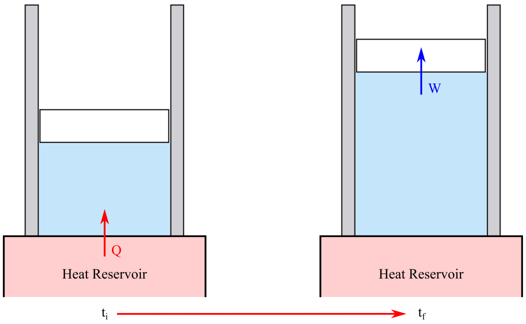
$$\boxed{s(p,V) = C_v \ln(pV^\gamma) + const.} \quad S(p,T) = ns(p,T) \tag{11.9}$$

   Note: $C_v \ln(pV^\gamma) = const.$ if $pV^\gamma = const.$ This is the case for an adiabatic and reversible process.

11.4 Energy Degradation

Lets again compare Isothermal Expansion vs. Joule Free Expansion, as in Chapter 6:

Isothermal Expansion



$\Delta U = 0$ (since $T = const.$) $\Rightarrow \Delta Q = \Delta W$

$$W_{i\to f} = \int_i^f p\mathrm{d}V = \int_i^f \frac{nRT}{V}\mathrm{d}V$$
$$= nRT\ln\left(\frac{V_f}{V_i}\right)$$

We apply

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V = 0$$

then it follows: $T\mathrm{d}S = p\mathrm{d}V = \Delta W$
Therefore:

$$\mathrm{d}S = \frac{nRT\ln\left(\frac{V_f}{V_i}\right)}{T}$$

Finally:

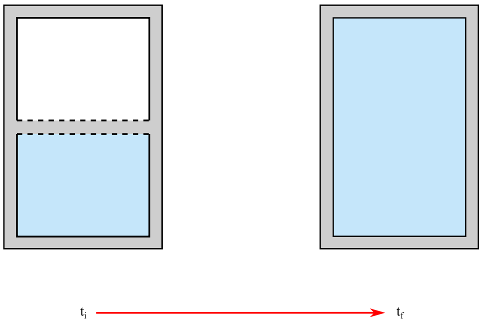
$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$$

The heat transferred from the reservoir was converted into work which was carried out by the piston (reversible process), therefore:

- $\Delta S_{gas} = \quad nR\ln\left(\frac{V_f}{V_i}\right)$
- $\Delta S_{res} = -nR\ln\left(\frac{V_f}{V_i}\right)$
- $\Delta S_{Universe} = \Delta S_{gas} + \Delta S_{res} = 0$

As would be expected since the process is reversible.

Free Joule Expansion



$\Delta Q = 0, \Delta W = 0, \Delta U = 0$
We know that for an ideal gas:

$$S = S(V,T) = nC_v\ln(T) + nR\ln(V) + const.$$

then

$$\Delta S = S_f - S_i = nR\ln\left(\frac{V_f}{V_i}\right) + \cancelto{0}{nR\ln\left(\frac{T_f}{T_i}\right)}$$

In the Joule Free Expansion the system is isolated from its vicinity ($vic.$), hence:

- $\Delta S_{gas} = nR\ln\left(\frac{V_f}{V_i}\right)$
- $\Delta S_{vic} = 0$
- $\Delta S_{Universe} = \Delta S_{gas} + \Delta S_{vic}$
  $= nR\ln\left(\frac{V_f}{V_i}\right)$

As expected the entropy of the Universe increases since the process is irreversible.

Question: Since in the Joule free expansion we have $\Delta Q = 0$, shouldn't we have $\Delta S = \frac{\Delta Q}{T} = 0$?

Answer: Wrong since $\mathrm{d}Q = T\mathrm{d}S$ is only valid for reversible processes. In this case we have $\Delta Q = 0$ and $\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$, therefore we verify the inequality $\Delta Q < T\Delta S$ for an irreversible process.

We verify that in the irreversible case of the Joule Free Expansion we have “wasted a potential quantity of work $W_{i\to f} = \Delta Q = T\Delta S$ which could have been used in case the process would have been carried out in a reversible fashion (as for an isothermal expansion).

This is a key concept for understanding Entropy: All the irreversibilities correspond to a degradation of energy, where we waste potential Work.

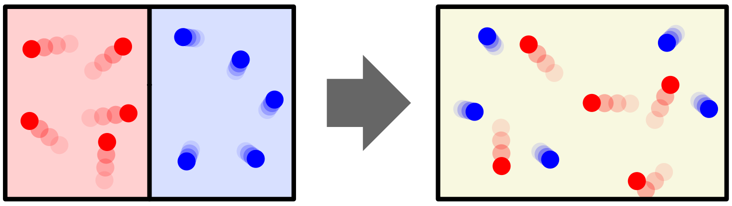
Some examples:

- Friction losses.
- Heat conduction $T_H \longrightarrow T_C$. These two heat sources/sinks could have been put to use in a Carnot machine.

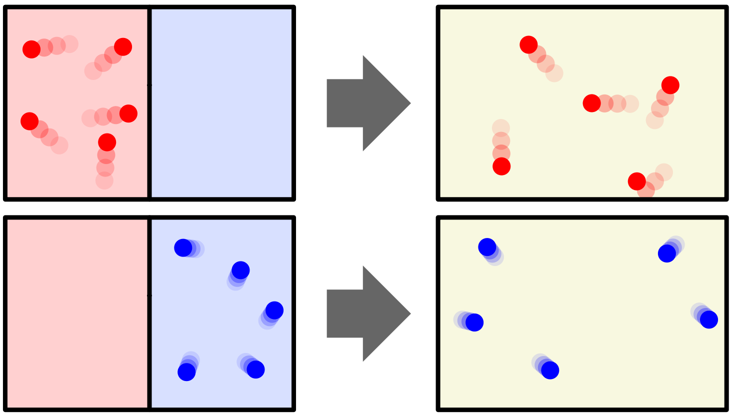
The Universe is inexorably evolving towards a **Heat Death** owing to the irreversibilities who diminish the ability of the **Universe** to perform **useful work** as **Entropy** S increases inexorably.

11.5 Some Examples of Irreversible Processes

11.5.1 Diffusion of a Gas into another



this corresponds to two Free Joule Expansions:



In case $V_1 = V_2$ we have:

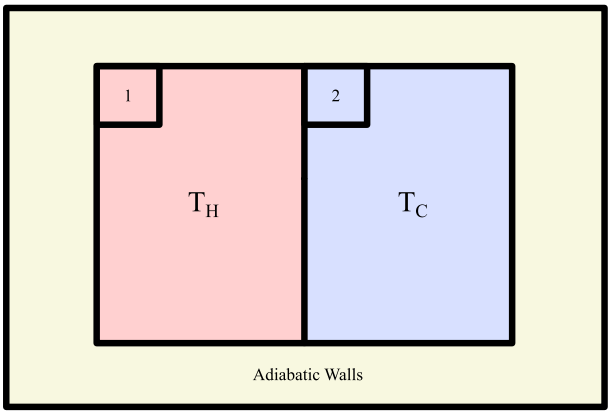
$$\begin{aligned}\Delta S &= 2nR\ln\left(\frac{V_1+V_2}{V_1}\right)\\ &= 2nR\ln(2)\end{aligned}$$

or in the general case $V_1 = x$; $V_2 = 1-x$:

$$\Delta S = nR\left[x\ln(x) + (1-x)\ln(1-x)\right]$$

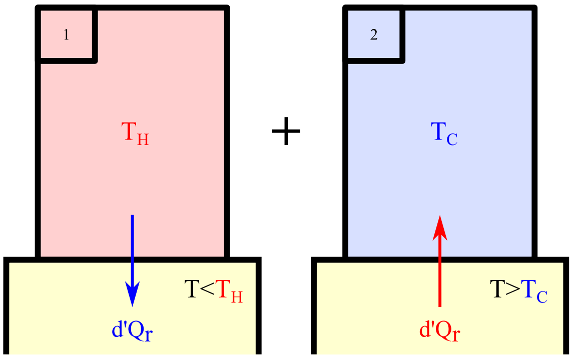
11.5.2 Heat conduction

Also an irreversible process!



Let us define the equivalent reversible process:

We take $\mathrm{d}'Q_r$ from 1 at T_H by using an intermediate thermal reservoir, and we give back $\mathrm{d}'Q_r$ to 2 by contact with another thermal reservoir at T_C:



For this reversible process we have:

$$\mathrm{d}S = \mathrm{d}S_H + \mathrm{d}S_C = -\frac{\mathrm{d}'Q_r}{T_H} + \frac{\mathrm{d}'Q_r}{T_C} = \mathrm{d}'Q_r\left(\frac{1}{T_C} - \frac{1}{T_H}\right)$$

If $m_H = m_C = m$ and $c_H = c_C = c$, $T_f = \dfrac{T_H + T_C}{2}$.

$$\begin{aligned}\Delta S = \Delta S_H + \Delta S_C &= \int_{T_H}^{T_f} \frac{\mathrm{d}'Q_r}{T} + \int_{T_C}^{T_f} \frac{\mathrm{d}'Q_r}{T} \\ &= mc \int_{T_H}^{T_f} \frac{\mathrm{d}T}{T} + mc \int_{T_C}^{T_f} \frac{\mathrm{d}T}{T} \quad = mc \ln\left(\frac{T_H}{T_H}\right) + mc \ln\left(\frac{T_f}{T_C}\right) \\ &= mc \ln\left(\frac{T_f^2}{T_H T_C}\right) \\ &= mc \ln\left[\frac{(T_H + T_C)^2}{4T_H T_C}\right]\end{aligned}$$

$$\Delta S = mc \ln\left[\frac{(T_H + T_C)^2}{4T_H T_C}\right]$$

since

$$(T_H + T_C)^2 = \underbrace{(T_H - T_C)^2}_{>0} + 4T_H T_C > 4T_H T_C$$

11.6 Statistic Basis of Entropy

We depart again from $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ and we rewrite $\mathrm{d}U$ as a function of its natural variable S and V:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-p} \mathrm{d}V$$

We have accordingly:

$$\begin{cases} T &= \left(\frac{\partial U}{\partial S}\right)_V \\ p &= -\left(\frac{\partial U}{\partial V}\right)_S \end{cases}$$

We rewrite:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$$

From **Chapter 2**, Eq. 2.6 we have[5]

$$\begin{aligned}\frac{1}{k_B T} &= \frac{\mathrm{d}\ln\Omega}{\mathrm{d}U} \\ \frac{1}{T} &= \frac{\mathrm{d}k_B \ln\Omega}{\mathrm{d}U}\end{aligned}$$

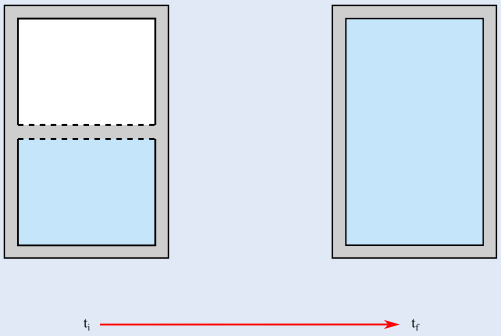
and we may accordingly identify S with $k_B \ln\Omega$:

$$\boxed{S = k_B \ln\Omega} \tag{11.10}$$

Which corresponds to the expression of the entropy of a system in a particular macrostate in terms of Ω, the number of associated microstates.

[5] we used E in Chapter 2 to describe the internal energy U

Example: Joule Expansion Revisited



After a Joule expansion for a mole of molecules, each of the may be in the left or right part of the container.

There are accordingly 2^{N_a} possible combinations for positioning the molecules, and the number of associated microstates for a gas occupying a volume twice (2x) as big is larger by a multiplicative factor of 2^{N_a}. The additional entropy is:

$$\Delta S = k_B \ln \Omega = k_B \ln \Omega = k_B \ln 2^{N_a} = k_B N_a \ln 2 = R \ln 2$$

Nomenclature

Variables:

- n: Number of moles $n = N/N_a$ [mol]
- N: Number of particles [-]
- p: Pressure [Pa]
- Q: Heat [J]
- S: Entropy [J/K]
- s: Molar Entropy [J/molK]
- t: Time [s]
- T: Temperature [K]
- U: Energy of a system [J]
- V: Volume [m^3]
- W: Work [J]

- C_p: Molar Specific Heat at Constant Pressure [J/molK]
- C_v: Molar Specific Heat at Constant Volume [J/molK]
- γ: Specific Heats ratio $\gamma = C_p/C_v$ [-]

- Ω: Microstate

Constants:

- $N_A = 6.02214076 \times 10^{23}$ [mol^{-1}]: Avogadro Number/Constant
- $R = 8.31447$ [J/molK]: Universal Gas Constant

Acronyms, subscripts and superscripts

- C: cold
- H: hot
- i: initial
- f: final
- eff: effective
- $friction$: friction
- $irrev$: irreversible
- rev: reversible
- $intrev$: internally reversible
- vic: vicinity
- res: reservoir

11.7 A Broader Understanding of Entropy

Entropy: A Macroscopic Vision

This text is retrieved from Schroeder, *an Introduction to Thermal Physics*, Chapter 3.

Historically, the relation $\mathrm{d}S = Q/T$ was the original *definition* of entropy. In 1865, Rudolf Clausius defined entropy to be the thing that increases by Q/T whenever heat Q enters a system at temperature T . Although this definition tells us nothing about what entropy actually is, it is still sufficient for many purposes, when the microscopic makeup of a system does not concern us. To illustrate this traditional view of entropy, consider again what happens when a hot object, A, is put in thermal contact with a cold object, B (see Figure 11.2). To be specific, suppose that $T_A = 500\,\mathrm{K}$ and $T_B = 300\,\mathrm{K}$. From experience we know that heat will flow from A to B. Let's say that during some time interval the amount of heat that flows is 1500 J, and that A and B are large enough objects that their temperatures don't change significantly due to the loss or gain of this amount of energy. Then during this time interval, the entropy of A changes by

$$\Delta S_A = \frac{-1500\,\mathrm{J}}{500\,\mathrm{K}} = -3\,\mathrm{J/K} \tag{11.11}$$

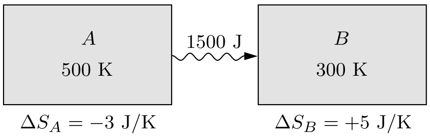


Figure 11.2: When 1500 J of heat leaves a 500 K object, its entropy decreases by 3 J/K. When this same heat enters a 300 K object, its entropy increases by 5 J/K.

Object A *loses* entropy, because heat is flowing out of it. Similarly, the entropy of B changes by

$$\Delta S_B = \frac{+1500\,\mathrm{J}}{300\,\mathrm{K}} = +5\,\mathrm{J/K} \tag{11.12}$$

Object B *gains* entropy, because heat is flowing into it. (Notice that the traditional entropy unit of J/K is quite convenient when we compute entropy changes in this way.)

Just as I often visualize energy as a "fluid" that can change forms and move around but never be created or destroyed, I sometimes imagine entropy, as well, to be a fluid. I imagine that, whenever energy enters or leaves a system in the form of heat, it is required (by law) to carry some entropy with it, in the amount Q/T. The weird thing about entropy, though, is that it is only half-conserved: It cannot be destroyed, but it can be created, and in fact, new entropy is created whenever heat flows between objects at different temperatures. As in the numerical example above, the entropy that is "carried by" the heat is more when it arrives at the cooler object than it was when it left the hotter object (see Figure 11.3). Only in the limit where there is no temperature difference between the two objects will no new entropy be created. In this limit, however, there is no tendency of heat to flow in the first place. It's important to remember that fundamentally, the net increase in entropy is the driving force behind the flow of heat. Fundamentally, though, entropy isn't a fluid at all and my model is simply wrong.

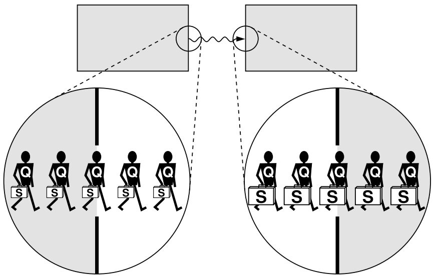


Figure 11.3: Each unit of heat energy (Q) that leaves a hot object is required to carry some entropy (Q/T) with it. When it enters a cooler object, the amount of entropy has increased.

But what is Entropy exactly?

- We have seen that the **2^{nd} Law** of Thermodynamics and Entropy S are very useful tools for the analysis and understanding of energetic systems.
- We considered the **Carnot cycle** to define the ideal machine which would convert a maximum amount of heat Q into work W. But **even this ideal machine has losses!** (eficiency $\eta < 100\%$).
    - "*The ideal Carnot engine produces the maximum of work possible, when the heat in the boiler is cooled down to the temperature of the condensor. The engine Carnot constructed worked without any loss; the work produced could be used again to heat the boiler to the starting temperature. That there are no engines more efficient than the Carnot engine in producing mechanical work is the original formulation of the second law of thermodynamics. Thus, actual engines have some irreversible losses; what is lost is not energy but capacity to do work. Entropy is a measure for that irreversible loss.*"[6]
- However at a more fundamental level, we are still not really quite certain of the meaning of Entropy...
- Let us go "*down the rabbit hole*" again and again travel to the microscopic world...

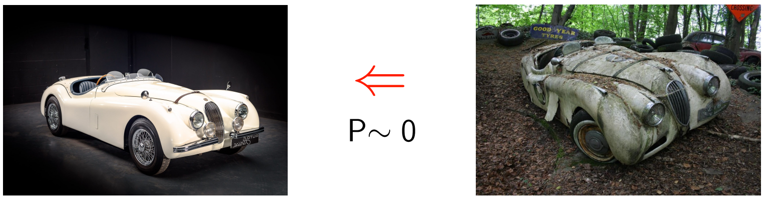
Entropy is a measure of disorder

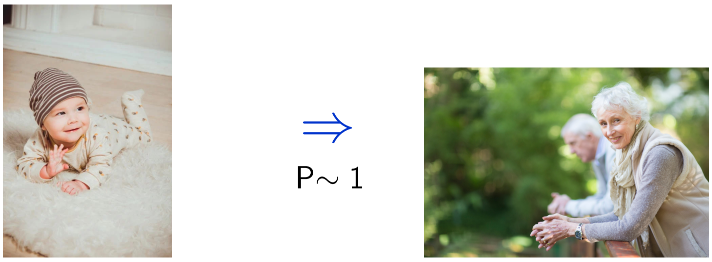
The underlying foundations of the 2^{nd} Law of Thermodynamics corresponds to its statistical interpretation where, for a large number of atoms and molecules, the most probable distribution of energy is so favorable in the probabilistic sense (think about 99.9999. . . % hypothesis), that all the other energy distributions, including those that invert the arrow of time (reverting irreversible processes and leading to a more organized system) are so unlikely that they may be ignored in practice[7].

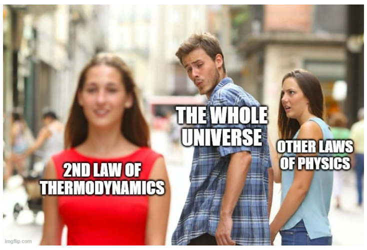
> "*the very foundation of the second law is in the statistical interpretation that, for a system containing a large number of atoms or molecules, the most probable distribution of energies is so highly favored that one can ignore all other distributions, including those that would carry the system backward in time to a more highly ordered state.*"
>
> Gordon, "*Thermodynamics and Society*", Science, 1981.

[6] D. T. Spreng, "*On the Entropy of Economic Systems*", 1980.

[7] (remember lecture 2 and the 100x coin toss. Going back in time is even more improbable than getting 100 faces or numbers in the coin toss outcomes)

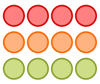




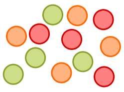


The 2^{nd} Law is inescapable!

Some examples of Order and Chaos



low entropy
low disorder



high entropy
high disorder

Your upcoming Thermodynamics exam

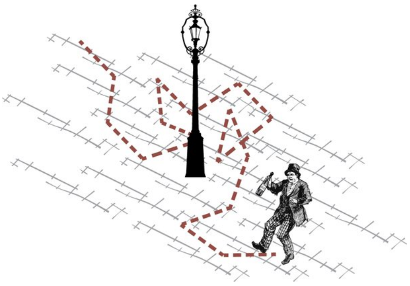
A Punk-Rock concert

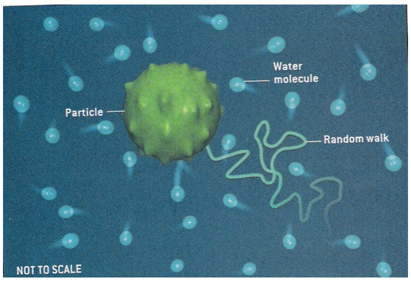
An example of Disorder: Brownian Movement

- Known to Physicists as the “drunkard’s walk”.
- We take a particle and we allow it to move one length unit in four possible directions (north, south, east, west) in a random fashion. We repeat the process for several particles.
- Corresponds to the macroscopic phenomena of diffusion: Diffusion (or Heat) equation.

$$\frac{\partial}{\partial t} f(x,t) = D \frac{\partial^2}{\partial x^2} f(x,t)$$

- Entropy (disorder) increases over time.





The Universe is inexorably walking towards a state of higher disorder

Any thermodynamic process will **increase the global Entropy** of the system + its surroundings.

DS > 0

"The increase of disorder or entropy is what distinguishes the past from the future, giving a direction to time"

Stephen Hawking, *"A Brief History of Time"*

- Entropy of the Universe at $t = 0$ (Big Bang): $S = 10^{88} k_B$
- Entropy do Universe today: $S = 10^{103} k_B$
- Entropy of the Black Hole at the center of our Galaxy: $S = 10^{91} k_B$
- Entropy at the time of the postulated[8] "Heat Death" of the Universe in $t = 10^{30}$ years: $S = 10^{123} k_B$

[8] This is a hypothetical end state of the universe. Other theories for the Ultimate End of the Universe exist.

Fatalistic Assertion: All Thermodynamic Processes hasten the Entropy increase of the Universe

All actions will increase entropy. Should we even get out of bed every morning?

Well, can we at least minimize Entropy production?

Statistical interpretation of Entropy

- Boltzmann Equation
  - $S = k_B \ln \Omega$
  - Ω corresponds to all the microstates of the macrostate (thermodynamic system, gas, or another) under study
  - Review Chapter 2. Demonstration: H Theorem
- **3^{rd} Law of Thermodynamics**: for $T = 0$, there is only one possible microstate (everything is at a standstill)
  - $S(T = 0) = k_B \ln \Omega = k_B \ln(1) = 0$
  - **The entropy of a system is 0 if this system is at absolute Zero (T = 0 K)**


Me: *Cleans my room to bring some order to the chaos of life*
Entropy:

Am I a joke to you?

Figure 11.4: Boltzmann's grave

The Answer is Cold

Heat is Chaos, Cold is Order

Icy Manipulator 4

Artifact

1, ⟳: Tap target artifact, creature, or land.

In fire there is the spark of chaos and destruction, the seed of life. In ice there is perfect tranquility, perfect order, and the silence of death.

Illus. Matt Cavotta

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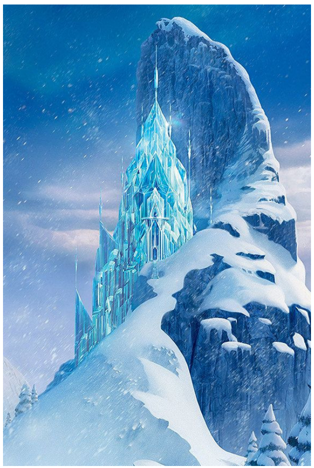


Order and Chaos

see `https://tvtropes.org/pmwiki/pmwiki.php/Main/OrderVersusChaos`

- Many creation myths start with a primordial sea of Chaos, from which Gods and creatures are born that eventually bring order to the Chaos and create the Earth.
- In mythological studies, there is a trope called "*Chaoskampf*". It is always along the lines of "storm god fights huge serpent/dragon, representing Order vs. Chaos". It appears in the form of
  - Indra vs Vritra (Hinduist mythology),
  - Zeus vs Typhon (Greek mythology),
  - Thor vs Jormungandr (Norse mythology),
  - Marduk vs Tiamat (Hinduist mythology),
  - YHWH vs Leviathan, followed by Christ vs The Ancient Serpent Satan (Judeo-Christian mythology),
  - and possibly Susano'o vs Orochi as well (Japanese mythology).
  - Yu the Great killing Xiangliu during his work stopping the Great Flood may also count, although Yu is not a storm god (Chinese mythology).

This is the conflict in physics between the theories of **General Relativity**, which describes an orderly and predictable universe, but is only applicable to large scales, and **Quantum Mechanics**, which describes a chaotic, random, near-nonsensical universe, but is only applicable to small scales.

Both theories are correct, even though they contradict each other. The purpose of a Unified Field Theory would be to resolve these conflicts and unite both theories.

11.7.1 Negentropy

Entropy and Life

Negentropy: A temporary condition in which matter is **hotter and more highly organised than the surrounding space**.

- Example: Earth (average temperature $T \simeq 15\,°\mathrm{C}/298\,\mathrm{K}$) and the surrounding vacuum in Space (from $T \simeq -100\,°\mathrm{C}/170\,\mathrm{K}$ in the Earth's shade to $T = 2.7\,\mathrm{K}$[9] in Outer Space).
  See Earth–Sun energy balace in Chapter 5
- Earth is a system in **thermodynamic nonequilibrium**.
- One would expect for thermodynamic nonequilibrium to create more chaos/disorder (see for example the phenomena of turbulence), however nonequilibrium may paradoxically create structure (Order from Chaos)[10] and ultimately, Life.
- **Earth collects Energy and Negentropy from the Sun**, and Life resorts to nonequilibrium thermodynamic processes to create ordered patterns and build structures[11]. Some examples include:
  - An human evolving from an unicellular embryo to a full fledged man/woman,
  - Humans building a city over decades/centuries.

Entropy balances on Earth

This text is retrieved from Spreng, D. T., *"On the Entropy of Economic Systems"*, 1984.

The global entropy balance

Let us first examine the Earth as an open thermodynamic system. The system has to be regarded as an open system due to the solar radiation it receives and the heat radiation it emits. The energy balance is very nearly zero, but the entropy balance certainly not; the incoming radiation has the temperature of the surface of the sun ($\sim 5000\,\mathrm{K}$) and the outgoing radiation the surface temperature of the Earth ($\sim 300\,\mathrm{K}$). What happens to the negative flux of entropy that enters this system or the positive flux that leaves it?

The solar negentropy flux is mostly used to drive the climate machine: the winds, the water cycle, the ocean currents, etc. However, all the negentropy input that goes into the climate machine is ultimately dissipated by mechanical friction. It looks like the total entropy of the Earth remains, in the very first approximation, about constant since

$$\mathrm{d_e}S \text{ (from the Sun)} \simeq \mathrm{d_i}S \text{ (due to friction of the climate machine).}$$

However, about 10% of the Solar negentropy flux falls on green leaves, photosynthesizes carbohydrates (at an efficiency of 1%), and leads to

[9] Thermal equilibrium Temperature with the cosmic microwave background

[10] See for example the regular turbulence patterns in the atmosphere of Jupiter

[11] See E. Schrödinger, *"What is Life?"*, 1944

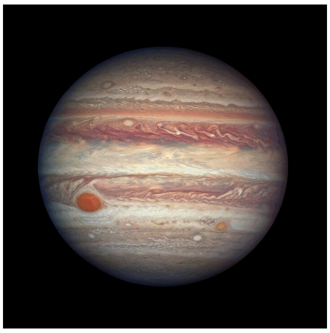
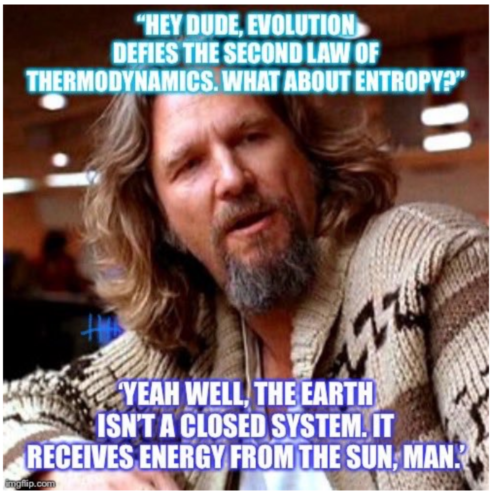


Figure 11.5: Jupiter dissipates the Negentropy it receives from the Sun exclusively through atmospheric friction processes (since no Life is known to exist in Jupiter).

many highly organized biological structures. It is the principle of self-organization that makes it possible to store the incoming entropy in the biosphere. (In case of the climate the situation is of course similar: the climate machine itself is a somewhat ordered structure that could build itself up due to the incoming negentropy flux.) The biosphere does however not grow and accumulate for ever; there is not only photosynthesis, but also respiration and decomposition. The total mass of the biosphere may be about constant, temporal decreases (for instance at the start of an ice age) are likely to be followed by temporal increases. Therefore, we may write in a first approximation also for the sunshine that reaches green leaves:

$$-\mathrm{d_e}S\,\text{(from photosynthesis)} \simeq \mathrm{d_i}S\,\text{(due to respiration and decomposition)}.$$



It thus seems that the incoming negentropy flux from the Sun is dissipated on Earth by natural processes. How does Man with all his technological activities fit into this picture? Let us examine this by looking at a typical example of Man's production machine.

11.7.2 Final Ponderings

Pondering Entropy: Parting Thoughts

We have briefly approached the far-reachings of the concept of **Entropy**, on how it relates to the arrow of time, the ultimate fate of the Universe, but also how Life may arise from **Negentropy** in nonequilibrium thermodynamic systems.

The student may:

- **Despair** at the thought of any action being futile, ultimately only leading to an increase of the global Entropy of the Universe,
- **Marvel** at the thought of Negative Entropy leading to the formation of structure and Life in planets such as Earth[12],
- **Ignore** all these other far-reaching and more philosophical implications of Entropy, focusing only on the practical engineering applications[13] for this additional State variable (which is also fine!)

Come what may, We conclude with a saying of the Western philosopher **Soren KIERKEGAARD**, who characterized Life as a dissipative thermodynamic structure 150 years ago:

“*Life can only be understood backwards but it must be lived forwards*”

---

[12] “*Value arises from living creatures experience of the quality of their lives, not from free energy or negative entropy*” Andrews, Env. Phil, 1984.

[13] see previous section of this chapter

Chapter Summary

- Clausius Inequality: $\oint \mathrm{d}Q/T = 0$ for a reversible process; $\oint \mathrm{d}Q/T > 0$ for an irreversible process;
- 2^{nd} Law of Thermodynamics: $\mathrm{D}S \geq 0$;
  - $\mathrm{d}Q = T\mathrm{d}S$: only true for reversible processes.
  - $\mathrm{d}W = -p\mathrm{d}V$: only true for reversible processes.
  - For irreversible processes $\mathrm{d}Q \leq T\mathrm{d}S$ and $\mathrm{d}W \geq -p\mathrm{d}V$
  - $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$: always true.
- $S = k_B \ln \Omega$. (Ω is the number of microstates associated to a system);
- 3^{rd} Law of Thermodynamics: for $T = 0$, there is only one possible microstate (everything is at a standstill);
  - The entropy of a system is 0 if this system is at absolute Zero ($T = 0\,\mathrm{K}$)

Recommended readings

- Blundell, "*Concepts in Thermal Physics*" [5], Chapter 14.
- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [7], Chapter 6.

Thermodynamics and Culture: Relevant Works

In Chapter 11 we have thouroghly discussed Entropy, a new state variable useful for the solving of thermodynamic problems. We have also explored the far-reaching meaning of the concept of Entropy, outlining its fundamental contribution to our understanding of thermodynamic processes of all kind, and the implications of the 2nd Law on the Ultimate Fate of Our Universe.

It is therefore not surprising that Entropy has been thouroughly appropriated by several works of writing, dating back to the 19th Century at the time this variable was being defined.

Philip K. Dick, Do Androids Dream of Electric Sheep? 1968

The famous 1968 novel by North–American science fiction writer Philip K. Dick which would go on to serve the basis for the 1982 World-acclaimed movie "Blade Runner". The novel is set in a post-apocalyptic San Francisco, where Earth's life has been greatly damaged by a nuclear global war. The main plot follows Rick Deckard, a bounty hunter who has to "retire" six escaped Nexus-6 model androids.

The novel is famous for, among other things, introducing "Kipple" as a metaphor for Entropy:

> “*Kipple is useless objects, like junk mail or match folders after you use the last match or gum wrappers or yesterday’s homeopape. When nobody’s around, kipple reproduces itself. For instance, if you go to bed leaving any kipple around your apartment, when you wake up the next morning there’s twice as much of it. It always gets more and more.*”
>
> “*I see*” The girl regarded him uncertainly, not knowing whether to believe him. Not sure if he meant it seriously.
>
> “*There’s the First Law of Kipple,*” he said. “*Kipple drives out nonkipple. Like Gresham’s law about bad money. And in these apartments there’s been nobody here to fight the kipple.*”
>
> “*So it has taken over completely,*” the girl finished. She nodded. “*Now I understand.*”
>
> “*Your place, here,*” he said, “*this apartment you’ve picked–it’s too kipple-ized to live in. We can roll the kipple-factor back; we can do like I said, raid the other apts. But–*” He broke off.
>
> “*But what?*”
>
> Isidore said, “*We can’t win.*”
>
> “*Why not?*” [...]
>
> “*No one can win against kipple,*” he said, “*except temporarily and maybe in one spot, like in my apartment I’ve sort of created a stasis between the pressure of kipple and nonkipple, for the time being. But eventually I’ll die or go away, and then the kipple will again take over. It’s a universal principle operating throughout the universe; the entire universe is moving toward a final state of total, absolute kippleization.*”

Percy Shelley, Ozymandias, 1818

“*Ozymandias*” is a sonnet written by the English Romantic poet Percy Bysshe Shelley (1792–1822). It was first published in the 11 January 1818 issue of The Examiner of London.

Although it is not contemporary to Clausius statement, this sonnet embodies our definition of Entropy. Here we have a great king, creator of massive monuments to his own greatness, and yet his works lie destroyed, eroded and buried by Entropy.

The poem is about the arrogance of Man himself, and it’s a cautionary tale for the creators of great monuments and creations which will be bound to decay, until they will be reclaimed by nature.

> I met a traveller from an antique land
> Who said: “*Two vast and trunkless legs of stone*
> *Stand in the desert. Near them on the sand,*
> *Half sunk, a shattered visage lies, whose frown*
> *And wrinkled lip and sneer of cold command*
> *Tell that its sculptor well those passions read*
> *Which yet survive, stamped on these lifeless things,*
> *The hand that mocked them and the heart that fed.*
> *And on the pedestal these words appear:*

> *'My name is Ozymandias, King of Kings:*
> *Look on my works, ye mighty, and despair!'*
> *Nothing beside remains. Round the decay*
> *Of that colossal wreck, boundless and bare,*
> *The lone and level sands stretch far away."*

H. G. Wells, The Time Machine, 1895

The work that popularized the concept of time travel. H. G. Wells depics a Victorian scientist known as the Time Traveller, who conceives and builds a time machine he then uses to travel to the year 802,701, and later to 30 million years into the future: where he witnesses a dying Earth under a red Sun (our Sun having evolved to a Red Giant).

> *"The darkness grew apace; a cold wind began to blow in freshening gusts from the east, and the showering white flakes in the air increased in number. From the edge of the sea came a ripple and whisper. Beyond these lifeless sounds the world was silent. Silent? It would be hard to convey the stillness of it. All the sounds of man, the bleating of sheep, the cries of birds, the hum of insects, the stir that makes the background of our lives—all that was over. As the darkness thickened, the eddying flakes grew more abundant, dancing before my eyes; and the cold of the air more intense. At last, one by one, swiftly, one after the other, the white peaks of the distant hills vanished into blackness. The breeze rose to a moaning wind. I saw the black central shadow of the eclipse sweeping towards me. In another moment the pale stars alone were visible. All else was rayless obscurity. The sky was absolutely black."*

Isaac Asimov, The Last Question, 1956

"INSUFFICIENT DATA FOR MEANINGFUL ANSWER."

"*The Last Question*" is one of Asimov's best-known works and is also the author's favorite short story written by himself. The story is written in the omniscient third-person narrative and primarily addresses the question of cosmic entropy in the universe, and the attempts of multiple future generations of human beings and computers trying to answer this question. The Last Question was first published in the November 1956 issue of the Science Fiction Quarterly.

Poul Anderson, Tau Zero, 1970

"for a moment infinitesimal and infinite, men, women, child, ship, and death were one. It"

"The universe is a symphony of chaos and harmony, and through exploration, we become part of its captivating melody."

The epic voyage of the spacecraft Leonora Christine will take her and her fifty-strong crew to a planet some thirty light-years distant. But, because the ship will accelerate to close to the speed of light, for those on board subjective time will slow and the journey will be of only a few years' duration. Then a buffeting by an interstellar dustcloud changes everything. The ship's deceleration system is damaged irreperably and soon she is gaining velocity. When she attains light-speed, tau zero itself, the disparity between ship-time and external time becomes almost impossibly great. Eons and galaxies hurtle by, and the crew of the Leonora Christine speeds into the unknown, beyond the end of the Universe.

Other works

Figure 11.6: Yuri Shwedoff, "*White Castle*", 2014.

12 Thermodynamic Cycles for Real Engines

This Chapter discusses the thermodynamic properties of **Insternal Combustion Engines (ICE)**.

The adopted conventions for the drawings presented here are: **Blue:** Air; **Green:** Air-fuel mixture; **Red:** Combustion; **Gray:** Combustion products.

12.1 Otto cycle

Otto cycle (1876): **four-stroke, two mechanical cycles engine**.

The piston goes up and down twice in a cycle. Typical piston cycle process: Piston compresses an air-fuel mixture; mixture is ignited releasing heat; the gas expands, pushing the piston.

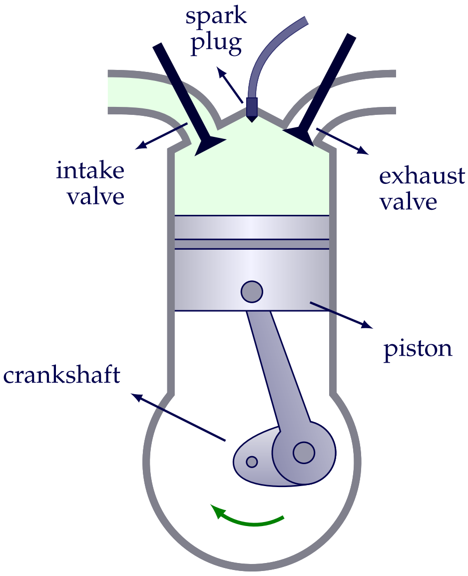


Figure 12.1: Four-Stroke Engine

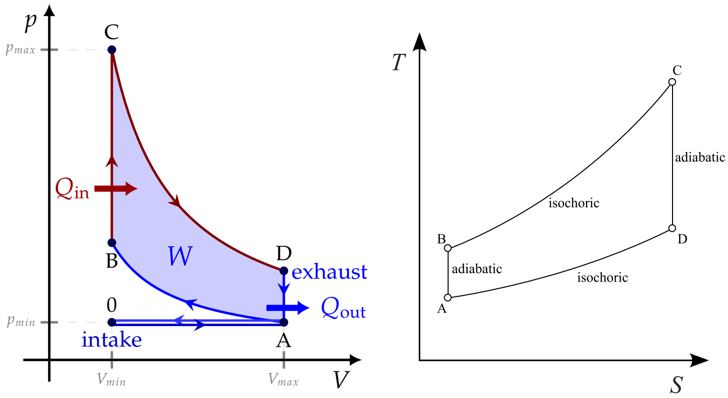
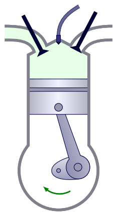


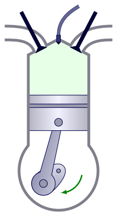
Figure 12.2: pV (left) and TS (right) diagrams for the Otto cycle

12.1.1 Otto cycle process

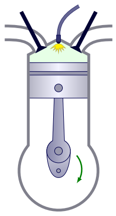
1. **Intake** $0 \longrightarrow A$: Fuel is injected at atmospheric pressure. $V_s \nearrow V_l$ (the piston makes room for filling the volume). Mass with chemical potential energy (air-fuel mixture) is allowed into the system.



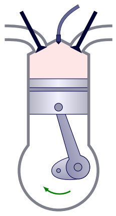
2. **Compression** $A \longrightarrow B$: Adiabatic compression to the initial volume $V_l \searrow V_s$. $\mathbf{W_{in}} < \mathbf{0}$, work is given to the system by the inertia of the moving piston. $T_A \nearrow T_B$ ($T_B > T_A$).



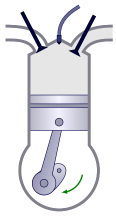
3. **Ignition** $B \longrightarrow C$: The spark initiates combustion. Very fast process ($V \simeq const.$). $P_B \nearrow P_C$; $T_B \nearrow T_C$. The chemical potential energy of the gas is converted into heat $\mathbf{Q_{in}}$



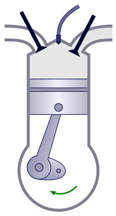
4. **Combustion/Power Stroke** $C \longrightarrow D$: The high-pressure, hot gas expands very rapidly (e.g. adiabatically), performing work $\mathbf{W_{out}} > \mathbf{0}$.



5. **Exhaust Valve Opens** $D \longrightarrow A$: $P_D \searrow P_A$; $T_D \searrow T_A$, again very rapidly. ($V \simeq const.$). Warm gas exits, evacuating heat $\mathbf{Q_{out}}$



6. **Exhaust Stroke** $A \longrightarrow 0$: The piston rises ($V_s \searrow V_l$) and purges the remaining combustion products. The cycle restarts in ① .



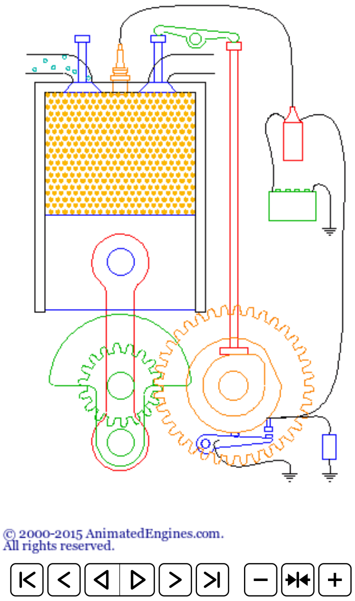


Figure 12.3: Otto cycle animation (from `https://animatedengines.com/otto.html`)

12.1.2 Efficiency of the Otto cycle

We consider the air-fuel mixture as an ideal gas.

$W = \oint p\mathrm{d}V$= cycle area.

$$\begin{aligned} W &= W_{AB} + W_{CD} + \underbrace{\cancelto{0}{W_{BC}} + \cancelto{0}{W_{DA}}}_{\mathrm{d}V\,=\,0\ \Rightarrow\ \mathrm{d}W\,=\,\int p\mathrm{d}V\,=\,0} \\ &= W_{AB} + W_{CD} \end{aligned}$$

For a cycle $\Delta U = 0$, $\mathbf{W} = Q_{in} - Q_{out}$

$$\begin{aligned} \Rightarrow \quad Q_{in} &= nC_v\Delta T = nC_v(T_C - T_B) \\ Q_{out} &= nC_v\Delta T = nC_v(T_D - T_A) \end{aligned}$$

$$\eta = \frac{\mathbf{W}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

We may now relate the different temperatures considering that for adiabatic processes $TV^{\gamma-1} = const.$:

$$\left.\begin{aligned} T_A V_A^{\gamma-1} &= T_B V_B^{\gamma-1} \\ T_C V_C^{\gamma-1} &= T_D V_D^{\gamma-1} \end{aligned}\right\} \begin{aligned} V_A &= V_D = V_{max} \\ V_B &= V_C = V_{min} \end{aligned} \quad \Rightarrow \quad \begin{aligned} T_A V_{max}^{\gamma-1} &= T_B V_{min}^{\gamma-1} \\ T_C V_{min}^{\gamma-1} &= T_D V_{max}^{\gamma-1} \end{aligned}$$

$$\begin{cases} T_A = T_B \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1} \\ T_D = T_C \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1} \end{cases} \Rightarrow \eta = 1 - \frac{T_D - T_A}{T_C - T_B}$$

$$= 1 - \frac{T_D - T_B \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1}}{T_D / \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1} - T_B}$$

$$= 1 - \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1} \cancelto{1}{\frac{T_D - T_B \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1}}{\left[T_D / \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1} - T_B\right] \left(\frac{V_{min}}{V_{max}}\right)^{\gamma-1}}}$$

$$\boxed{\eta_{\text{Otto}} = 1 - r^{1-\gamma}} \tag{12.1}$$

with $r = \frac{V_{max}}{V_{min}}$ is the compression ratio of the engine. From Eq. 12.1, it follows that the efficiency of the cycle will increase as the compression rate increases. Fig. 12.4 plots the theoretical efficiency curve η as a function of r, and presents some "real-life" engine efficiencies as a comparison. Naturally these are below the theoretical limit as the result of losses not considered in an idealized engine (for example the compression/expansion processes are never truly isentropic (adiabatic+reversible) nor even adiabatic since the strokes are not infinitely fast $t \longrightarrow 0$ and some heat transfer to the walls occurs through conduction). Combustion is also not 100% efficient, and friction losses need to be accounted for.

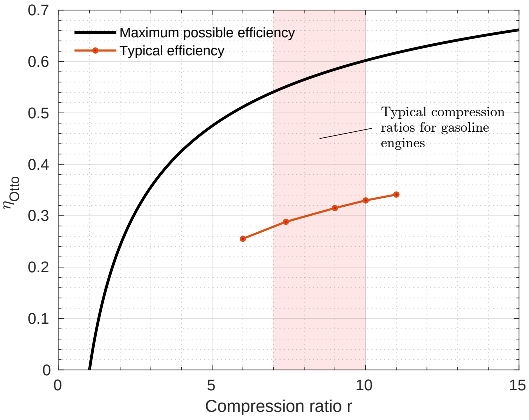


Figure 12.4: Theoretical efficiency of the Otto cycle as a factor of the compression ratio r, and real-life engine efficiencies.

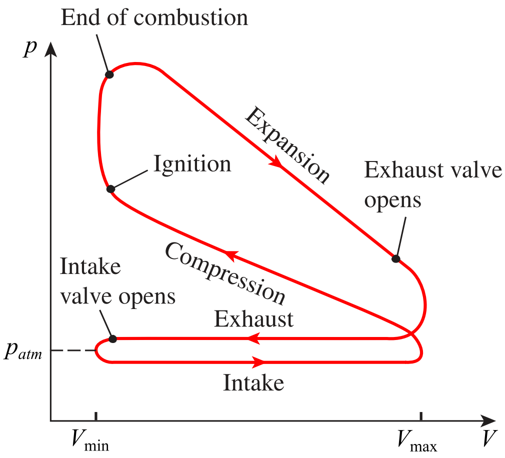


Figure 12.5: Real Otto cycle. Figure adapted from Cengel, *Thermodynamics, and Engineering Approach, 5th Ed.*

Comparison with a Carnot cycle

We may now express the efficiency of the Otto cycle in terms of Temperatures considering:

$$\left(\frac{V_{max}}{V_{min}}\right)^{\gamma-1} = \frac{T_A}{T_B} = \frac{T_D}{T_C}$$

We accordingly have:

$$\eta_{\text{Otto}} = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

Since $T_C > T_B > T_D > T_A$ we have for an equivalent Carnot cycle:

$$\eta_{\text{Carnot}} = 1 - \frac{T_A}{T_C} >= \eta_{\text{Otto}} = 1 - \frac{T_A}{T_B}$$

as it should!

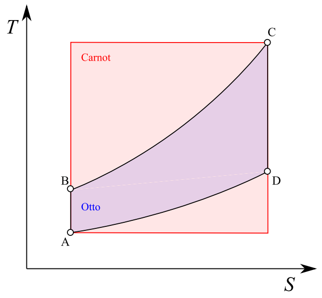


Figure 12.6: Otto and Carnot cycles TS diagram

12.2 Diesel cycle

Diesel cycle (1893–1895): **also four-stroke, two mechanical cycles engine**.

Very similar to the Otto cycle with two key differences:

1. The fuel is directly injected in the chamber during the cycle instead of being premixed to the air. This mass addition increases the volume from V_{min} to V_{cut}.
2. There is no spark ignition of the mixture, instead the mixture is auto-ignited as a consequence of the higher compression ratios of such engines.

This leads to a slight difference compared to the Otto cycle, as heat addition through combustion now occurs at constant pressure as the fuel is injected and expands the piston (for the Otto cycle, combustion is very fast and occurs at constant Volume).

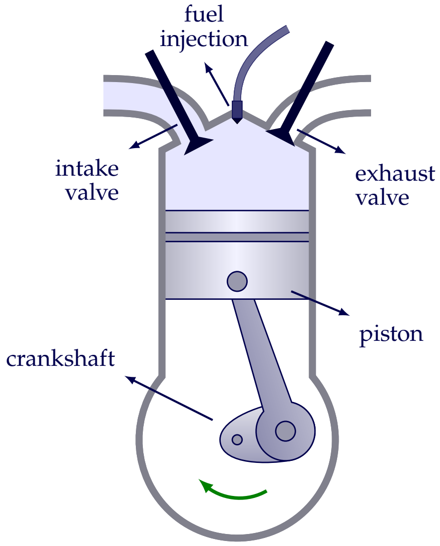


Figure 12.7: Diesel Engine

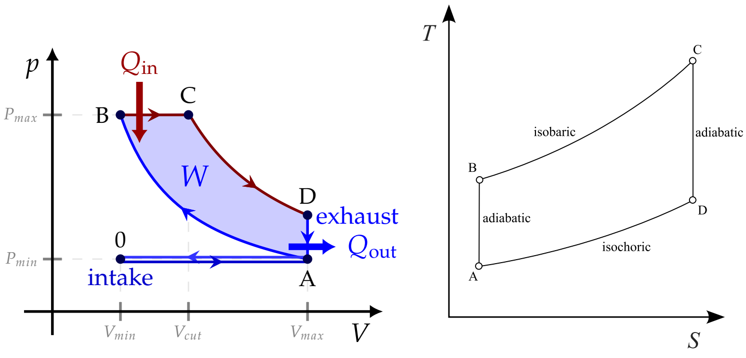
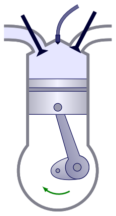


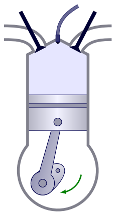
Figure 12.8: pV (left) and TS (right) diagrams for the Diesel cycle

12.2.1 Diesel cycle process

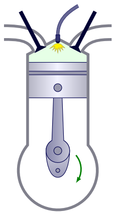
1. **Intake** $0 \longrightarrow A$: Air (instead of an Air-Fuel mixture) is injected at atmospheric pressure. The rest is identical to the Otto cycle.



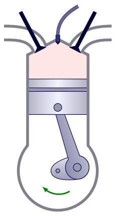
2. **Compression** $A \longrightarrow B$: Adiabatic compression identical to the Otto cycle. Usually for Diesel engines, the compression factor is much higher and the gas volume at the end of compression is very small. The final temperature is accordingly very high.



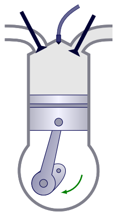
3. **Fuel Injection** $B \longrightarrow C$: The Temperature is high enough to ensure the auto-ignition of the Air-Fuel mixture without the aid of a spark plug (as in the Otto engine).



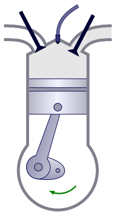
4. **Explosion** $C \longrightarrow D$: Adiabatic expansion to V_{max}



5. **Exhaust Valve Opens** $D \longrightarrow A$: Energy leaves the system (Q_{out}), identical to the Otto cycle



6. **Exhaust Stroke** $A \longrightarrow 0$: Identical to the Otto cycle.



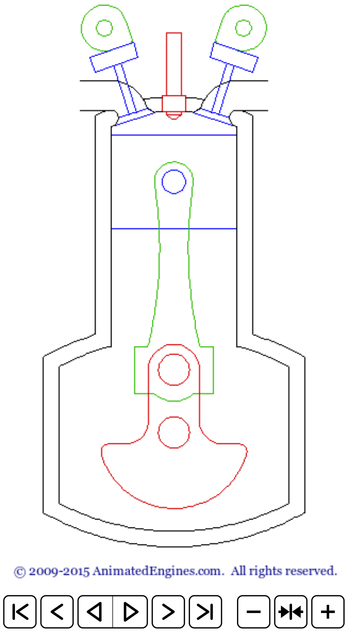


Figure 12.9: Diesel cycle animation (from `https://animatedengines.com/diesel.html`)

12.2.2 Otto and Diesel cycle comparisons

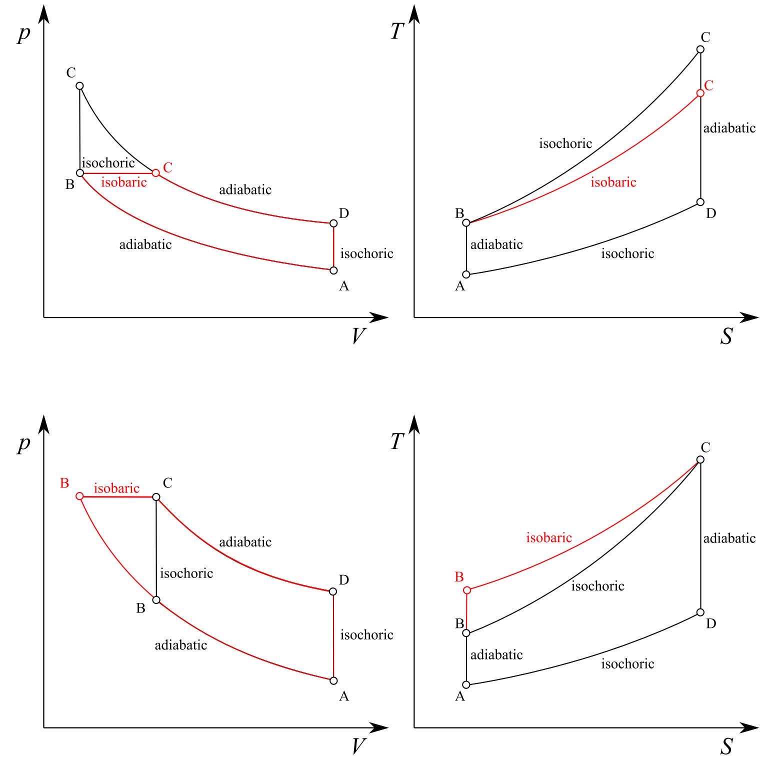


Figure 12.10: pV (left) and TS (right) diagram comparisons for the Otto and Diesel cycles. Same compression rate r on top; same p_{max}, T_{max} on bottom. **red:** Diesel cycle. **black:** Otto cycle.

- For an identical compression rate r: $\eta_{\text{Otto}} > \eta_{\text{Diesel}}$
- For identical p_{max}, T_{max}: $\eta_{\text{Otto}} < \eta_{\text{Diesel}}$

12.2.3 Efficiency of the Diesel cycle

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} \begin{cases} Q_{out} = nC_v(T_D - T_A) \text{ (DA: constant volume process)} \\ Q_{in} = nC_p(T_C - T_B) \text{ (BC: constant pressure process)} \end{cases}$$

$$\begin{aligned} \eta &= 1 - \frac{C_v}{C_p}\frac{T_D - T_A}{T_C - T_B} \\ &= 1 - \frac{1}{\gamma}\frac{T_D - T_A}{T_C - T_B} \end{aligned}$$

$$\frac{T_D - T_A}{T_C - T_B} = \frac{p_D V_{max} - p_A V_{max}}{p_B V_{cut} - p_B V_{min}} = \frac{p_D - p_A}{p_B}\frac{V_{max}}{V_{cut} - V_{min}} = \frac{p_D/p_B - p_A/p_B}{V_{cut}/V_{max} - V_{min}/V_{max}}$$

$$\begin{aligned} p_D V_{max}^{\gamma} &= p_B V_{cut}^{\gamma} \rightarrow p_D/p_B = (V_{cut}/V_{max})^{\gamma} = 1/(V_{max}/V_{cut})^{\gamma} \\ p_A V_{max}^{\gamma} &= p_B V_{min}^{\gamma} \rightarrow p_A/p_B = (V_{min}/V_{max})^{\gamma} = 1/(V_{max}/V_{min})^{\gamma} \end{aligned}$$

$$\eta = 1 - \frac{1}{\gamma}\frac{(V_{max}/V_{cut})^{-\gamma} - (V_{max}/V_{min})^{-\gamma}}{(V_{max}/V_{cut})^{-1} - (V_{max}/V_{min})^{-1}}$$

we define $r = V_{max}/V_{min}$ as for the Otto cycle, and $r_e = V_{max}/V_{cut}$ in addition. We may then write the efficiency as:

$$\boxed{\eta = 1 - \frac{1}{\gamma}\frac{r_e^{-\gamma} - r^{-\gamma}}{r_e^{-1} - r^{-1}}} \tag{12.2}$$

12.3 Stirling cycle

Stirling cycle (1816): **Regenerative Closed Cycle with a Heat Exchanger**.

In a Stirling cycle, a working fluid in a gaseous state is exposed to a hot and a cold boundary, leading to the cyclic expansion and compression of the gas. This gas in turn pushes/pulls a piston, resulting in a net conversion of heat energy to mechanical work.

This cycle has many advantages: The working gas always remains in the engine (there is no gases admission/exhaust as in the Otto/Diesel cycles. Stirling engines are therefore very simple and particularly silent.

During its first years, the Stirling cycle was a credible rival to the other steam engine designs. However, several disadvantages for this process precluded its more widespread use: the power/weight ratio is smaller than in other steam engines, preventing its application to locomotion engines; the starting/shutdown times are quite long; complexity of the heat exchangers required for this engine; need for the boiler to be manufactured from heat-resistant materials to achieve large energy densities; need for more exotic gases (typically hydrogen/helium) to achieve good

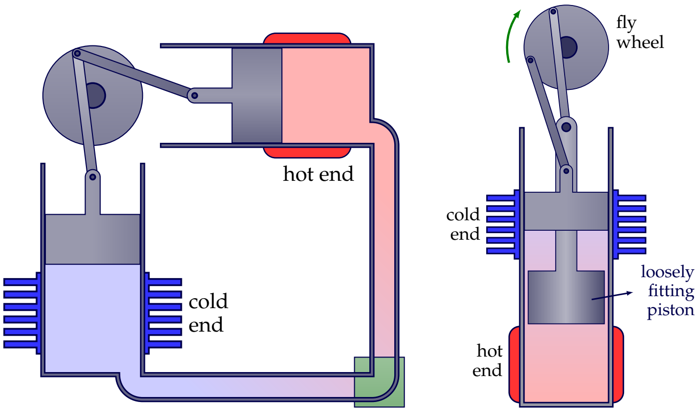


Figure 12.11: Two-cylinder – alpha (left) and One-cylinder – beta (right) Stirling Engine

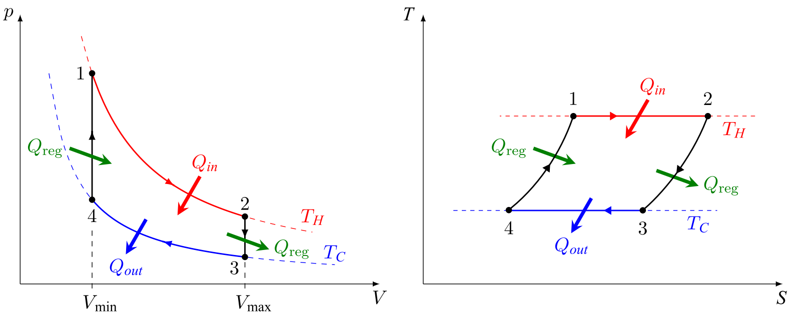


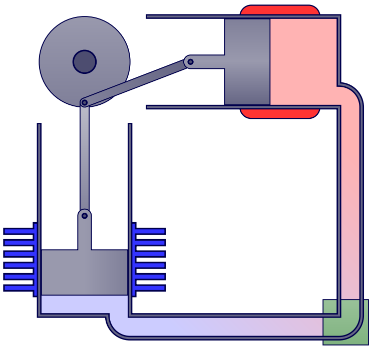
Figure 12.12: pV (left) and TS (right) diagrams for the Stirling cycle

performances.

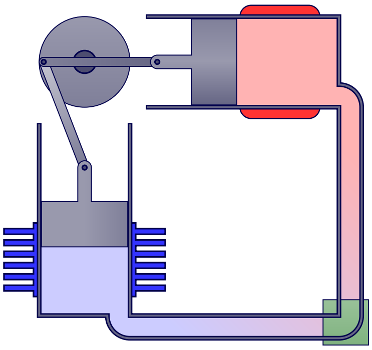
The Stirling cycle is nowadays used in cryogenic applications (production and research on low-temperature materials) where this cycle is used reversibly as a heat pump. As an example, the Rankine cycle (to be discussed in Lecture 12), which is the common cycle for refrigerators, is limited to minimum temperatures of $-40\,°\mathrm{C}/-30\,°\mathrm{C}$. However the Stirling cycle allows reaching Temperatures down to $-200\,°\mathrm{C}$, which is for example enough for liquefying air. The Rankine cycle cannot reach such low temperatures owing to the absence of a refrigeration fluid with practical applications with a vaporization temperature as low as that temperature.

12.3.1 Stirling Alpha cycle process

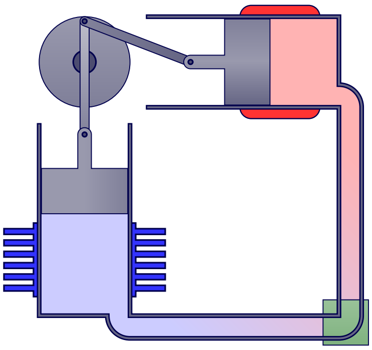
1. **Isothermal Expansion** $A \longrightarrow B$:
   Most of the gas in the system has just been driven into the hot cylinder. The gas heats and expands driving both pistons outward.



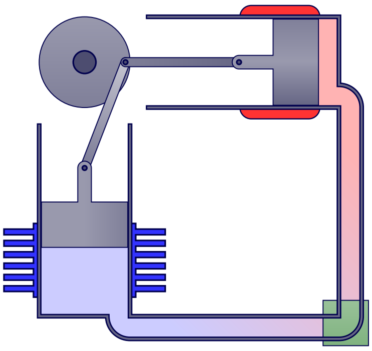
2. **Isochoric Transfer** $B \longrightarrow C$:
   The gas has expanded (typically about 3 times). Most of the gas (about 2/3) is still located in the hot cylinder. Flywheel momentum carries the crankshaft the next 90 degrees, transferring the bulk of the gas to the cool cylinder.



3. **Isothermal Contraction** $C \longrightarrow D$:
   The majority of the expanded gas has shifted to the cool cylinder. It cools and contracts, drawing both pistons inward.



4. **Isochoric Transfer** $D \longrightarrow A$:
   The contracted gas is still located in the cool cylinder. Flywheel momentum carries the crank another 90 degrees, transferring the gas to back to the hot cylinder to complete the cycle.



This engine also features a regenerator, illustrated in green. The regenerator is constructed of material that readily conducts heat and has a high surface area, typically a mesh of closely spaced, thin metal plates. When hot gas is transferred to the cool cylinder, it is first driven through the regenerator, where a portion of the heat is deposited. When the cool gas is transferred back, this heat is reclaimed; thus the regenerator “pre-heats” and “pre-cools” the working gas, dramatically improving efficiency.

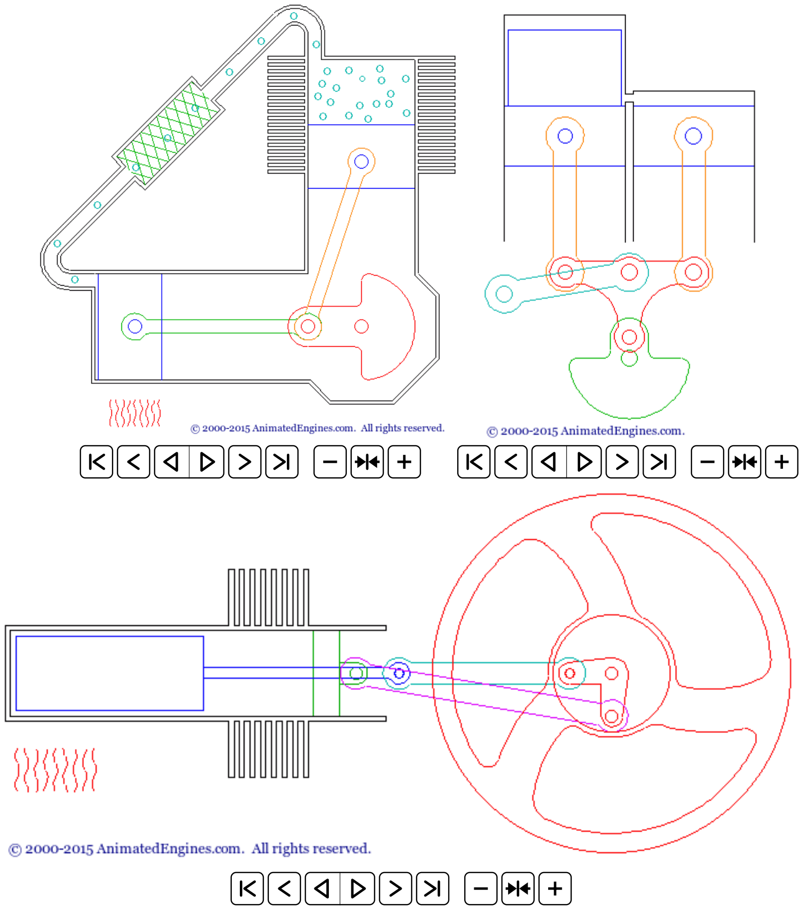


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Figure 12.13: Left: Stirling cycle, Alpha configuration, animation (from `https://animatedengines.com/vstirling.html`); Right: Stirling cycle, Ross Yoke (Gamma) configuration, animation (from `https://animatedengines.com/ross.html`); Bottom: Stirling cycle, Beta configuration, animation (from `https://animatedengines.com/stirling.html`)

12.3.2 Efficiency of the Stirling cycle

We have two isotherms and two isochors. Let us calculate the net work **W** and the net heat input Q'_{in} to the system. Here we need to account not only for the heat transferred to the gas by the hot source Q_{in} but also the heat supplied to the regenerator Q_{reg}:

$$\begin{aligned} \mathbf{W} &= nRT_H \ln\left(\frac{V_{max}}{V_{min}}\right) - nRT_C \ln\left(\frac{V_{max}}{V_{min}}\right) \\ &= nR\left(T_H - T_C\right)\ln\left(\frac{V_{max}}{V_{min}}\right) \end{aligned}$$

$$\begin{aligned} Q'_{in} &= Q_{in} + Q_{reg} \\ &= nRT_H \ln\left(\frac{V_{max}}{V_{min}}\right) + nC_v\left(T_H - T_C\right) \end{aligned}$$

We may now state the efficiency η of the cycle:

$$\eta = \frac{\mathbf{W}}{Q'_{in}} = \frac{nR\left(T_H - T_C\right)\ln\left(\frac{V_{max}}{V_{min}}\right)}{nRT_H \ln\left(\frac{V_{max}}{V_{min}}\right) + nC_v\left(T_H - T_C\right)} \qquad (12.3)$$

(note that the calculation for the efficiency was very straightforward given that this cycle only has a hot T_H and a cold T_C temperature, and no fancy calculations are needed unlike the case of the Otto and Diesel cycles)

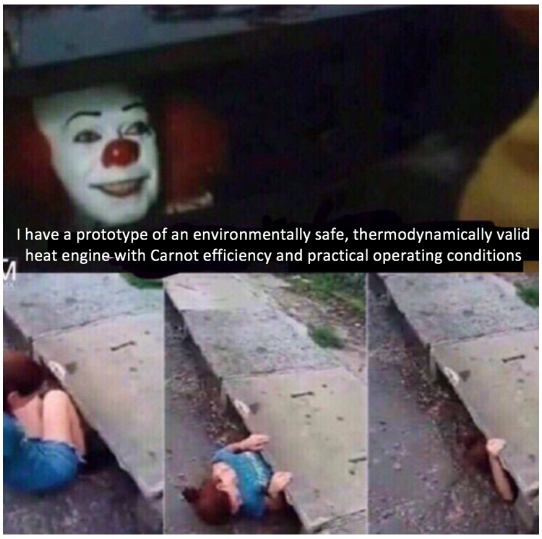
We now divide the upper and lower terms, respectively, by $nR\ln\left(\frac{V_{max}}{V_{min}}\right)$ ① and T_H ②

$$\eta = \frac{\mathbf{W}}{Q'_{in}} = \frac{(T_H - T_C)}{T_H + \frac{C_v}{R}\,\frac{(T_H - T_C)}{\ln(V_{max}/V_{min})}} \qquad \textcircled{1}$$
$$= \frac{\cancelto{\eta_{\text{carnot}}}{1 - T_C/T_H}}{\frac{C_v}{R\ln(V_{max}/V_{min})}\left(\cancelto{\eta_{\text{carnot}}}{1 - \frac{T_C}{T_H}}\right) + 1} \qquad \textcircled{2}$$
$$= \frac{\eta_{\text{carnot}}}{1 + \eta_{\text{carnot}}\frac{C_v}{R\ln(V_{max}/V_{min})}} < \eta_{\text{carnot}}. \tag{12.4}$$

We now may note that we considered the energy Q_{reg} given to the regenerator to be lost. However, this energy is reclaimed by the fluid once it traverses the regenerator in the opposite direction. If we consider that the regenerator is 100% efficient (regenerators with efficiencies of up to 95% are considered to be practically feasible [1]), then we may remove the term $nC_v\,(T_H - T_C)$ corresponding to Q_{reg} from the efficiency expression in Eq. 12.3, since this input energy is later reclaimed. Then, the efficiency in Eq. 12.3 becomes simply the Carnot efficiency η_{carnot}.

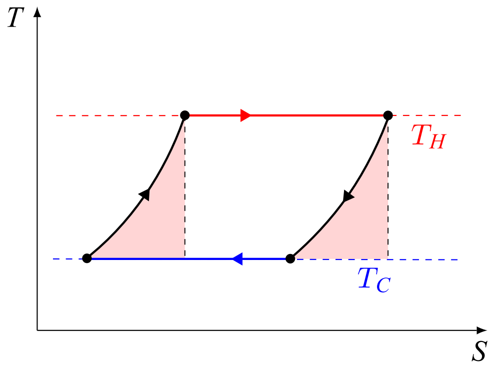
[1]: Nielsen et al. (2019), *Stirling engine regenerators: How to attain over 95% regenerator effectiveness with sub-regenerators and thermal mass ratios*

How can this be? Is it possible to have a *real* engine that is equivalent to the idealized Carnot engine?



Well, yes and no...

Indeed, the idealized cycle corresponds to a Carnot cycle, if we assume 100% efficiency in heat transfer from the regenerator. Looking at the T–S diagram, we immediately understand that the areas for the Stirling cycle and an equivalent Carnot cycle between T_H and T_C are equivalent:



Nevertheless, "real-life" irreversibilities work to bring the efficiencies of the Stirling cycle well below the Carnot cycle. We need to once again re-examine our regenerator properties. Although 95% efficiencies in heat transfer are nothing to scoff at, one needs to consider that the regenerator will induce a considerable amount of drag in the fluid movement, and the friction losses will be considerable, requiring more work from the piston to be allocated to moving the fluid back and forth. Further, and analogously to other cycles, the four processes won't be exactly isothermal or isochoric. A comparison of the ideal Stirling cycle with a real one is presented in Fig. 12.14.

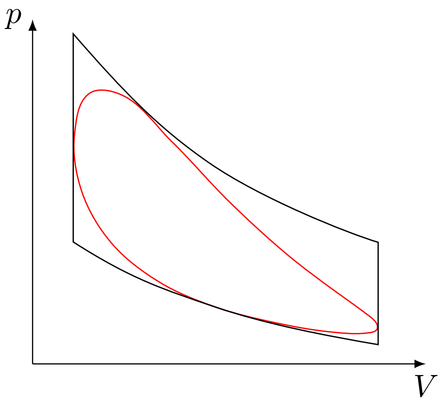


Figure 12.14: Stirling cycle: Ideal (black) vs. real (red).

All things said, the fact that this cycle operates with an external heat source, with combustion operating as a steady-process, means that the potential for optimization is considerable. Since the working fluid is enclosed in the machine, we may further optimize it, using stable, inert, and highly conductive gases like hydrogen or helium.

Clearly, research on this class of engines is still ongoing at a steady pace, and who knows what improvements the future will bring us from the minds of bright engineers?

What future for Piston engines?

It is likely that we will soon look at Otto and Diesel piston engines as we look at piston steam-engines from the 19th Century: Great inventions that were superseded by more efficient technologies, better adapted to the realities of the 21st Century. Nowadays, the de-carbonization of the different World economies moves at a steady pace, and electric vehicles are slowly displacing ICE (Internal Combustion Engine) vehicles, owing to a key advantage which is that these vehicles do not produce greenhouse and other polluting gases, and their batteries may be charged by renewable power sources.

"Yet, despite their drawbacks, classic engines still have something mythical about them – their intricate mechanisms are synchronized together to create carefully controlled conditions for harnessing fire in a truly Promethean way." (from `https://ciechanow.ski/internal-combustion-engine/`)

Figure 12.15: Prometheus Brings Fire to Mankind – Painting by Heinrich Fuger

Supplementary Material

Don't forget to check this excellent webpage and its animations which will teach you all you need to know about the inner workings of an Otto cycle gasoline engine: `https://ciechanow.ski/internal-combustion-engine/`

Nomenclature

Variables:

- n: Number of moles $n = N/N_a$ [mol]
- N: Number of particles [-]
- p: Pressure [Pa]
- Q: Heat [J]
- S: Entropy [J/K]
- T: Temperature [K]
- V: Volume [m^3]
- W: Work [J]

- r: Compression ratio of an engine [-]
- r_e: Power stroke ratio for a Diesel engine [-]
- C_v: Molar Specific Heat at Constant Pressure [J/(mol K)]
- C_v: Molar Specific Heat at Constant Volume [J/(mol K)]
- γ: Specific Heats ratio $\gamma = C_p/C_v$ [-]
- η: Efficiency of an Engine $\eta = W/Q_{in}$ [-]

Constants:

- $R = 8.31447$ [J/(mol K)]: Universal Gas Constant

Acronyms, subscripts and superscripts

- C: cold
- H: hot
- min: minimum
- max: maximum
- in: from the outside towards the system
- out: from the system towards the outside
- reg: regenerator

Chapter Summary

- Otto Cycle (Gasoline Engine);
  - Cycle: adiabatic, isochoric, adiabatic, isochoric;
  - Efficiency: $\eta = 1 - r^{(}1 - \gamma)$ with $r = V_{max}/V_{min}$ (engine compression ratio)
- Diesel Cycle;
  - Cycle: adiabatic, isobaric, adiabatic, isochoric;
  - Efficiency: $\eta = 1-(1-\gamma)\times[r_c^{(}-\gamma)-r^{(}-\gamma)]/[r_c^{(}-1)-r^{(}-1)]$ with $r = V_{max}/V_{min}$ (engine compression ratio), and $r_c = V_{max}/V_{cut}$ (engine cutoff ratio);
- Stirling Cycle;
  - Cycle: isothermal, isochoric, isothermal, isochoric;
  - Efficiency: $\eta = \eta_{Carnot}/\{1+\eta_{Carnot}[C_v/R \ln(V_{max}/V_{min})]\}$ with $r = V_{max}/V_{min}$ (engine compression ratio).

Recommended readings

- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [2], for Chapters 9.0, 9.1, 9.2, 9.3, 9.8.

Thermodynamics and Culture: Relevant Works

Chapter 12 has discussed the internal combustion engine (ICE), a mainstay of the 20th Century of ground, sea and air transportation. The internal combustion engine made automobiles possible, and the development of mass production techniques in the 1920's made the Automobile available for increasingly higher fractions of the population in industrialized countries.

The focus of this chapter's section on Thermodynamics and Culture is simple the Automobile, whose prevalence in our modern societies has made it a Cultural Icon.

Automobiles have revolutionized transportation, reshaped cities and suburbs, stimulated economic growth, and transformed social interactions. Prior to the automobile, travel was limited by the constraints of horse-drawn carriages and the reach of railroads. Cars enabled individuals and families to travel farther and more conveniently, fostering a new sense of independence. The open road became a symbol of freedom, adventure.

Beyond the practicalities of transportation, the automobile represents the ability to explore new frontiers, seek opportunities, and achieve personal independence. The pride associated with car ownership, from the first family vehicle to the dream car in the garage, speaks to a broader narrative of success and achievement that resonates across generations.

Yet, starting in the 70's, more dark undertones have been associated to automobiles, with the newfound awareness of the negative ecological impact of internal combustion engines, and the fear of dwindling resources which may ultimately lead to societal collapse.

Our selected work of art is accordingly the original movien from The Mad Max series. These have for a generation embodied our darker societal phantasms, depicting a near-future of societal collapse with lawfulness and anarchy reigning in the wasteland at the hands of marauders roving in supercharged vehicles, fighting for the last scraps of our fallen civilization.

George Miller, "*Mad Max*", 1979

"She's the last of the V8s. She sucks nitro... with Phase 4 heads! 600 horsepower through the wheels! She's meanness set to music and the bitch is born to run!"

Barry, Main Force Patrol Garage Mechanic

12.A Appendix: Superchargers and Turbochargers

The Otto cycle design described in this chapter corresponds to a *naturally aspired* internal combustion engine. The power these engines may create is limited by the amount of air the pistons can pull into the cylinders.

This limitation can be critical for car engines traveling at high altitudes, and more importantly, for piston aircraft where flying at higher altitudes/lower densities leads to significant reductions in engine power.

To overcome this limitation, so-called *Superchargers* and *Turbochargers* have been designed to force more air into the volume compressed by the piston engine, by using a compressor that increases the pressure of the air which is delivered to the engine. The difference between both concepts lies in the way this compressor is powered:

1. for *Superchargers*, the compressor is directly driven by the engine crankshaft through a belt drive;
2. for *Turbochargers*, the compressor is driven by a small turbine, powered by the engine exhaust gases which exit the engine at pressures above atmospheric pressure.

An additional device that can be added between the compressor and the engine is an *Intercooler* which will bring down the temperature of the compressed gas and allow injecting higher quantities of gas (since the density of the gas will increase as it is cooled).

The diagrams for both systems are presented in Fig. 12.16. Engineering schematics for both systems are presented in Fig. 12.17. The corresponding thermodinamic cycle is presented in Fig. 12.18.

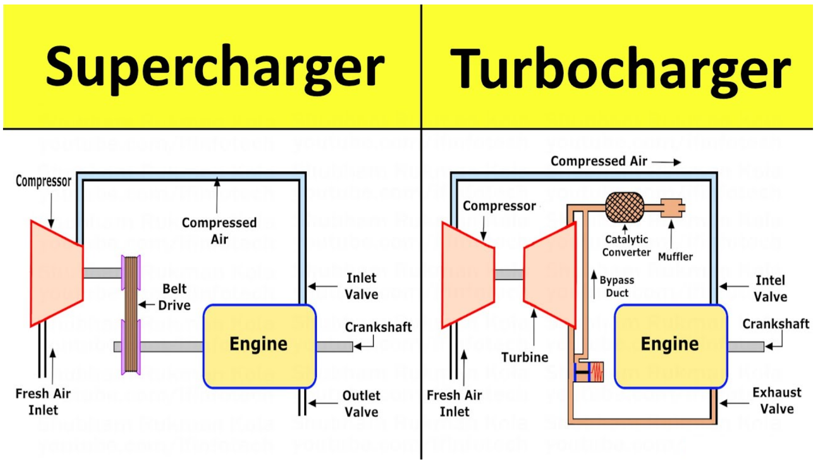


Figure 12.16: Supercharger and Turbocharger diagrams

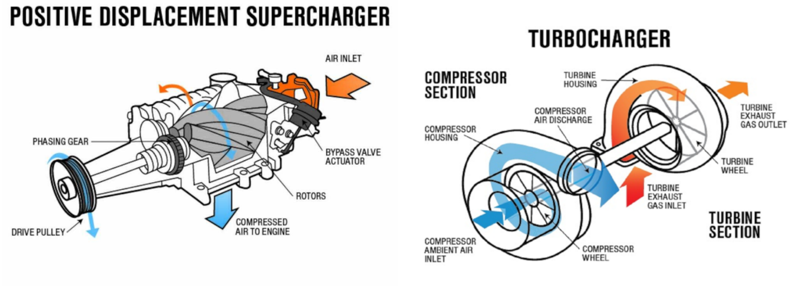


Figure 12.17: Supercharger and Turbocharger schematics

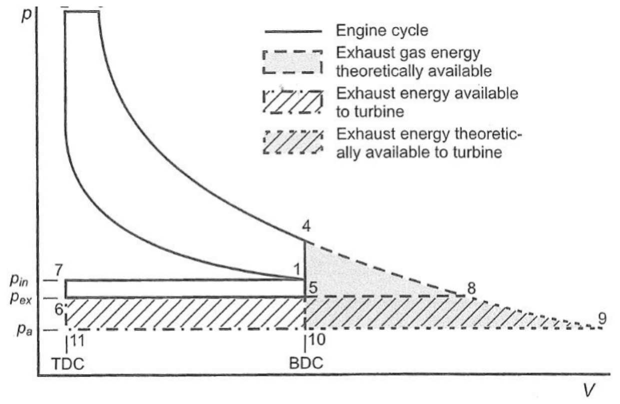


Figure 12.18: Ideal pV diagram for a turbocharged engine; adapted from: Nicholas C. Baines, Fundamentals of Turbocharging. Vermont: Concepts NREC, 2004.

The advantages and drawbacks for each system may be defined as follows:

- Supercharger: compressor powered by engine output;
  - No turbo-lag;
  - Does not impact exhaust treatment;
  - Less efficient than turbo-charging;
- Turbocharger: compressor powered by exhaust turbine;
  - More direct utilization of exhaust energy;
  - Turbo-lag problem;
  - Affects exhaust treatment;
- Intercooler:
  - Increase charge density (hence output power) by cooling the charge;
  - Lowers NOx emissions;
  - Suppresses knock;

12.A.1 Supercharging Power

The power required for driving the supercharger is determined according to the equation:

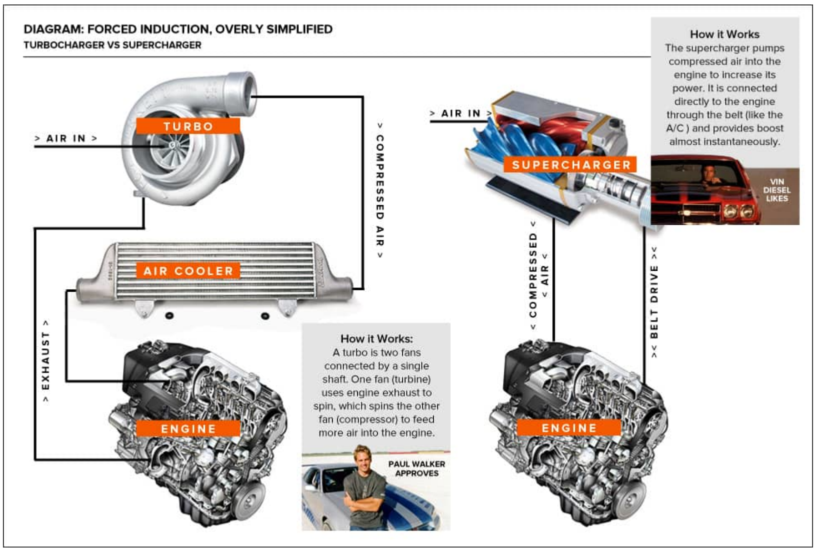
$$W_c = m_1 C_p^{atm} T_1/\eta \left[\left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \tag{12.5}$$

Where:

- η: Isentropic efficiency of the supercharger;
- p_1,T_1: atmospheric air pressure and temperature;
- p_2,T_2: atmospheric air pressure and temperature at end of compression.

This power is supplied either by:

- Gas turbine driven by exhaust gas energy of the engine;
- Separate drive by motor or any other prime mover driving the supercharger;
- Connecting the supercharger to the engine output shaft.



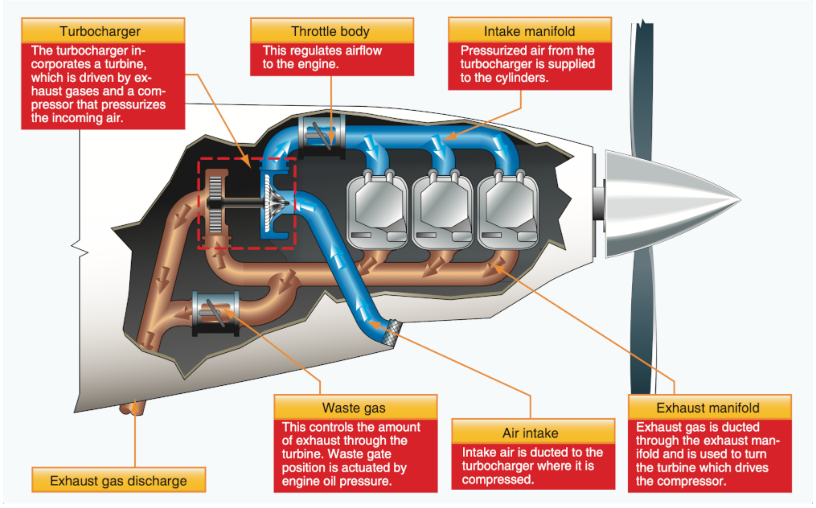
How it Works
The supercharger pumps compressed air into the engine to increase its power. It is connected directly to the engine through the belt (like the A/C) and provides boost almost instantaneously.

How it Works:
A turbo is two fans connected by a single shaft. One fan (turbine) uses engine exhaust to spin, which spins the other fan (compressor) to feed more air into the engine.

Figure 12.19: Additional diagrams.

12.A.2 Turbocharged Aircraft Piston Engines

Aircraft piston engines are typically turbocharged. See Fig. 12.20 for a schematic example.


Turbocharger
The turbocharger incorporates a turbine, which is driven by exhaust gases and a compressor that pressurizes the incoming air.

Throttle body
This regulates airflow to the engine.

Intake manifold
Pressurized air from the turbocharger is supplied to the cylinders.

Waste gas
This controls the amount of exhaust through the turbine. Waste gate position is actuated by engine oil pressure.

Air intake
Intake air is ducted to the turbocharger where it is compressed.

Exhaust manifold
Exhaust gas is ducted through the exhaust manifold and is used to turn the turbine which drives the compressor.

Figure 12.20: Aeronautic Turbocharged Engine

One of the most successful aircraft engines of the World War II era was the British Rolls-Royce Merlin, a liquid-cooled V–12 piston engine with 27-litre capacity, first ran in 1933, with mass production launched in 1936. The first operational aircraft to enter service using the Merlin were the Fairey Battle, Hawker Hurricane and Supermarine Spitfire.

The Merlin continued to benefit from a series of rapidly-applied developments, which markedly improved the engine's performance and durability. Starting at 1,000 horsepower (750 kW) for the first production models, most late war versions produced just under 1,800 horsepower (1300 kW), and the very latest version as used in the de Havilland Hornet over 2,000 horsepower (1500 kW).

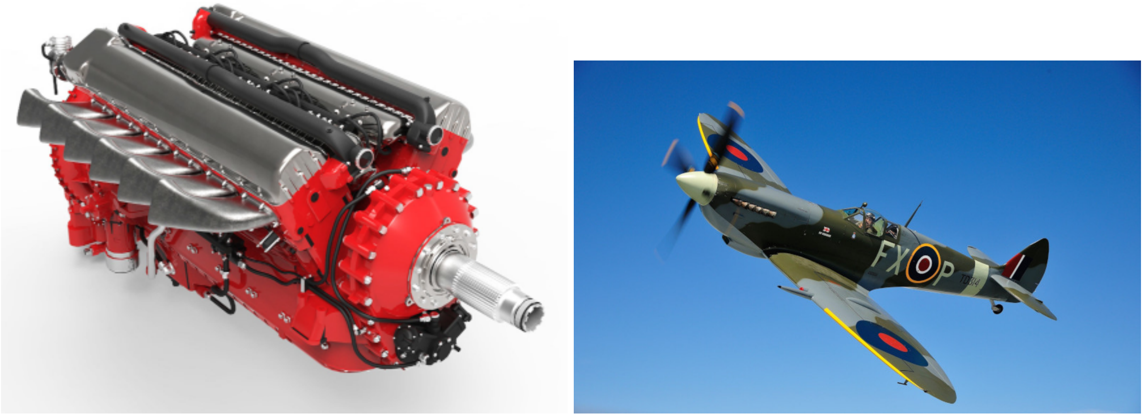


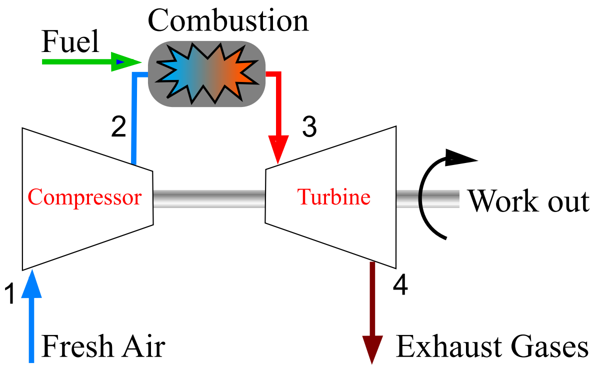
Figure 12.21: Rolls–Royce Merlin V–12 engine that powered the Supermarine Spitfire, the legendary WWII plane.

13 Control Volumes, Gas and Vapor Power Systems

- Aeronautics
- Trains
- Shipping
- Electrical Generators
- Pumps
- Gas Compressors
- Tanks

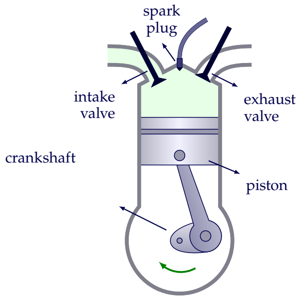
Working Principles

- Axial Compressor and Axial Turbine connected by a shaft
- The turbine is acted by a hot gas which expands and performs work
- The work exerted on the turbine acts the compressor, which returns a part of the work to the incoming fluid, compressing it
- The combustion chamber heats the gas between the compressor and the turbine



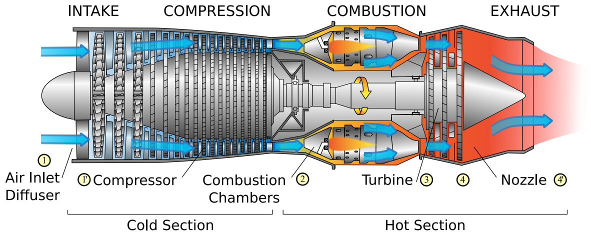
Thermodynamic cycles

Closed cycle



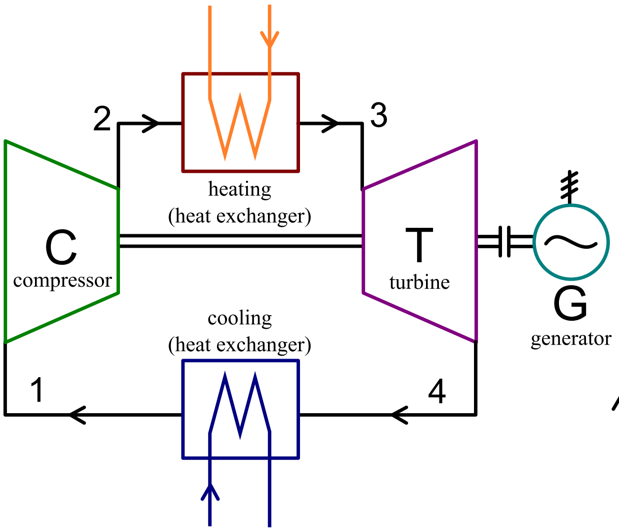
The thermodynamic processes occur in a closed volume

Open cycle

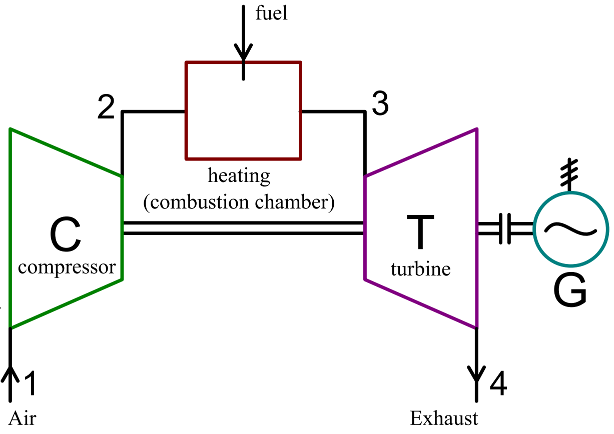


The working fluid is injected, travels inside the engine, and is expelled at the end of the process

Closed cycle

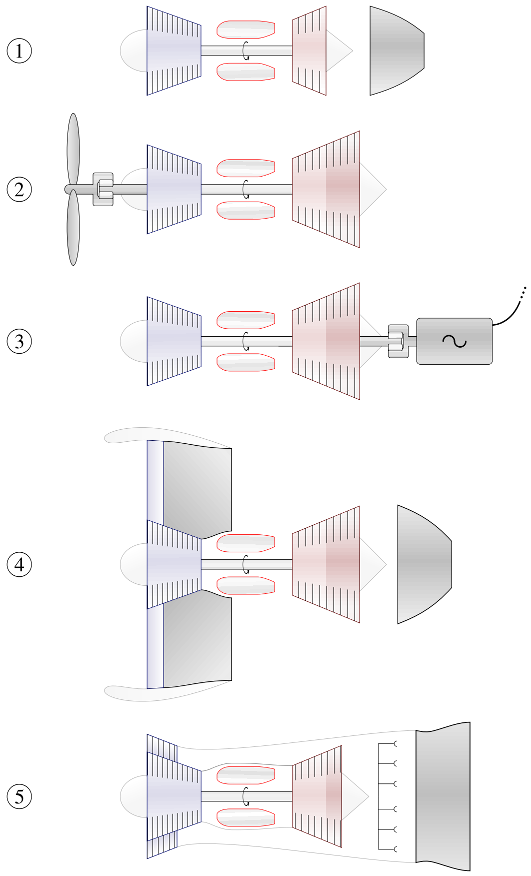


Open cycle



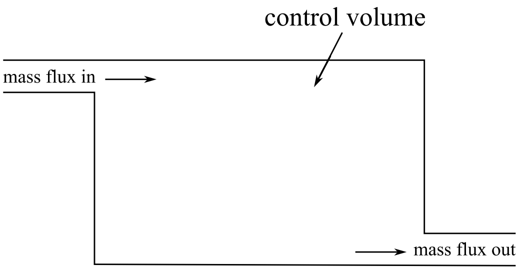
Different Gas engine types

- ① Turbojet
- ② Turboprop
- ③ Turboshaft (Generator)
- ④ Turbofan
- ⑤ Turbofan with afterburner

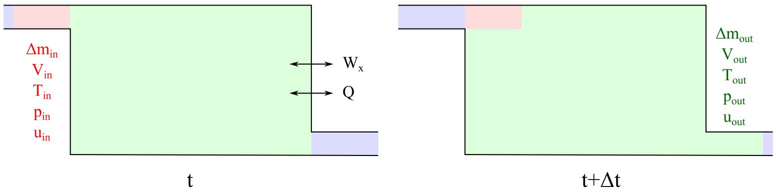


13.1 Open Thermodynamic Cycles and Control Volumes

We define a control volume such as:



We will now consider a given amount of matter Δm_{in} joining the rest of the matter in the control volume, pushing an amount of matter Δm_{out} from the same control volume after a time interval Δt.



Let us define: $E(t)$ the energy in the control volume at time t, and $E(t+\Delta t)$ the energy in the control volume at time $t + \Delta t$.

On a first approach, we will ignore the potential energy U_p and the kinetic energy K of the fluid.

We accordingly consider $E \equiv U$

$$
① \begin{cases} U_1 = U(t) \qquad +\Delta m_{in} u_{in} \quad &: \text{energy of the “system” at } t \\ U_2 = U(t+\Delta t) + \Delta m_{out} u_{out} &: \text{energy of the “system” at } t+\Delta t \end{cases}
$$

$$
② \begin{cases} U_2 - U_1 = Q - W \\ W = W_x - p_{in} V_{in} + p_{out} V_{out} \end{cases}
$$

Here W is the work performed ont the “system” (where “system”≡quantity of matter in consideration) and W_x is the work performed on the control volume. Here the state variables (p, V, m, u) define the red “system” 🟥 (in subscript) and the green “system” 🟩 (out subscript).

We now adjoin ① + ②, replace Volume V [m^3] by the product of the Specific Volume and Mass $v \times \Delta m$ [m^3/kg] × [kg] and we may write:

$$U(t+\Delta t) - U(t) + \Delta m_{out} u_{out} - \Delta m_{in} u_{in} = Q - W_x + p_{in} V_{in} - p_{out} V_{out}$$

Let us now divide this expression by Δt:

$$\frac{U(t+\Delta t) - U(t)}{\Delta t} = \frac{Q}{\Delta t} - \frac{W_x}{\Delta t} + p_{in} v_{in} \frac{\Delta m_{in}}{\Delta t} - p_{out} v_{out} \frac{\Delta m_{out}}{\Delta t} + \frac{\Delta m_{in}}{\Delta t} u_{in} - \frac{\Delta m_{out}}{\Delta t} u_{out}$$

In the limit $\Delta t \longrightarrow 0$,

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{Q} - \dot{W}_x + \dot{m}_{in} \underbrace{(p_{in} v_{in} + u_{in})}_{h_{in}} - \dot{m}_{out} \underbrace{(p_{out} v_{out} + u_{out})}_{h_{out}}$$

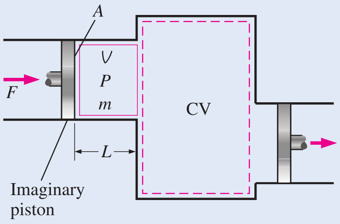
where h is the specific enthalpy (see Chapter 6).

If we further consider the system to be in the stationary regime, we have $\mathrm{d}U/\mathrm{d}t = 0$ and $\dot{m}_{in} = \dot{m}_{out}$ (this means that there is a steady mass flow at a rate measured in kg/s). The equation above simplifies to:

$$\boxed{\dot{Q} - \dot{W}_x + \dot{m}\,(h_{in} - h_{out}) = 0} \qquad (13.1)$$

Work of a Fluid: Demonstration:

Let us consider the fluid as an imaginary piston which pushes the fluid element into the control volume:



We have $F = pA$.

Let us now consider that the fluid must perform work throughout a length L to push the overall fluid element into the control volume: $W_{fluido} = F \cdot L$. We obtain:

$$W_{fluid} = FL = pAL = pV$$

accordingly, the work per unit mass will be:

$$w_{fluido}\,[\mathrm{J/kg}] = p\,[\mathrm{Pa}]V\,[\mathrm{m^3/kg}]$$

where v is now the specific volume.

13.1.1 Accounting for the fluid potential and kinetic energy

Potential energy

Let us consider the case of a water dam where the potential energy is converted into work **W**:

Here the work is produced through the decrease of the potential energy ΔU_p of the water and we have

$$\Delta \dot{U}_p = \dot{m}_{out} g z_{out} - \dot{m}_{in} g z_{in}$$

Kinetic energy

The fluid may have an inlet velocity v_{in} and an outlet velocity v_{out} with different magnitudes.

We accordingly have:

$$\Delta \dot{K} = \frac{1}{2}\dot{m}_{out} v_{out}^2 - \frac{1}{2}\dot{m}_{in} v_{in}^2$$

General form for the Energy balance equation (1st Law) for a control volume

The inclusion of the flow potential energy and kinetic energy changes yields the general equation for the 1st Law in terms of control volumes:

$$\boxed{\dot{Q} - \dot{W}_x + \dot{m}\left(h_{in} + \frac{v_{in}^2}{2} + g z_{in} - h_{out} - \frac{v_{out}^2}{2} - g z_{out}\right) = 0} \tag{13.2}$$

This energy balance equation may also be expressed in mass unit terms:

$$\dot{q} - \dot{w}_x + h_{in} + \frac{v_{in}^2}{2} + g z_{in} - h_{out} - \frac{v_{out}^2}{2} - g z_{out} = 0 \tag{13.3}$$

with $\dot{q} = \frac{\dot{Q}}{m}$ and $\dot{w}_x = \frac{\dot{W}_x}{m}$ in J/(kg s) units.

13.1.2 Mass balance in a stationary regime

For a stationary regime:

$$\sum_{in} \dot{m} = \sum_{out} \dot{m} \text{ [kg/s]}$$

The mass flux may be defined as a function of the flow density ρ, its normal velocity to the flow cross-section area v_n and its cross-section area A:

$$\dot{m} = \int_A \rho v_n \mathrm{d}A$$

For a quasi-1D flow we will accordingly have:

$$\dot{m} = \rho A v$$

If we consider the mass balance in a steady-flow regime ($\dot{m}_{in} = \dot{m}_{out}$) we have:

$$\boxed{\rho_{in} A_{in} v_{in} = \rho_{out} A_{out} v_{out}} \tag{13.4}$$

For the particular case of an incompressible fluid (for example a liquid) we may further simplify the previous expression to:

$$A_{in} v_{in} = A_{out} v_{out}$$

13.1.3 Entropy balance in a stationary regime

For a closed system we have:

$$\Delta S_{sys.} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen.} = \sum_k \frac{Q_k}{T_k} + S_{gen.}$$

The entropy change of a closed system during a process is equal to the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

For a control volume we have:

$$\frac{\mathrm{d}S_{cont.vol.}}{dt} = \sum_i \frac{\dot{Q}_i}{T_i} + \dot{m}_{in} s_{in} - \dot{m}_{out} s_{out} + \dot{S}_{gen.}$$

The rate of entropy change within the control volume during a process is equal to the sum of the rate of entropy transfer through the control volume boundary by heat transfer, the net rate of entropy transfer into the control volume by mass flow, and the rate of entropy generation within the boundaries of the control volume as a result of irreversibilities.

If we have a constant mass flux then we have $\frac{\mathrm{d}S_{cont.vol.}}{dt} = 0$ and the above expression simplifies to:

$$-\dot{S}_{gen.} = \sum_i \frac{\dot{Q}_i}{T_i} + \dot{m}\left(s_{in} - s_{out}\right)$$

Further, if the wall is adiabatic ($\dot{Q} = 0$):

$$-\dot{S}_{gen.} = \dot{m}\left(s_{in} - s_{out}\right)$$

13.2 Ideal Gas Turbine Cycle: The Brayton Cycle

Proposed in 1870.

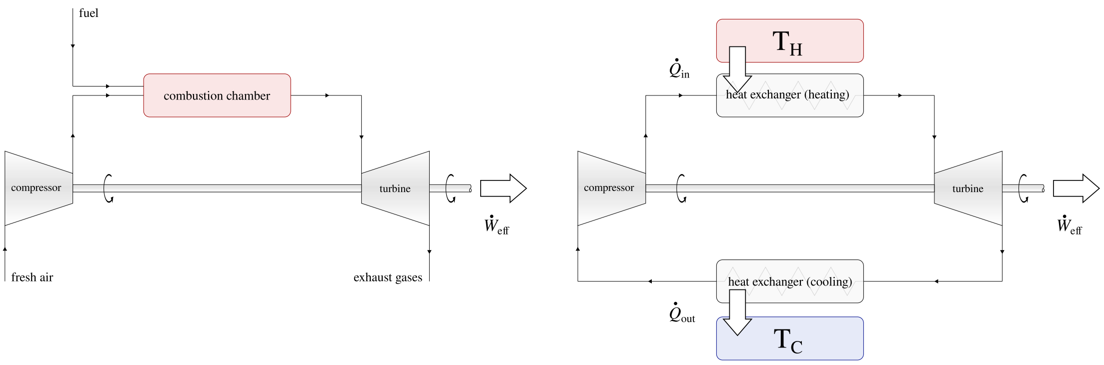


Figure 13.1: Open (left) and closed (right) Brayton cycles

The cycle is composed by four reversible processes:

- $1 \longrightarrow 2$: **Isentropic Compression** in the Compressor.
- $2 \longrightarrow 3$: **Isobaric (constant p) Heat Addition** in the Combustion Chamber (open cycle)/Heat exchanger (closed cycle).
- $3 \longrightarrow 4$: **Isentropic Expansion** in the Turbine.
- $4 \longrightarrow 1$: **Isobaric (constant p) Heat Rejection** in the Exhaust (open cycle)/Heat exchanger (closed cycle).

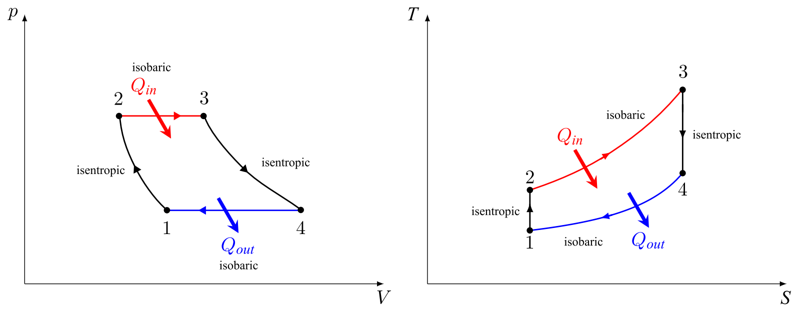


Figure 13.2: pV (left) and TS (right) diagrams for the Brayton cycle

13.3 Efficiency of the Brayton Cycle

Since the working fluid is constantly being injected into the engine, we need to use the expression of the 1st Law for a control volume in mass units (Eq. 13.3):

$$(q_{in} - q_{out}) + (w_{in} - w_{out}) = h_{out} - h_{in}$$

For the heat addition and removal parts of the cycle, $W_{in} = W_{out} = 0$. Considering that $\Delta h = C_p \Delta T$ we have:

$$\begin{cases} q_{in} = h_3 - h_2 = C_p(T_3 - T_2) \\ q_{out} = h_4 - h_1 = C_p(T_4 - T_1) \end{cases},$$

and we may accordingly calculate in a straightforward fashion the efficiency[1] for the Brayton cycle:

$$\eta_{\text{Brayton}} = \frac{W_{eff}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{C_p(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)} \quad (13.5)$$

As processes 1 ⟶ 2 and 3 ⟶ 4 are isentropic, and as processes 2 ⟶ 3 and 4 ⟶ 1 are constant pressure we have:

$$\begin{cases} p_2 = p_3; \quad p_4 = p_1 \\ \dfrac{T_2}{T_1} = \left(\dfrac{p_2}{p_1}\right)^{\dfrac{\gamma - 1}{\gamma}} = \left(\dfrac{p_3}{p_4}\right)^{\dfrac{\gamma - 1}{\gamma}} = \dfrac{T_3}{T_4} \end{cases},$$

And we accordingly have

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \Rightarrow T_4 = \frac{T_1 T_3}{T_2}$$

Replacing T_4 in Eq. 13.5 we have:

$$\begin{aligned} \eta_{\text{Brayton}} &= 1 - \frac{T_1(\cancel{T_1}T_3/T_2/\cancel{T_1} - 1)}{T_2(T_3/T_2 - 1)} \\ &= 1 - \frac{T_1\cancel{(T_3/T_2 - 1)}}{T_2\cancel{(T_3/T_2 - 1)}} \\ &= 1 - \frac{T_1}{T_2} = 1 - \frac{1}{T_2/T_1} \end{aligned}$$

Since $\frac{T_2}{T_1} = \left(\dfrac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$ we have

[1] $W_{eff} = W_{turb} - W_{comp}$. The turbine uses part of the work received by the fluid to act the compressor. Only the remaining work is available in the machine.

$$\boxed{\eta_{\text{Brayton}} = 1 - \frac{1}{r_p^{\left(\frac{\gamma-1}{\gamma}\right)}}} \tag{13.6}$$

where $r_p = p_2/p_1$ is the pressure ratio.

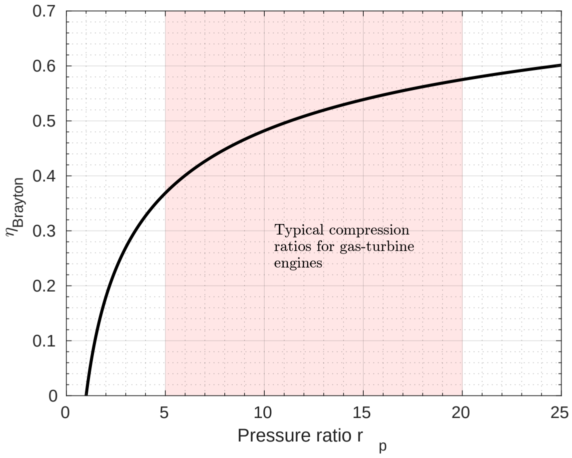


Figure 13.3: Theoretical efficiency of the Brayton cycle as a factor of the pressure ratio r_p.

Gas turbines are typically limited by the maximum temperature at turbine inlet (T_3), owing to the metallurgical limitations of these devices (excessively high temperatures may deform the turbine blades and seize the turbine.

Since the invention of the first turbines in the 1940's until today, progress in metallurgy, compounded with new techniques for the internal cooling of turbine blades, and further compounded with the spray addition of protective ceramic coatings, have brought the maximum temperature T_3^{max} from about 540 °C in 1940 up to 1425 °C (or more) today.

Accounting for these temperature limitations, we may verify that there is an optimized value for the pressure ratio r_p for which the cycle work may be maximized:

13.3.1 Application to Aeronautic Gas Turbines

In the case of an aeronautic gas turbine, the main goal is to obtain the maximum amount of *thrust* (e.g. maximize the quantity of movement $T = m_{flow} v_{flow}$ that the engine sends backward so that the aircraft may advance forward (according to Newton's action/reaction principle). In this specific case the turbine only produces the minimum amount of work required for acting the compresssor, and the exhaust gases exit the turbine at a pressure above the atmospheric pressure, performing less work.

There is an additional phase in the cycle where the addition of a nozzle will contract the gas, leading to its acceleration according to the

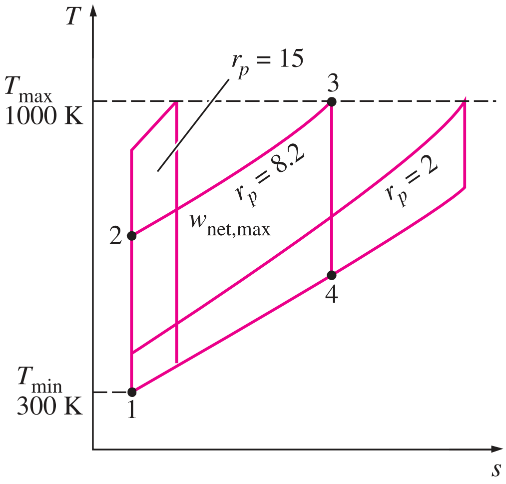


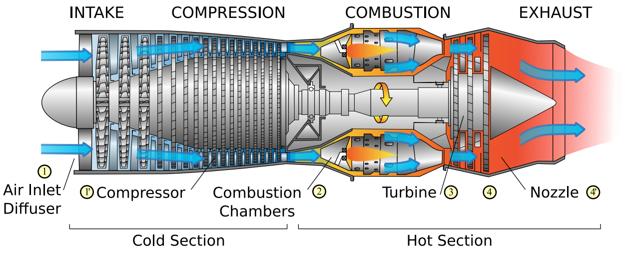
Figure 13.4: For fixed values of T_{min} and T_{max}, the net work of the Brayton cycle first increases with the pressure ratio, then reaches a maximum at $r_p = (T_{max}/T_{min})^{\gamma/[2(\gamma-1)]}$, and finally decreases.

mass conservation principle $\rho A v = const.$. Analogously, a diffuser is added in front of the compressor, which operates in an opposite fashion, expanding (and accordingly decelerating) the gas before compressor inlet.

We may invoke the Bernoulli principle:

$$\boxed{\frac{v^2}{2} + \frac{p}{\rho} + \overset{\text{usually ignored}}{\cancel{gz}} = const.}$$

to conclude that the pressure of the fluid will be inversely proportional to the square of its velocity[2]



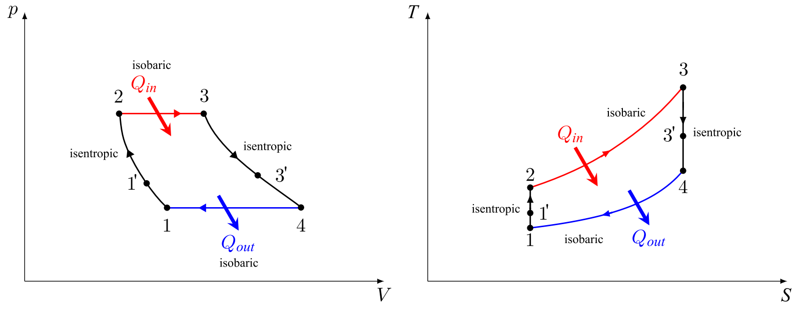


Figure 13.5: pV (left) and TS (right) diagrams for the Aeronautic Brayton cycle

One may further note that modern aeronautical gas turbines generate additional work to action *turbofans* or *turboprops* which further accelerate the fluid (externally to the engine), further increasing the efficiency of

[2] in the case of a liquid or an incompressible gas this simplifies to $p + \frac{v^2}{2} = const.$

the momentum transfer (think of a person rowing a boat. maximum efficiency is achieved by relatively slow paddling, but displacing a high aount of water).

For these cases, the efficiency is calculated as:

$$\begin{aligned} W_p &= \dot{m}\left(v_{out}^{gas} - v_{in}^{gas}\right) v_{aircraft} \quad [\text{kW}] \\ \Rightarrow\ \eta &= \frac{\dot{W}_p}{\dot{Q}_{in}} \end{aligned}$$

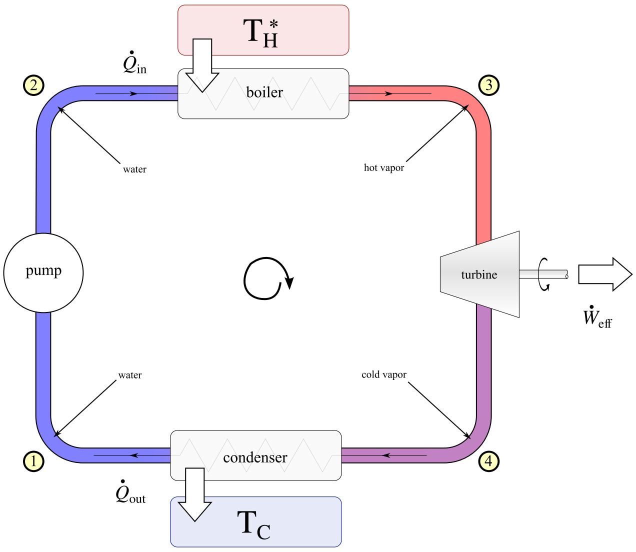
where W_p is the "propulsive power" and Q_{in} is the added heat.

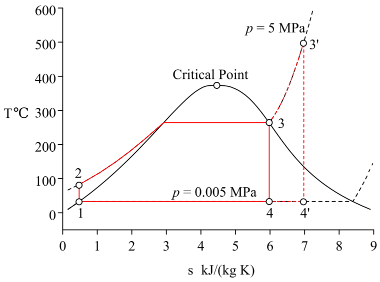
13.4 The Rankine Cycle

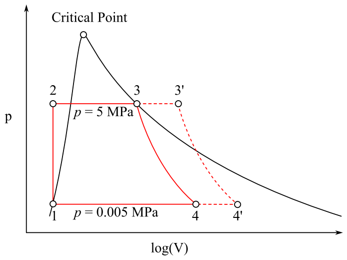
- The Rankine cycle is an idealized cycle for "steam operated engines"
- About 80% of the electricity production around the work is carried out according to the Rankine cycle. And this is not only for fossil fuels, but for a wide array of heat sources (coal, natural gas, biomass, nuclear, or solar)
- This cycle is often referred as a practical implementation of a Carnot cycle, since its T–S diagram is very similar to the one from the Carnot cycle
- The main difference lies in the heat addition (boiler) and heat rejection (condenser) processes are isobaric instead of isothermal as in Carnot's cycle
- One part of the cycle is performed in the gas phase, the other one in the liquid phase. Same as a 19th Century vapor engine (see Lecture 6).
- One key advantage of a phase change in the cycle is that the liquid water phase is incompressible, and therefore very little energy is needed to significantly raise its pressure, compared to the energy necessary to compress a gas. The pump usually consumes the equivalent of 1-3% of the energy output of a turbine, and this energy is frequently omitted in thermodynamic cycles calculations.
- The Rankine cycle efficiency is limited by the kind of fluid that is utilized. The temperature range varies between 500–600 °C at turbine inlet and 30 °C at condenser outlet.
- For such a temperature range the Carnot efficiency is:

  $$\eta_{carnot} = 1 - \frac{30 + 273.15}{600 + 273.15} \simeq 66\% \tag{13.7}$$

  The real efficiency of the best vapor centrals is $\eta = 42\%$.
- The fluid runs on a closed cycle and is constantly re-utilized. This is different from the Otto/Diesel cycles where the working fluid is renovated after each cycle.
- One of the favorite liquids for this cycle is simply water: non-toxic, cheap, plentiful, and with good thermodynamic properties







One of the main advantage for this cycle is the low amount of work that the pump needs to supply to increase the pressure of the fluid: Since the fluid is in the liquid phase, and is essentially incompressible, very little work needs to be done by the pump ($W = \int p\mathrm{d}V \sim 0$ since $\mathrm{d}V \longrightarrow 0$).

Typically the pump will only consume around 1–3% of the power supplied by the turbine.

The usual 4 processes are:

- $1 \longrightarrow 2$: The fluid in its liquid phase is compressed from p_{low} to p_{high}. The pump spends a low amount of energy (adiabatic, reversible $\longrightarrow$ isentropic process).
- $2 \longrightarrow 3$: The high-pressure liquid is heated in the boiler at $p = const.$, where heat is added by an external source (usually combustion, but also heating from nuclear fission reactions). The liquid temperature raises up until the liquid starts evaporating at $T = const.$
- $3 \longrightarrow 4$: The vapor expands in the turbine, performing work. T and p decrease (adiabatic, reversible expansion).
- $3' \longrightarrow 4'$: We may improve the cycle and perform more work if we add additional heat, bringing the fluid to a superheated vapor, and then injecting it into the turbine. Turbine designs work better it the quality of the steam is high (e.g. little to no condensated water during the $3' \longrightarrow 4'$ cycle).

- $4 \longrightarrow 1$: Constant pressure heat rejection in the condenser, transforming vapor into water.

Note that we do not have an ideal gas in this cycle, but instead a much more complex two-phase flow. It is not possible to straightforwardly calculate efficiency η from a pV diagram. In practical applications we note that this cycle involves two temperature limits (T_H and T_C) and two pressure limits (p_{low} and p_{high}), so we will be instead using steam tables at given pairs of temperature T and pressure p.

Why using Enthalpy?

The enthalpy of an ideal gas is independent of its pressure or volume, and depends only on its temperature, which correlates to its thermal energy. Real gases at common temperatures and pressures often closely approximate this behavior, which simplifies practical thermodynamic design and analysis.
Noting that the total energy of a flowing fluid is equal to its enthalpy when the kinetic and potential energies are negligible, we may then use thermodynamic tables to perform cycle analysis more straightforwardly.

From the definition of Enthalpy we have

$$H = U + pV, \tag{13.8}$$

and from the First Law we have

$$\Delta U = Q - W = Q - p\mathrm{d}V. \tag{13.9}$$

For processes at constant pressure, we have

$$\Delta H = \Delta U + p\Delta V \tag{13.10}$$

and injecting Eq. 13.9 into 13.10 we may write

$$\Delta H = \Delta Q$$

which means that

$$(\mathrm{d}H)_p = (\mathrm{d}Q)_p.$$

Since heat addition and rejection is carried out at constant pressure, the amount of added/rejected heat Q_{in}/Q_{out} is simply $H_3 - H_2$ and $H_4 - H_1$ respectively[3], and the efficiency η of the cycle is simply:

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{H_4 - H_1}{H_3 - H_2} \simeq 1 - \frac{H_4 - H_1}{H_3 - H_1}$$

[3] 3: for practical calculations we instead use the specific enthalpy h considering $H = mh$

since liquids are incompressible $\mathrm{d}V \sim 0$ and the pump work $W = p\mathrm{d}V \simeq 0$ adds very little energy to the water. We accordingly have $H_2 \simeq H_1$.

To close the calculation of the cycle, we may then assume than in process $3 \longrightarrow 4$ there is no entropy variation, and we may use the steam tables assuming[4] that $S_4 = S_3$ and then finding out the corresponding enthalpy H_4 that has the enthalpy S_3 at the lower pressure $p_4 = p_{low}$. The work supplied by the flow to the turbine is simply:

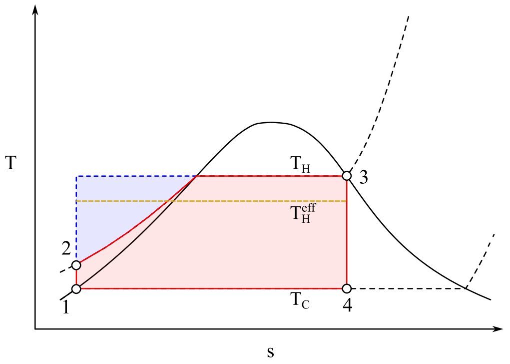
$$-\dot{W} = \dot{m}(h_4 - h_3)$$

13.4.1 Efficiency of the Rankine Cycle

Considering $Q = T\Delta S$ and $S_1 = S_2$; $S_3 = S_4$ we have:

$$Q_C = T_C \Delta S_C = T_C(S_4 - S_1)$$
$$Q_H = T_H \Delta S_H = T_H^{eff}(S_3 - S_2)$$

where T_H^{eff} is an average "effective" temperature for the heat exchange with the hot source.



In the figure above, the corresponding Carnot cycle has an additional area which corresponds to the light blue triangle, therefore by visual inspection we verify that the Rankine cycle adds less heat Q_{in} that the equivalent Carnot cycle, Q_{out} being identical to the Carnot cycle.

Here, T_H^{eff} will yield a rectangle in the $T - S$ diagram with the same area than the Rankine cycle represented in red.

We then may write:

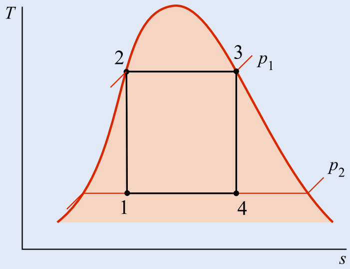
$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H^{eff}} < 1 - \frac{T_C}{T_H} < \eta_{Carnot}$$

since $T_H^{eff} < T_3 = T_H$.

[4] for non-isentropic processes, we may consider a lower efficiency η for the turbine, and then $S_4 = S_3/\eta$

Why not Carnot?

We notice that in a Rankine cycle, heat addition/rejection processes may be carried out isothermally it they are carried out exclusively under the saturated liquid curve, which is great since these are the optimal theoretical heat addition/rejection processes in a Carnot cycle. Then, if we account the pumps and turbines in typical Rankine cycles have very high efficiencies (up to 96%), we may then treat the compression and expansion processes as fully adiabatic and reversible, hence isentropic.
This means that we have a practical way to achieve a real-life Carnot cycle. So why don't we do so?



There are several practical reasons why this kind of Carnot cycle is not possible in "real life":

1. Low-quality steam with a certain amount of condensed water will cause erosion and wear in turbine blades.
2. Compressors typically handle the gas or the liquid phase and are designed differently. It is impractical to design a compressor that handles both phases.
3. It is difficult to control the condensation process to end-up precisely in point 1 as desired.

Hence the Rankine cycle is the closest to a Carnot cycle we can achieve in "real life":

"Rankine converted Carnot's idea into a practical working heat engine. He realized a real-life machine cannot be reversible. He also realized that one major constraint of the Carnot engine is its isothermal heat addition and heat rejection which limits the hot reservoir temperature and thus limits the capability of an engine to produce the amount of work. Rankine conceived an isobaric heat addition/rejection instead of an isothermal process of Carnot. An isobaric process does maximum thermodynamic work since it receives heat from outside in proportion to the work it does to keep the pressure constant. Outside heat continuously compensates for dP in the heat engine and keeps $\mathrm{d}P = \mathtt{const}$. *Therefore, while Carnot focused on* $\mathrm{d}E = 0$, *Rankine conceived* $\mathrm{d}P = \mathtt{const}$. *Thus while Carnot got maximum efficiency Rankine achieved the maximum volume of work.*
This opened the opportunity for Rankine to choose any temperature (superheat) and maximize the hot reservoir temperature that the system can tolerate. This is how Rankine converted Carnot's ideal machine into a real practical machine.[a]*"*

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[a] from: `https://www.linkedin.com/pulse/carnot-vs-rankine-cycle-nikhilesh-mukherjee-x3orf/`:

Nomenclature

Variables:

- A: Cross-Sectional Area [m^2]
- g: Acceleration of gravity [m/s^2]
- H: Enthalpy [J]
- h: Specific Enthalpy [J/Kg]
- m: Mass [Kg]
- n: Number of moles $n = N/N_a$ [mol]
- p: Pressure [Pa]
- Q: Heat [W]
- q: Specific Heat [J/Kg]
- r_p: Pressure ratio of an engine [-]
- t: Time [s]
- T: Temperature [K]
- U: Energy of a system [J]
- u: Energy of a flow unit [J]
- V: Volume [m^3]
- v: Specific Volume [m^3/Kg]
- v: Velocity [m/s]
- v_n: Velocity normal to a surface [m/s]
- W: Work [J]
- W_p: Propulsive power [W]
- W_x: Work performed on the control volume [J]
- w_x: Specific Work performed on the control volume [J/Kg]
- z: Height [m]

- C_v: Molar Specific Heat at Constant Pressure [J/molK]
- ρ: Density [Kg/m^3]
- γ: Specific Heats ratio $\gamma = C_p/C_v$ [-]
- η: Efficiency of an Engine [-]

Constants:

- $R = 8.31447$ [J/molK]: Universal Gas Constant

Acronyms, subscripts and superscripts

- C: cold
- H: hot
- p: constant pressure
- min: minimum
- max: maximum
- eff: effective
- in: from the outside towards the system
- out: from the system towards the outside

Chapter Summary

- 1^{st} Law for Control Volumes in stationary regime:
  $\dot{Q} - \dot{W}_x + \dot{m}(h_{in} + v_{in}^2/2 + gz_{in} - h_{out} + v_{out}^2/2 + gz_{out}) = 0$;
  - Mass balance in a steady-state quasi-1D flow regime:
    $m = \rho A v = constant$;
- Brayton Cycle (Gas Turbine);
  - Cycle: isentropic, isobaric, isentropic, isobaric;
  - Efficiency: $\eta = 1 - 1/r^(\gamma - 1/\gamma)$ with $r_p = p_2/p_1$ (pressure ratio);
  - Bernoulli principle: $v^2/2 + p/\rho = constant$;
- Rankine Cycle (Vapor Turbine);
  - Cycle: isentropic, isobaric, isentropic, isobaric, inside the saturation curve;
  - Efficiency: $\eta = (h_4 - h_1)/(h_3 - h_2) \approx (h_4 - h_1)/(h_3 - h_1)$.

Recommended readings

- Moran & Shapiro, "*Fundamentals of Engineering Thermodynamics*" [7], for Chapters 9.5, 9.6, 9.7, 9.11, 8.1, and 8.2.

Thermodynamics and Culture: Relevant Works

Chapter 13 discusses the theoretical foundations of gas turbine cycles, which has allowed developing gas turbines that power most of today's commercial and military planes. Since this topic is pervasive to the discipline of aeronautics, it is only fitting to select a "cool plane" action movie as our reference work of art for illustrating this chapter. The honour goes to:

Clint Eastwood, "*Firefox*", 1982

Figure 13.6: Firefox Poster, Art by Rodrigo Barraza, 2022.

Firefox is a 1982 action movie based upon a 1977 novel of the same name by Craig Thomas. This techno-thriller action film was produced and directed by Clint Eastwood, who also stars as the main actor.

The movie focuses on a plot to steal a Soviet MiG–31, NATO reporting name "Firefox", and bring it back to a friendly base where it can be analysed.

This highly advanced stealth interceptor aircraft, is capable of flying up to Mach 6, and deploys an innovative thought-control weapons system which gives its pilot a 2–3 seconds edge in air-to-air dogfights.

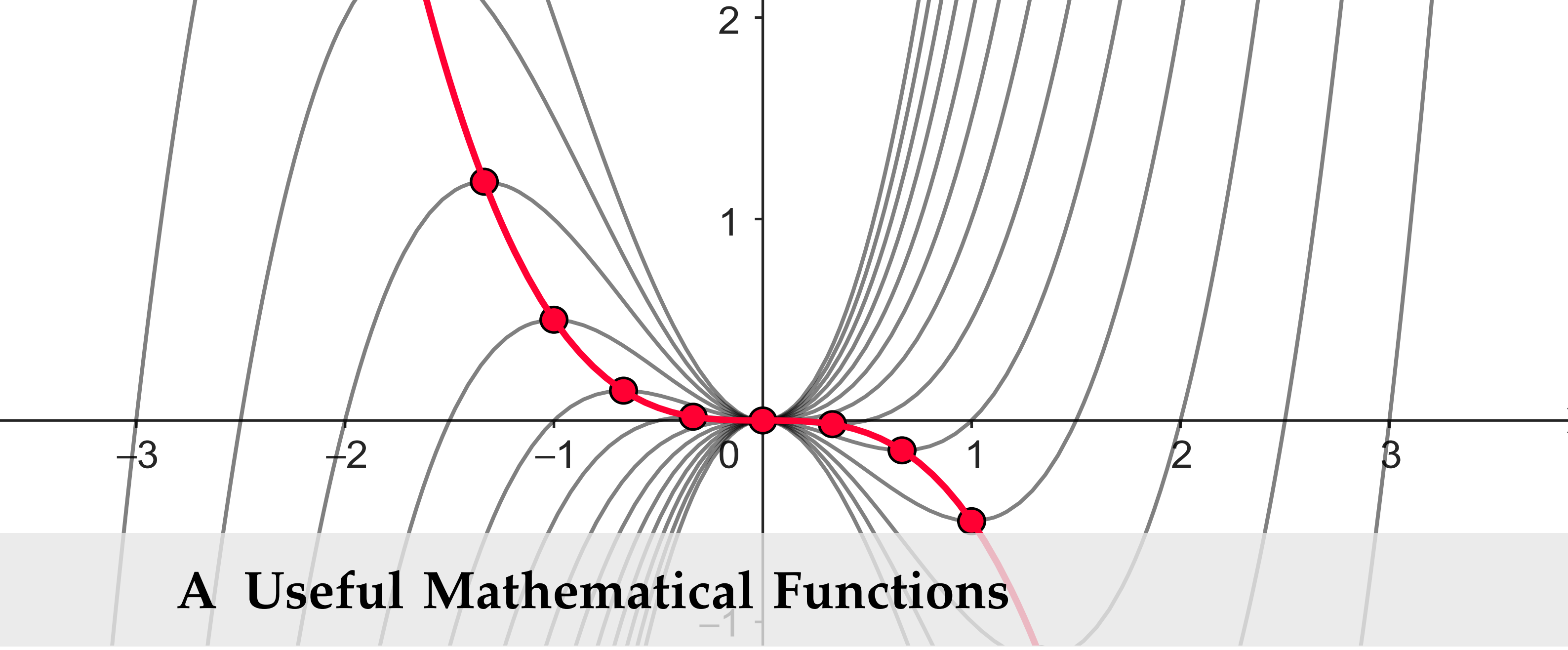
The protagonist will have to fly this experimental plane through Soviet airspace, evading interceptions up until he can reach friendly airspace.

The fictional specifications of the plane are described in the defunct website thinkinrussian.org.

Of particular interest to us is the aircraft twin gas turbine powerplant, which consisted on a fictional evolution of the Tumansky R-15BD–300 gas turbine which powered the real-life Mig–25, NATO reporting name "Foxbat" at 100 kN thrust (with afterburners on). This fictional Tumansky R-15BD–600 would supply an astounding 222 kN of thrust apiece. The aircraft would also have 6 fictional Soyuz/Komarov solid rocket boosters, providing an extra 70 kN of thrust, available during take-off or high-speed dash acceleration.

Overall the aircraft's powerplant would allow sustained cruise speeds between Mach 3.8 to 5.2 at 85,000–95,000 ft (26–29 km) altitudes.

APPENDIX



A Useful Mathematical Functions

A.1 The Factorial Integral

This appendix is taken from Blundell, *"Concepts in Thermal Physics"*, 2^{nd} Ed., Appendix C1 and C2.

One of the most useful integrals in thermodynamics problems is the following one (which is worth memorizing):

$$\boxed{n! = \int_0^\infty x^n \mathrm{e}^{-x} \mathrm{d}x} \tag{A.1}$$

This integral is simple to prove by induction as follows. First, show that it is true for the case $n = 0$. Then assume it is true for $n = k$ and prove it is true for $n = k + 1$. (Hint: integrate $(k + 1)! = \int_0^\infty x^{k+1} \mathrm{e}^{-x} \mathrm{d}x$ by parts.)

A.1.1 The Gamma Function

It allows you to define the factorial of non-integer numbers. This is so useful that the integral is given a special name, the gamma function. The traditional definition of the gamma function is

$$\boxed{\Gamma(n) = \int_0^\infty x^{n-1} \mathrm{e}^{-x} \mathrm{d}x} \tag{A.2}$$

so that $\Gamma(n) = (n - 1)!$, i.e., the factorial function and the gamma function are "out of step" with each other, a rather confusing feature. The gamma function is plotted in Fig. C.1 and has a surprisingly complicated structure for negative n. Selected values of the gamma function are listed in Table A.1. The gamma function will appear again in later integrals.

z	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	4
$\Gamma(z)$	$\frac{4\sqrt{\pi}}{3}$	$-2\sqrt{\pi}$	$\sqrt{\pi}$	1	$\frac{\sqrt{\pi}}{2}$	1	$\frac{3\sqrt{\pi}}{4}$	2	$\frac{15\sqrt{\pi}}{8}$	6

Table A.1: Selected values of the gamma function. Other values can be generated using $\Gamma(z + 1) = z\Gamma(z)$.

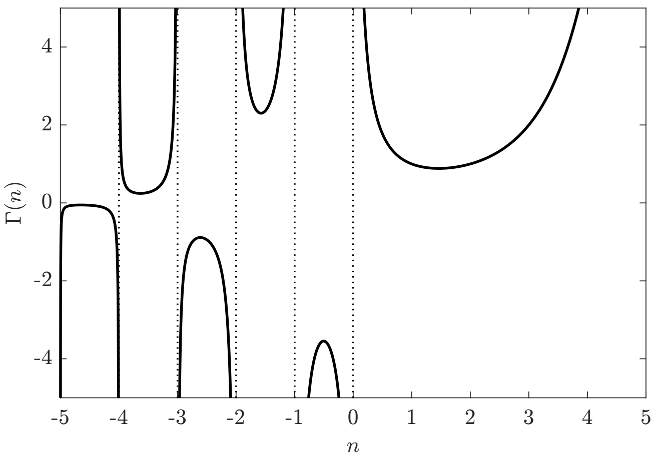


Figure A.1: The gamma function $\Gamma(n)$ showing the singularities for integer values of $n \leq 0$. For positive, integer n, $\Gamma(n) = (n-1)!$.

A.2 the Gaussian Integral

The Gaussian is a function of the form $\mathrm{e}^{-\alpha x^2}$, and is plotted in Fig. C.2. It has a maximum at $x = 0$ and a shape that has been likened to that of a bell. It turns up in many statistical problems, often under the name of the **normal distribution**. The integral of a Gaussian is another extremely useful integral:

$$\boxed{\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}} \tag{A.3}$$

It can be proved by evaluating the two-dimensional integral

$$\begin{aligned} \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y\, \mathrm{e}^{-\alpha x^2 + y^2} &= \left(\int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{e}^{-\alpha x^2}\right)\left(\int_{-\infty}^{\infty} \mathrm{d}y\, \mathrm{e}^{-\alpha y^2}\right) \\ &= I^2, \end{aligned} \tag{A.4}$$

where I is our desired integral. We can evaluate the left-hand side using polar coordinates, so that

$$I^2 = \int_0^{2\pi} \mathrm{d}\theta \int_0^{\infty} \mathrm{d}r\, r \mathrm{e}^{-\alpha r^2}, \tag{A.5}$$

which with the substitution $z = \alpha r^2$ (and hence $dz = 2\alpha r \mathrm{d}r$) gives

$$I^2 = 2\pi \times \frac{1}{2\alpha} \int_0^{\infty} \mathrm{d}z\, \mathrm{e}^{z} = \frac{\pi}{\alpha}, \tag{A.6}$$

and hence $I = \sqrt{\pi/\alpha}$ is proved.

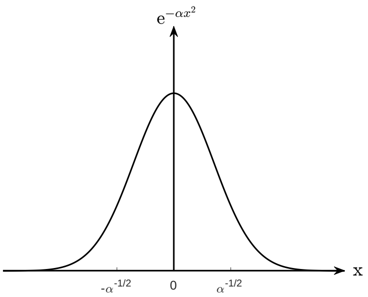


Figure A.2: A Gaussian $\mathrm{e}^{-\alpha x^2}$.

Even more fun begins when we employ a cunning stratagem: we differentiate both sides of the equation with respect to α. Because x does not depend on α, this is easy to do. Hence $(\mathrm{d}/\mathrm{d}\alpha)\mathrm{e}^{-\alpha x^2} = -x^2 \mathrm{e}^{-\alpha x^2}$ and $(\mathrm{d}/\mathrm{d}\alpha)\sqrt{\pi/\alpha} = -\sqrt{\pi}/2\alpha^{3/2}$ so that

$$\boxed{\int_{-\infty}^{\infty} x^2 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}} \tag{A.7}$$

This trick can be repeated with equal ease. Differentiating again gives

$$\boxed{\int_{-\infty}^{\infty} x^4 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{3}{4}\sqrt{\frac{\pi}{\alpha^5}}} \tag{A.8}$$

Therefore we have a way of generating the integrals between $-\infty$ and ∞ of $x^{2n}\mathrm{e}^{-\alpha x^2}$, where $n \geq 0$ is an integer[1]. Because these functions are even, the integrals of the same functions between 0 and ∞ are just *half* of these results:

$$\int_0^{\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}, \tag{A.9}$$

$$\int_0^{\infty} x^2 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}}, \tag{A.10}$$

$$\int_0^{\infty} x^4 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}}. \tag{A.11}$$

To integrate $x^{2n+1}\mathrm{e}^{-\alpha x^2}$ between $-\infty$ and ∞ is easy: the functions are all odd and so the integrals are all zero. To integrate between 0 and ∞, start off with $\int_0^{\infty} x\mathrm{e}^{-\alpha x^2}\mathrm{d}x$, which can be evaluated by noticing that $x\mathrm{e}^{-\alpha x^2}$ is almost what you get when you differentiate $\mathrm{e}^{-\alpha x^2}$. All the odd powers of x can now be obtained [2] by differentiating that integral with respect to α. Hence,

$$\int_0^{\infty} x \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2\alpha}, \tag{A.12}$$

$$\int_0^{\infty} x^3 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{2\alpha^2}, \tag{A.13}$$

$$\int_0^{\infty} x^5 \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \frac{1}{\alpha^3}. \tag{A.14}$$

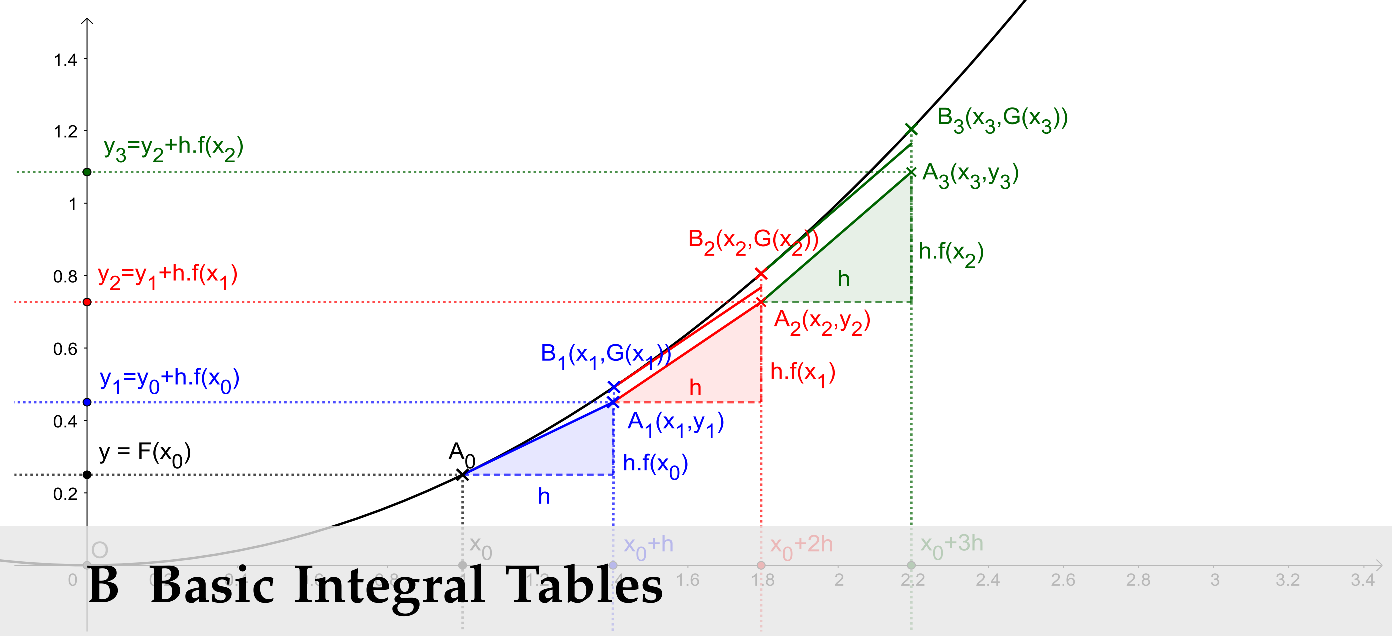
A useful expression for a normalized Gaussian (one whose integral is unity) is

$$\frac{1}{\sqrt{2\pi\sigma^2}}\mathrm{e}^{-(x-\mu)^2/2\sigma^2} \tag{A.15}$$

This has mean $\langle x \rangle = \mu$ and variance $\langle (x - \langle x \rangle)^2 \rangle = \sigma^2$.

[1] A general formula is $\int_{-\infty}^{\infty} x^{2n}\mathrm{e}^{-\alpha x^2}\mathrm{d}x = \frac{(2n)!}{n!2^{2n}}\sqrt{\frac{\pi}{\alpha^{2n+1}}}$, for integer $n \geq 0$.

[2] A general formula is $\int_{-\infty}^{\infty} x^{2n+1}\mathrm{e}^{-\alpha x^2}\mathrm{d}x = \frac{n!}{2\alpha^{n+1}}$, for integer $n \geq 0$.



B Basic Integral Tables

$$\int x^n \,\mathrm{d}x = \frac{1}{n+1}x^{n+1}, \quad n \neq -1 \tag{B.1}$$

$$\int \frac{1}{x}\,\mathrm{d}x = \ln|x| \tag{B.2}$$

$$\int u \,\mathrm{d}v = uv - \int v \,\mathrm{d}v \tag{B.3}$$

$$\int e^x \,\mathrm{d}x = e^x \tag{B.4}$$

$$\int a^x \,\mathrm{d}x = \frac{1}{\ln a}a^x \tag{B.5}$$

$$\int \ln x \,\mathrm{d}x = x\ln x - x \tag{B.6}$$

$$\int \sin x \,\mathrm{d}x = -\cos x \tag{B.7}$$

$$\int \cos x \,\mathrm{d}x = \sin x \tag{B.8}$$

$$\int \tan x \,\mathrm{d}x = \ln|\sec x| \tag{B.9}$$

$$\int \sec x \,\mathrm{d}x = \ln|\sec x + \tan x| \tag{B.10}$$

$$\int \sec^2 x \,\mathrm{d}x = \tan x \tag{B.11}$$

$$\int \sec x \tan x \,\mathrm{d}x = \sec x \tag{B.12}$$

$$\int \frac{a}{a^2+x^2}\,\mathrm{d}x = \tan^{-1}\frac{x}{a} \tag{B.13}$$

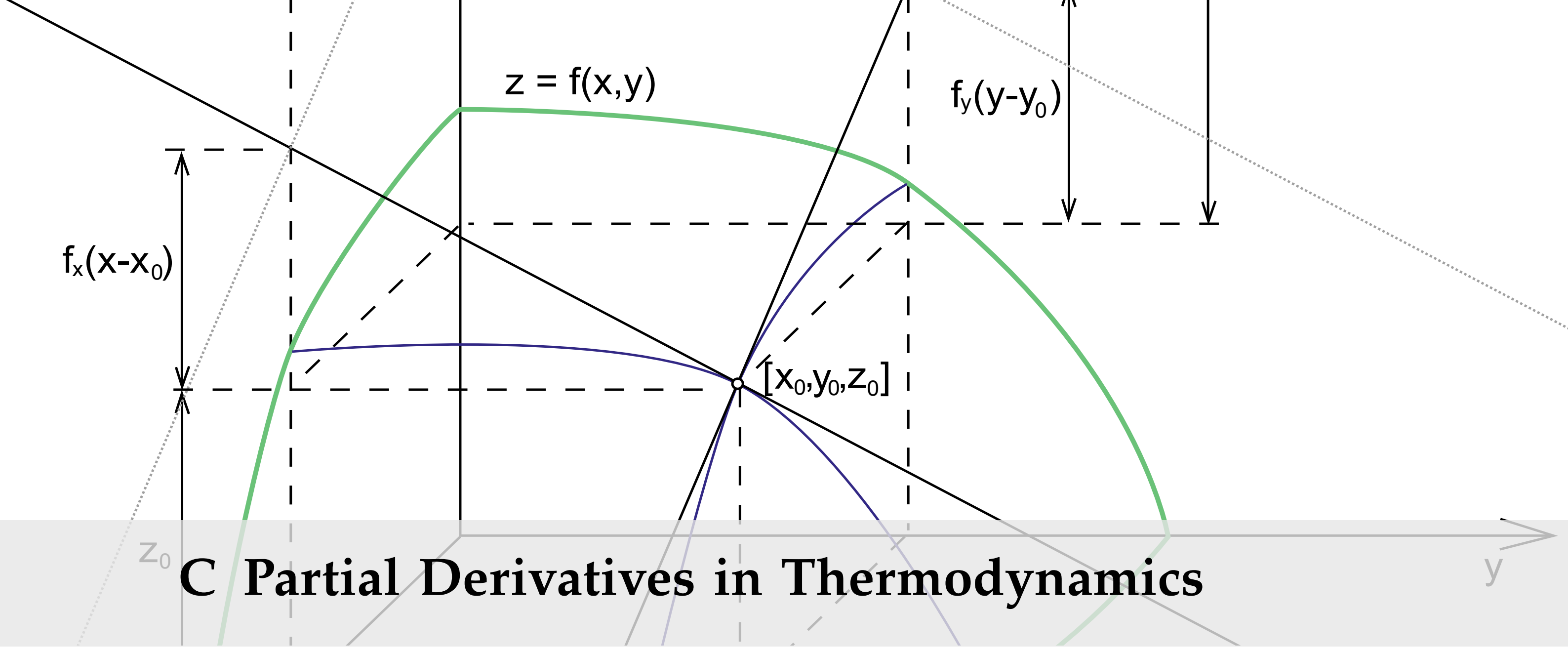
$$\int \frac{a}{a^2-x^2}\,\mathrm{d}x = \frac{1}{2}\ln\left|\frac{x+a}{x-a}\right| \tag{B.14}$$

$$\int \frac{1}{\sqrt{a^2-x^2}}\,\mathrm{d}x = \sin^{-1}\frac{x}{a} \tag{B.15}$$

$$\int \frac{a}{x\sqrt{x^2-a^2}}\,\mathrm{d}x = \sec^{-1}\frac{x}{a} \tag{B.16}$$

$$\begin{aligned}\int \frac{1}{\sqrt{x^2-a^2}}\,\mathrm{d}x &= \cosh^{-1}\frac{x}{a}\\ &= \ln(x+\sqrt{x^2-a^2})\end{aligned} \tag{B.17}$$

$$\begin{aligned}\int \frac{1}{\sqrt{x^2+a^2}}\,\mathrm{d}x &= \sinh^{-1}\frac{x}{a}\\ &= \ln(x+\sqrt{x^2+a^2})\end{aligned} \tag{B.18}$$



C Partial Derivatives in Thermodynamics

C.1 Introduction

Any text on thermodynamics is sure to be liberally sprinkled with partial derivatives on many pages, so it may be helpful to give a brief summary of some of the more useful formulas involving partial derivatives are used in this textbook suite.

C.2 Partial Derivatives

The equation

$$z = z(x,\ y) \tag{C.1}$$

represents a two-dimensional surface in three-dimensional space. The surface intersects the plane y = constant in a plane curve in which z is a function of x. One can then easily imagine calculating the slope or gradient of this curve in the plane y = constant. This slope is $\left(\frac{\partial z}{\partial x}\right)_y$ – the partial derivative of z with respect to x, with y being held constant. For example, if

$$z = y \ln x, \tag{C.2}$$

then

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{y}{x}, \tag{C.3}$$

y being treated as though it were a constant, which, in the plane y = constant, it is. In a similar manner the partial derivative of z with respect to y, with x being held constant, is

This section is borrowed practically *verbatim* from Chapter 2 of the book "Heat and Thermodynamics" by Prof. Jeremy Tatum, from the University of Victoria, Canada. The book is available online at `https://phys.libretexts.org/Bookshelves/Thermodynamics_and_Statistical_Mechanics/Heat_and_Thermodynamics_(Tatum)`

$$\left(\frac{\partial z}{\partial y}\right)_x = \ln x \tag{C.4}$$

When you have only three variables – as in this example – it is usually obvious which of them is being held constant. Thus $\partial z/\partial y$ can hardly mean anything other than at constant x. For that reason, the subscript is often omitted. In thermodynamics, there are often more than three variables, and it is usually (One would say always) essential to indicate by a subscript which quantities are being held constant.

Let us suppose that we have evaluated z at $(x,\ y)$. Now if you increase x by δx, what will the resulting increase in z be? Obviously, to first order, it is $\frac{\partial x}{\partial x}\delta x$. And if y increases by δy, the increase in z will be $\frac{\partial z}{\partial y}\delta y$. And if both x and y increase, the corresponding increase in z, to first order, will be

$$\delta z = \frac{\partial z}{\partial x}\delta x + \frac{\partial z}{\partial y}\delta y \tag{C.5}$$

No great and difficult mathematical proof is needed to "derive" this; it is just a plain English statement of an obvious truism. The increase in z is equal to the rate of increase of z with respect to x times the increase in x plus the rate of increase of z with respect to y times the increase in y.

Likewise if x and y are increasing with time at rates $\frac{dx}{dt}$ and $\frac{dy}{dt}$, the rate of increase of z with respect to time is

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\frac{dx}{dt} + \frac{\partial z}{\partial y}\frac{dy}{dt}. \tag{C.6}$$

C.3 Implicit Differentiation

Equation C.5 can be used to solve the problem of differentiation of an implicit function. Consider, for example, the unlikely equation

$$\ln(xy) = x^2y^3 \tag{C.7}$$

Calculate the derivative dy/dx. It would be easy if only one could write this in the form y = something; but it is difficult (impossible as far as we know) to write y explicitly as a function of x. Equation C.7 implicitly relates y to x. How are we going to calculate dy/dx?

The curve $f(x,\ y) = 0$ might be considered as being the intersection of the surface $z = f(x,\ y)$ with the plane $z = 0$. Seen thus, the derivative dy/dx can be thought of as the limit as δx and δy approach zero of the ratio $\delta y/\delta x$ within the plane $z = 0$; that is, keeping z constant and hence δz equal to zero. Thus equation C.5 gives us that

$$\frac{dy}{dx} = -\left(\frac{\partial f}{\partial x}\right)/\left(\frac{\partial f}{\partial y}\right). \tag{C.8}$$

For example, show that, for Equation C.7,

$$\frac{dy}{dx} = \frac{y(2x^2y^3 - 1)}{x(1 - 3x^2y^3)}. \tag{C.9}$$

C.4 Product of Three Partial Derivatives

Suppose x, y and z are related by some equation and that, by suitable algebraic manipulation, we can write any one of the variables explicitly in terms of the other two. That is, we can write

$$x = f(y,\ z), \tag{C.10a}$$

$$y = y(z,\ x), \tag{C.10b}$$

$$z = z(x,\ y). \tag{C.10c}$$

Then

$$\delta x = \frac{\partial x}{\partial y}\delta y + \frac{\partial x}{\partial z}\delta z, \tag{C.11a}$$

$$\delta y = \frac{\partial y}{\partial z}\delta z + \frac{\partial y}{\partial x}\delta x \tag{C.11b}$$

$$\delta z = \frac{\partial z}{\partial x}\delta x + \frac{\partial z}{\partial y}\delta y. \tag{C.11c}$$

Eliminating δy from Equations C.11a and C.11b and δz from Equations C.11a and C.11c:

$$\delta x\left(1 - \frac{\partial x}{\partial y}\frac{\partial y}{\partial x}\right) = \delta z\left(\frac{\partial x}{\partial z} + \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\right), \tag{C.12a}$$

$$\delta x\left(1 - \frac{\partial x}{\partial z}\frac{\partial z}{\partial x}\right) = \delta y\left(\frac{\partial x}{\partial y} + \frac{\partial x}{\partial z}\frac{\partial z}{\partial y}\right). \tag{C.12b}$$

Since z and x can be varied independently, and x and y can be varied independently, the only way in which Equations C.12a and C.12b can always be true is for all of the expressions in parentheses to be zero. Equating the left-hand parentheses to zero shows that

$$\frac{\partial x}{\partial y} = 1/\frac{\partial y}{\partial x} \tag{C.13a}$$

$$\frac{\partial x}{\partial z} = 1/\frac{\partial z}{\partial x}. \tag{C.13b}$$

These results may seem to be trivial and "obvious" – and so they are, provided that the same quantity is being kept constant in the derivatives of both sides of each equation. In thermodynamics we are often dealing with more variables than just x, y and z, and we must be careful to specify which quantities are being held constant. If, for example, we are dealing with several variables, such as u, v, w, x, y, z, it is not in general true that $\frac{\partial u}{\partial y} = 1/\frac{\partial y}{\partial u}$, unless the same variables are being held constant on both sides of the equation.

Let us return now to Equation C.12a. The left hand parenthesis is zero, and this, together with Equation C.13b, results in the important relation:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{C.14}$$

C.5 Second Derivatives and Exact Differentials

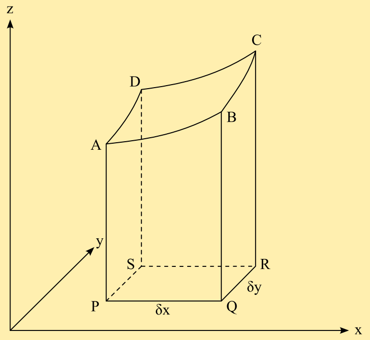
If $z = z(x,\ y)$, we can go through the motions of calculating $\frac{\partial z}{\partial x}$ and $\frac{\partial z}{\partial y}$, and we can then further calculate the second derivatives $\frac{\partial^2 z}{\partial x^2}$, $\frac{\partial^2 x}{\partial y^2}$, $\frac{\partial^2 z}{\partial y \partial x}$ and $\frac{\partial^2 z}{\partial y \partial x}$. It will usually be found that the last two, the mixed second derivatives, are equal; that is, it doesn't matter in which order we perform the differentiations.

Example C.5.1
Let $z = x \sin y$. Show that

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} = \cos y. \tag{C.15}$$

Solution

We examine in this section what conditions must be satisfied if the mixed derivatives are to be equal.
Figure C.5.1 depicts z as a "well-behaved" function of x and y. By "well-behaved" in this context we mean that z is everywhere single-valued (that is, given x and y there is just one value of z), finite and continuous, and that its derivatives are everywhere continuous (that is, no sudden discontinuities in either the function itself or its slope). "Good behaviour" in this sense is the sufficient condition that the mixed second derivatives are equal.



Let us calculate the difference δz in the heights of A and C. We can go from A to C via B or via D, and δz is route-independent. That is, to first order,

$$\delta z = \left(\frac{\partial z}{\partial x}\right)_y^{(A)} \delta x + \left(\frac{\partial z}{\partial y}\right)_x^{(B)} \delta y = \left(\frac{\partial z}{\partial y}\right)_x^{(A)} \delta y + \left(\frac{\partial z}{\partial x}\right)_y^{(D)} \delta x. \tag{C.16}$$

Here the superscript (A) means “evaluated at A”.

Divide both sides by $\delta x \delta y$:

$$\frac{\left(\frac{\partial z}{\partial y}\right)_x^{(B)} - \left(\frac{\partial z}{\partial y}\right)_x^{(A)}}{\partial x} = \frac{\left(\frac{\partial z}{\partial x}\right)_y^{(D)} - \left(\frac{\partial z}{\partial x}\right)_y^{(A)}}{\partial y}. \tag{C.17}$$

If we now go to the limit as δx and δy approach zero (the equation now becomes exact rather than merely “to first order”), this becomes:

$$\frac{\partial^2 z}{\partial x \delta y} = \frac{\partial^2 z}{\partial y \delta x}. \tag{C.18}$$

A further property of a function that is well-behaved in the sense described is that if the differential dz can be written in the form

$$dz = A(x,\ y)dx + B(x,\ y)dy, \tag{C.19}$$

then Equation C.17 implies that,

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}. \tag{C.20}$$

A differential dz is said to be exact if the following conditions are satisfied: The integral of dz between two points is route-independent, and the integral around a closed path (i.e. you end up where you started) is zero, and if equations C.17 and C.19 are satisfied.

If a differential such as Equation C.18 is exact – i.e., if it is found to satisfy the conditions for exactness – then it should be possible to integrate it and determine $z(x,\ y)$. Let us look at an example. Suppose that

$$dz = (4x - 3y - 1)dx + (-3x + 2y + 4)dy. \tag{C.21}$$

It is readily seen that this is exact. The problem now, therefore, is to find $z(x,\ y)$.

Let $u = \int (4x - 3y - 1)dx$

So that

$$u = 2x^2 - 3yx - x + g(y). \tag{C.22}$$

Note that we are treating y as constant. The “constant” of integration depends on the value of y – i.e. it is an arbitrary function of y.

Of course u is not the same as z – unless we can find a particular function $g(y)$ such that u indeed is the same as z.

Now $du = \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y}dy$; that is,

$$du = (4x - 3y - 1)dx + \left(-3x + \frac{dg}{dy}\right)dy. \tag{C.23}$$

Then $du = dz$ (and $u = z$ plus an arbitrary constant) provided that

$\frac{dg}{dy} = 2y + 4$. That is,

$$g(y) = y^2 + 4y + \text{constant}. \tag{C.24}$$

Thus

$$z = 2x^2 - 3xy + y^2 - x + 4y + \text{constant} \tag{C.25}$$

The reader should verify that this satisfies equation C.20. The reader should also try letting

$$v = -3xy + y^2 + 4y + f(x) \tag{C.26}$$

(where did this come from?) and go through a similar argument to arrive again at equation C.24.

Consider another example,

Example C.5.2

$$dz = 3 \ln y \; dx + \frac{x}{y} dy. \tag{C.27}$$

You should immediately find that this differential is not exact, and, to emphasize that, we shall use the symbol ${\mathchar'26\mkern-12mu d}z$, the special symbol ${\mathchar'26\mkern-12mu d}$ indicating an inexact differential. However, given an inexact differential ${\mathchar'26\mkern-12mu d}z$, it is very often possible to find a function $H(x,\ y)$ such that the differential $dw = H(x,\ y){\mathchar'26\mkern-12mu d}z$ is exact, and dw can then be integrated to find w as a function of x and y. The function $H(x,\ y)$ is called an integrating factor. There may be more than one possible integrating factor; indeed it may be possible to find one simply of the form $F(x)$ or maybe $G(y)$. There are several ways for finding an integrating factor. We'll do a simple and straightforward one. Let us try and find an integrating factor for the inexact differential ${\mathchar'26\mkern-12mu d}z$ above. Thus, let $dw = F(x)dz$, so that

$$dw = 3F \ln y \; dx + \frac{xF}{y} dy. \tag{C.28}$$

For dw to be exact, we must have

$$\frac{\partial}{\partial y}(3F \ln y) = \frac{\partial}{\partial x}\left(\frac{xF}{y}\right). \tag{C.29}$$

That is,

$$\frac{3F}{y} = \frac{1}{y}\left(F + x\frac{dF}{dx}\right). \tag{C.30}$$

Upon integration and simplification we find that

$$F = x^2, \tag{C.31}$$

or any multiple thereof, is an integrating factor, and therefore

$$dw = 3x^2 \ln y \; dx + \frac{x^3}{y} dy \tag{C.32}$$

is an exact differential. The reader should confirm that this is an exact differential, and from there show that

$$w = x^3 \ln y + \text{constant} \tag{C.33}$$

To anticipate – what has this to do with thermodynamics? To give an example, the state of many simple thermodynamical systems can be specified by giving the values of three intensive state variables, p, V and T, the pressure, molar volume and temperature. That is, the state of the system can be represented by a point in pVT space. Often, there will be a known relation (known as the equation of state) between the variables; for example, if the substance involved is an ideal gas, the variables will be related by $pV = RT$, which is the equation of state for an ideal gas; and the point representing the state of the system will then be represented by a point that is constrained to lie on the two-dimensional surface $pV = RT$ in three-dimensional pVT space. In that case it will be necessary to specify only two of the three variables. On the other hand, if the equation of state of a particular substance is unknown, you will have to give the values of all three variables.

Now there are certain quantities that one meets in thermodynamics that are functions of state. Two that come to mind are entropy S and internal energy U. By function of state it is meant that S and U are uniquely determined by the state (i.e. by p, V and T). If you know p, V and T, you can calculate S and U or any other function of state. In that case, the differentials dS and dU are exact differentials.

The internal energy U of a system is defined in such a manner that when you add a quantity dQ of heat to a system and also do an amount of work dW on the system, the increase dU in the internal energy of the system is given by

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W. \tag{C.34}$$

Here dU is an exact differential, but dQ and dW are clearly not. You can achieve the same increase in internal energy by any combination of heat and work, and the heat you add to the system and the work you do on it are clearly not functions of the state of the system.

Some authors like to use a special symbol, such as đ, to denote an inexact differential (but beware, this symbol has been used used to denote an exact differential in some sources!). We shall not in general do this, because there are many contexts in which the distinction is not important, or, if it is, it is obvious from the context whether a given differential is exact or not. If, however, there is some context in which the distinction is important (and there are many) and in which it may not be obvious which is which, we may, with advance warning, use a special đ for an inexact differential, and indeed we have already done so earlier in this section.

C.6 Euler's Theorem for Homogeneous Functions

There is a theorem, usually credited to Euler, concerning homogenous functions that we might be making use of.

A homogenous function of degree n of the variables x, y, z is a function in which all terms are of degree n. For example, the function $f(x,\ y,\ z) = Ax^3 + By^3 + Cz^3 + Dxy^2 + Exz^2 + Gyx^2 + Hzx^2 + Izy^2 + Jxyz$ is a homogenous function of x, y, z, in which all terms are of degree three.

The reader will find it easy to evaluate the partial derivatives $\frac{\partial f}{\partial x}, \frac{\partial f}{\partial x}, \frac{\partial f}{\partial x}$ and equally easy (if slightly tedious) to evaluate the expression $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z}$. Tedious or not, we do urge the reader to do it. You should find that the answer is $3Ax^3 + 3By^3 + 3Cz^3 + 3Dxy^2 + 3Exz^2 + 3Fyz^2 + 3Gyx^2 + 3Hzx^2 + 3Izy^2 + 3Jxyz$.

In other words, $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = 3f$. If you do the same thing with a homogenous function of degree 2, you will find that $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = 2f$. And if you do it with a homogenous function of degree 1, such as $Ax + By + Cz$, you will find that $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = f$. In general, for a homogenous function of $x, y, z...$ of degree n, it is always the case that

$$x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} + ... = nf. \tag{C.35}$$

This is Euler's theorem for homogenous functions.

C.7 Undetermined Multipliers

Let $\psi(x, y, z)$ be some function of x, y and z. Then if x, y and z are independent variables, one would ordinarily understand that, where ψ is a maximum, the derivatives are zero:

$$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial z} = 0. \tag{C.36}$$

However, if x, y and z are not completely independent, but are related by some constraining equation such as $f(x, y, z) = 0$, the situation is slightly less simple. (In a thermodynamical context, the three variables may be, for example, three "intensive state variables", p, V and T, and ψ might be the entropy, which is a function of state. However the intensive state variables may not be completely independent, since they are related by an "equation of state", such as $pV = RT$.)

If we move by infinitesimal displacements dx, dy, dz from a point where ψ is a maximum, the corresponding changes in ψ and f will both be zero, and therefore both of the following equations must be satisfied.

$$d\psi = \frac{\partial \psi}{\partial x}dx + \frac{\partial \psi}{\partial y}dy + \frac{\partial \psi}{\partial z}dz = 0, \tag{C.37}$$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0. \tag{C.38}$$

Consequently any linear combination of ψ and f, such as $\phi = \psi + \lambda f$, where λ is an arbitrary constant, also satisfies a similar equation. The constant λ is sometimes called an "undetermined multiplier" or a "Lagrangian multiplier", although often some additional information in an actual problem enables the constant to be identified.

In summary, the conditions that ψ is a maximum (or minimum or saddle point), if x, y and z are related by a functional constraint $f(x, y, z) = 0$, are

$$\tfrac{\partial \Phi}{\partial x} = 0 \quad \tfrac{\partial \Phi}{\partial y} = 0, \quad \tfrac{\partial \Phi}{\partial z} = 0, \tag{C.39}$$

where

$$\Phi = \psi + \lambda f. \tag{C.40}$$

Of course, if ψ is a function of many variables $x_1, x_2, x_3...$, and the variables are subjected to several constraints, such as $f = 0, g = 0, h = 0$, etc., where f, g, h, etc..., are functions connecting all or some of the variables, the conditions for ψ to be a maximum (etc...) are

$$\frac{\partial \psi}{\partial x_i} + \lambda\frac{\partial \psi}{\partial x_i} + \mu\frac{\partial \psi}{\partial x_i} + \nu\frac{\partial \psi}{\partial x_i} + ... = 0, \ i = 1,\ 2,\ 3 \tag{C.41}$$

C.8 Dee and Delta

We have discussed the special meanings of the symbols ∂ and $đ$, but we also need to be clear about the meanings of the more familiar differential symbols Δ, δ, and d. It is often convenient to use the symbol Δ to indicate an increment (not necessarily a particularly small increment) in some quantity. We can then use the symbol δ to mean a small increment. We can then say that if, for example, $y = x^2$, and if x were to increase by a small amount δx, the corresponding increment in y would be given approximately by

$$\delta y \cong 2x\delta x \tag{C.42}$$

That is,

$$\frac{\partial y}{\partial x} \cong 2x. \tag{C.43}$$

This doesn't become exact until we take the limit as δx and δy approach zero. We write this limit as $\frac{dy}{dx}$ and then it is exactly true that

$$\frac{dy}{dx} = 2x. \tag{C.44}$$

There is a valid point of view that would argue that you cannot write dx or dy alone, since both are zero; you can write only the ratio $\frac{dx}{dy}$. It would be wrong, for example, to write

$$dy = 2x\,dx, \tag{C.45}$$

or at best it is tantamount to writing $0 = 0$. We are not going to contradict that argument, but, at the risk of incurring the wrath of some readers, we are often going to write equations such as Equation C.45, or, more likely, in a thermodynamical context, equations such as

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V, \tag{C.46}$$

even though you may prefer one to say that, for small increments,

$$\delta U \cong T\delta S - p\delta V. \tag{C.47}$$

We are going to argue that, in the limit of infinitesimal increments, it is exactly true that $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$. After all, the smaller the increments, the closer it becomes to being true, and, in the limit when the increments are infinitesimally small, it is exactly true, even if it does just mean that zero equals zero. We hope this does not cause too many conceptual problems.

D Thermodynamic Cycles

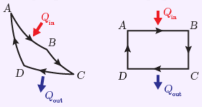
Heat Engines & Pumps

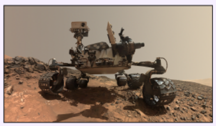
P-V **T-s**

Nicolas Léonard Sadi Carnot is often called the "father of thermodynamics".

Carnot

Theoretical ideal cycle. Provides upper limit on heat engine and heat pump efficiency.



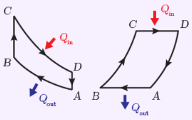


The Chemistry and Mineralogy instrument aboard the Mars Curiosity rover uses a Ricor Stirling cryocooler.

Stirling

aka Philips

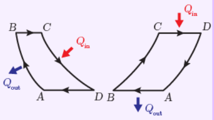
Heat Engine: External combustion. Used in electrical power generation and cogeneration.
Heat Pump: Regenerative. Used in cryocoolers.



An Ericsson cycle steam engine propelled the caloric ship "Ericsson".

Ericsson

Heat Engine: External combustion.
Heat Pump: Regenerative.
No current commercial usage.

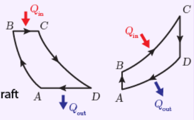


The Boeing 747-8 uses four General Electric turbofans for propulsion.

Brayton

aka Joule-Brayton, Bell Coleman (reverse)

Heat Engine: Typically internal combustion. Used in gas turbines.
Heat Pump: Recuperative. Used in cryocoolers, gas liquefaction, and aircraft air conditioning.



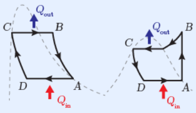
Heat Pumps

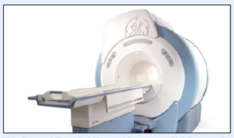
P-V **T-s**

This LG refrigerator runs R600a refrigerant in a vapor compression cycle.

Vapor Compression

Used in building and automobile air conditioning; domestic, commercial, and industrial refrigeration.

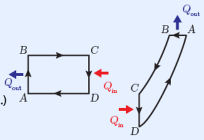


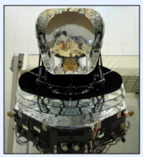


This General Electric MRI machine uses a SHI Cryogenics Gifford-McMahon cryocooler to cool its magnets.

Gifford-McMahon

Regenerative. Used in cryocoolers. (PV diagram shown for cold volume.)



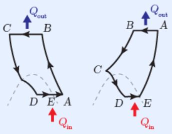


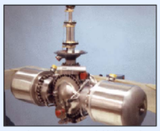
The Planck space observatory used a Joule-Thomson cryocooler to cool its sensors.

Joule-Thomson

aka Linde, Hampson-Linde

Recuperative. Used in cryocoolers and gas liquefaction.

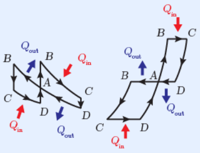




The Hi-Cap cooler was a research Vuilleumier cryocooler developed by Hughes Aircraft Company

Vuilleumier

Regenerative. Variation of the Stirling cycle. No current commercial usage.



Heat Engines

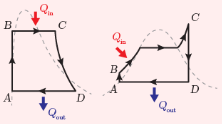
P-V **T-s**

Siemens steam turbines drive electrical generators at the Eemshaven power plant.

Rankine

aka Clausius-Rankine, Hirn

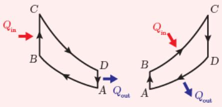
External combustion. Used in steam turbines and engines.



The 1966 Oldsmobile Torondo was powered by a 425 ci 385 hp big-block V-8 engine.

Otto

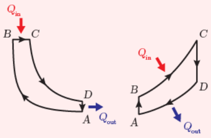
Internal combustion. Used in gasoline engines.



"Eleonora Mærsk" is powered by the Wärtsilä RT-flex96C, the largest combustion engine in the world.

Diesel

Internal combustion. Used in lower speed diesel engines.

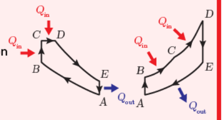


The Freightliner 122SD is powered by a 906 ci 505 hp I-6 diesel engine.

Dual

aka Mixed, Sabathe, Trinkler, Seiliger

Internal combustion. Combination of Otto and Diesel cycles. Used in higher speed diesel engines.

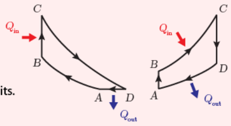


This micro cogeneration unit uses Honda's Extended Expansion Linkage Engine.

Atkinson

aka Humphrey

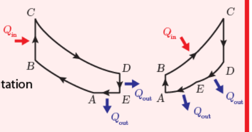
Internal combustion. Used in gas-powered cogeneration units.



Many hybrid automobiles, like the Toyota Prius, simulate the ideal Atkinson cycle through variable valve timing.

Miller

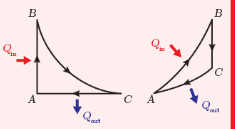
Internal combustion. Used in some gasoline and diesel engines. Practical implementation of the Atkinson cycle.



The Enics E95M target drone is propelled by a pulse jet engine.

Lenoir

Internal combustion. Used in pulse jet engines.



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Credit: erk070, `https://www.reddit.com/r/thermodynamics/comments/qu80be/i_compiled_this_image_describing_a_bunch_of/`

E Numerical Scripts

The scripts presented here were originally developed in Matlab language. They have been translated to python language using the ChatGPT AI assistant.

E.1 Boltzmann Distribution

This python3 script (requiring the numpy and matplotlib libraries) is invoked in Cahpter 2, Section 2.1.2. It runs 3 different examples:

1. Creates a 10x10 grid square with one particle in each box. Pressing space aleatorily takes a particle from a box and puts it in another one. 20 manual steps.
2. Same as 1) for a 10x10 grid except now the code runs automatically for 1000 iterations with a 0.2 s pause for the first 100 and an infinitesimal pause for the remainder ones.
3. The code makes the same 100,000 iterations for a 100x100 grid and just displays the final distribution.

Which all yield a Boltzmann distribution for a sufficiently large number of events.

```
import numpy as np
import matplotlib.pyplot as plt

# Function to display options and get user input
def choose_option():
    print(’Choose an option: 1, 2, or 3’)
    print(’Option 1: Press space to aleatorily take a particle from a box and put it in another in a 10x10 grid square. 20 manual steps’)
    print(’Option 2: Code runs automatically to aleatorily take a particle from a box and put it in another in a 10x10 grid square. 1000 steps’)
    print(’Option 3: Code runs automatically to take a particle from a box and put it in another in a 100x100 grid square. 100,000 steps’)
    example = int(input(’Enter a number: ’))
```

```
    return example

# Get the chosen option
example = choose_option()

# Setup variables based on the chosen option
if example == 1:
    boxsize = 10
    iterations = 20
    plot_iter = True
    pause_iter = True
elif example == 2:
    boxsize = 10
    iterations = 1000
    plot_iter = True
    pause_iter = False
elif example == 3:
    boxsize = 100
    iterations = 100000
    plot_iter = False
    pause_iter = False

# Initialize the box
box = np.ones((boxsize, boxsize))

# Create the figure
fig, (ax1, ax2) = plt.subplots(1, 2, figsize=(12, 6))
ax1.set_title('Box State')
ax2.set_title('Histogram')

# Display the initial state
heatmap = ax1.imshow(box, cmap='jet', vmin=0, vmax=9)
plt.colorbar(heatmap, ax=ax1)
histogram = ax2.hist(box.ravel(), bins=np.arange(-0.5, 10.5, 1), edgecolor='black')
ax2.set_xlim([-0.5, 10])
ax2.set_ylim([0, 100])
plt.pause(0.01)  # To allow the figure to render

if example == 1:
    input("Press Enter to continue...")

# Main iteration loop
for i in range(1, iterations + 1):
    initial = [np.random.randint(1, boxsize + 1), np.random.randint(1, boxsize + 1)]
    final = [np.random.randint(1, boxsize + 1), np.random.randint(1, boxsize + 1)]

    if box[initial[0] - 1, initial[1] - 1] != 0:  # Check if there is a particle
        box[initial[0] - 1, initial[1] - 1] -= 1
        box[final[0] - 1, final[1] - 1] += 1

    if plot_iter:
        heatmap.set_data(box)
      # plt.colorbar(heatmap, ax=ax1) # commented otherwise it is doing new colormap over and over
```

```
        ax2.clear()
        ax2.hist(box.ravel(), bins=np.arange(-0.5, 10.5, 1), edgecolor=’black’)
        ax2.set_xlim([-0.5, 10])
        ax2.set_ylim([0, 100])

        # Slow down first 100 iterations in example 2
        if example == 2 and i < 100:
            plt.pause(0.2)

        plt.pause(0.000001)

        if pause_iter:
            input("Press Enter to continue...")

    print(f’iteration {i}’)

# Final display
heatmap.set_data(box)
# plt.colorbar(heatmap, ax=ax1) # commented otherwise it is doing new colormap over and over
ax2.clear()
ax2.hist(box.ravel(), bins=np.arange(-0.5, 10.5, 1), edgecolor=’black’)

if example == 3:
    ax2.set_yscale(’log’)

plt.show()
```

E.2 Random Walk

This python3 script (requiring the numpy, matplotlib, and tkinter libraries) is invoked in Chapter **??**, Section **??**. It simulates the random walk motion of N particles whith an equivalent diffusion coefficient D, for a set of time intervals $\mathrm{d}t$. The values can be adjusted by the user using a small Graphical User Interface.

The user can for example run the simulation with the following parameters: $N = 1000$, $D = 10$, $\mathrm{d}t = 10$.

```
import tkinter as tk
from tkinter import messagebox
import numpy as np
import matplotlib.pyplot as plt

class RunMeApp:
    def __init__(self, master):
        self.master = master
        master.title("Run Me App")

        self.isrun = False

        self.N_label = tk.Label(master, text="N:")
        self.N_label.pack()
        self.N_entry = tk.Entry(master)
```

```python
        self.N_entry.pack()

        self.D_label = tk.Label(master, text="D:")
        self.D_label.pack()
        self.D_entry = tk.Entry(master)
        self.D_entry.pack()

        self.dt_label = tk.Label(master, text="dt:")
        self.dt_label.pack()
        self.dt_entry = tk.Entry(master)
        self.dt_entry.pack()

        self.dx_label = tk.Label(master, text="dx:")
        self.dx_label.pack()
        self.dx_entry = tk.Entry(master)
        self.dx_entry.config(state='readonly')
        self.dx_entry.pack()

        self.track_var = tk.BooleanVar()
        self.track_check = tk.Checkbutton(master, text="Track", variable=self.track_var)
        self.track_check.pack()

        self.run_button = tk.Button(master, text="Run", command=self.run_simulation)
        self.run_button.pack()

        self.stop_button = tk.Button(master, text="Stop", command=self.stop_simulation)
        self.stop_button.pack()

        self.canvas = None

    def run_simulation(self):
        self.isrun = True
        self.clear_canvas()

        N = int(self.N_entry.get())
        D = float(self.D_entry.get())
        dt = float(self.dt_entry.get())
        dx = np.sqrt(dt * D)

        self.dx_entry.config(state='normal')
        self.dx_entry.delete(0, tk.END)
        self.dx_entry.insert(0, f"{dx:.6f}")
        self.dx_entry.config(state='readonly')

        L2 = 100 * dx  # axes limits
        r = np.zeros((2, N))  # points positions

        plt.ion()
        self.figure, self.ax = plt.subplots()
        hp, = self.ax.plot(r[0, :], r[1, :], 'k.')

        if self.track_var.get():
            rhist1 = np.zeros((2, 1))  # position history for particle #1
            rhist2 = np.zeros((2, 1))  # position history for
```

```
    particle #2
            histp1, = self.ax.plot(rhist1[0, :], rhist1[1, :], ’b-’, linewidth=1.5)
            histp2, = self.ax.plot(rhist2[0, :], rhist2[1, :], ’r-’, linewidth=1.5)

        self.ax.set_xlim([-L2, L2])
        self.ax.set_ylim([-L2, L2])
        self.ax.set_aspect(’equal’)

        while self.isrun:
            r += dx * np.random.randn(2, N)
            hp.set_xdata(r[0, :])
            hp.set_ydata(r[1, :])

            if self.track_var.get():
                rhist1 = np.hstack((rhist1, r[:, 0:1]))
                rhist2 = np.hstack((rhist2, r[:, 1:2]))
                histp1.set_xdata(rhist1[0, :])
                histp1.set_ydata(rhist1[1, :])
                histp2.set_xdata(rhist2[0, :])
                histp2.set_ydata(rhist2[1, :])

            plt.xlim([-L2, L2])
            plt.ylim([-L2, L2])
            plt.draw()
            plt.pause(0.01)  # brief pause to update the plot

    def stop_simulation(self):
        self.isrun = False

    def clear_canvas(self):
        if self.canvas is not None:
            self.canvas.delete("all")

if __name__ == "__main__":
    root = tk.Tk()
    app = RunMeApp(root)
    root.mainloop()
```