

Principles of thermodynamics

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ABSTRACT. This is an introduction to thermodynamics and statistical mechanics, assuming basic calculus known. We first discuss the notions of temperature and pressure, starting from basic everyday experiments, such as reading a thermometer or a manometer, and what that means. Then we embark on the process of understanding all this mathematically, first with some basic thermodynamics, mainly concerned with the geometry of the state space of ideal gases, then with more advanced thermodynamics, and then with the kinetic theory of gases and statistical mechanics, from the basics up to advanced topics. Finally, we discuss as well a number of more advanced questions, such as heat diffusion, states of matter, exotic matter, and heat quantization.

Preface

You have probably heard about $PV = kT$, with this being the main equation of thermodynamics, going back to work of Boyle, Charles, Avogadro, Gay-Lussac, Clapeyron and others from the 17th, 18th and 19th centuries. But what does this equation mean? This is no easy question, even for the modern scientist, and things get even worse if you relax a bit, and look at $PV = kT$ from your sofa, with a glass of wine in hand:

(1) Regarding V , that is the volume of the gas, at least we know one thing. With the remark however that V does not tell us if the gas is enclosed in a cylinder, sphere, cube or some more bizarre container, which might play a role in all this. But let us not bother for the moment with such things, V is the usual V , and that is a good thing.

(2) Regarding P , that is the pressure, coming by reading a manometer. However, if you think at what happens inside that manometer, things are quite complicated there, with gas molecules pushing a piston, and P coming out of that. Thus, P is in fact a statistical quantity, eventually coming from the statistics of the molecular speeds.

(3) Regarding T , that is the temperature, coming by reading a thermometer. But, as for the manometer, what happens inside the thermometer is no easy business, and in fact is even more complicated, due to joint presence of solids, liquids and gases. Again, T looks like a statistical quantity, coming from the statistics of molecular speeds.

(4) Regarding k , that is a constant, so very good, the conclusion being that $PV = kT$ tells us that “pressure and temperature are the same thing”. With this being something non-trivial, that “same thing” referring to the mathematical machinery producing, via manometer or thermometer, the pressure and temperature out of molecular speeds.

All this is, obviously, quite subtle, and makes thermodynamics, which is the branch of physics concerned with $PV = kT$ and related topics, fall into four classes, depending on the attitude that you would like to adopt, with respect to this equation:

(I) Basic thermodynamics, which is usually high school matter, is about getting familiar with P, T and their basic properties. Heat does not flow from cold to warm, heat can be converted into work and vice versa, refrigerators are inverse engines, there is something called $0^\circ K$, and finally a bit about $PV = kT$. All magical and useful things.

(II) Advanced thermodynamics, usually an undergraduate matter, assumes the basic properties of P, T known, and starts with $PV = kT$, with the aim of improving this, by looking at more complicated, “non-ideal” gases, and with a look into liquids and solids too. There is a lot of interesting mathematics here, of differential geometry flavor.

(III) Basic statistical mechanics, which is traditionally advanced undergraduate material, assumes $PV = kT$ unknown, with the aim of proving this equation, and many other laws and formulae of thermodynamics, out of nothing, meaning just molecules colliding. Again, the mathematics here is quite exciting, of rather probabilistic flavor.

(IV) Advanced statistical mechanics, which is quite often of graduate level, attempts to go, by using statistical mechanics methods, beyond what you know from thermodynamics. Here both the physics and the mathematics can be quite complicated, eventually needing you to know a bit about everything, both in mathematics and physics.

The present book is an introduction to thermodynamics and statistical mechanics, by following the above standard I-II-III-IV scheme. We will assume basic calculus known, and with this making the originality of the book. That is, if you have some college, and enjoyed calculus from there, but skipped physics classes both in high school and as an undergrad, and want to know about thermodynamics, this book might be for you. Of course, if you already know some physics, you might find some pleasure reading or using this book too, perhaps starting with Part II, or why not with Part III.

It is a pleasure to thank my former teachers, former students, and friends and colleagues, mathematicians and physicists, for various things that I learned from them, quite often used in this book. Many thanks go as well to my cats, for advice in regards with thermodynamically efficient diet, and for some help with computations.

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Part I

Pressure and heat

*In the heat of the night
I lose control in the heat of the night
But I can't stand it anymore
I lose control in the heat of the night*

CHAPTER 1

Temperature

1a. Temperature

Welcome to thermodynamics. We will discuss here the foundations of the theory, starting from 0 or almost, with this meaning some basic common sense, complemented with some basic knowledge of calculus. Normally calculus will be explained, whenever needed, but in case you are interested in more detailed explanations on that, you can check my calculus book [9], which is mathematical, but physics friendly. In what regards non-thermodynamics physics, this will be explained too, whenever needed, and for more you have here my introductory physics book [10]. Finally, if looking for more, the present book is undergraduate, but will be followed by a graduate book on lattice models [11], dealing more in detail with several advanced aspects of statistical mechanics.

So, what is thermodynamics? The answer here is very simple, as follows:

DEFINITION 1.1. *Thermodynamics is the science concerned with the study of various materials, such as solids, liquids or gases, under the influence of heat.*

In practice now, you already know quite a lot about this, thermodynamics, and this since childhood. Ice melting, water boiling, wind blowing, rain falling, and many other interesting phenomena, all obviously in relation with warm and cold. Overall, the idea is that various materials, be them solids, liquids or gases, can change their properties, and also interact with their environment, depending on their temperature T .

Getting now to physics, as a first requirement, in order to have some theory running, we would need a good understanding of the temperature T , as a real number:

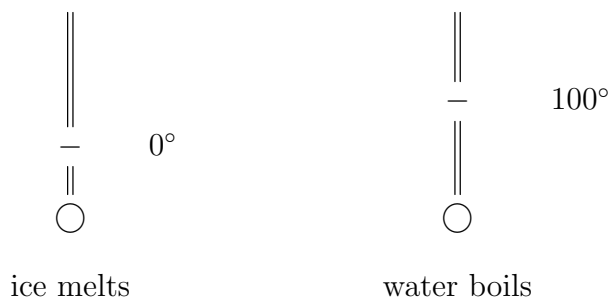
$$T \in \mathbb{R}$$

You would probably say that this is what comes out when reading a thermometer, but passed the fact that the thermometer is a quite complicated device, whose functioning we will have to understand well, we are already stuck, with a basic question, namely:

QUESTION 1.2. *Shall we use Celsius or Fahrenheit degrees?*

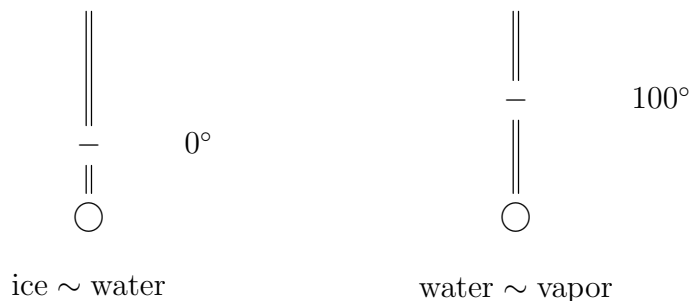
This question is in fact more subtle than it seems, because properly calibrating a thermometer is no easy business, but more on this later, when talking thermometers. For the moment, let us answer our question. Many things can be said here, but with me

writing this book, let us agree on Celsius. This is quite nice and logical, and we can even call it scientific, 0°C being where ice melts, and 100°C being where water boils:



Observe that there is in fact a bit of a problem here, because it is not clear, on the left, whether we should say that ice melts, or that water freezes, with these two temperatures being not exactly identical, and with this being most likely due to the usual “laziness” of nature, when it comes of doing things, like melting or freezing.

The solution to this problem is that of calling 0°C the temperature where both ice and water coexist peacefully, in equilibrium. A same discussion goes for the left, at 100°C , with boiling vs condensation, so our thermometer calibration becomes:



However, we are not done yet with our answer to Question 1.2. Indeed, you might know this from hiking, and cooking a meal in the mountains, but water boils differently depending on altitude, with a pot cover being very useful, as you go high up. The rule here, which is best stated in feet and degrees Celsius, and please forgive me everyone, on

both sides, for doing such profanities, is that you lose 1°C for any 1000 feet:

altitude (feet)	boiling point
0	100°
1000	99°
2000	98°
3000	97°
4000	96°

Hang on, we are not done yet. Indeed, you might know this also from hiking, but unless you hunt a big animal and cook it over a huge fire, a bit like Vikings did, a windy day will affect your dinner preparation. So, in order not to mess up things here, let us avoid wind, and formulate our answer to Question 1.2 as follows:

ANSWER 1.3. We will go for Celsius, namely water freezes at 0°C and boils at 100°C , and with our thermometer being calibrated at sea level, on a non-windy day.

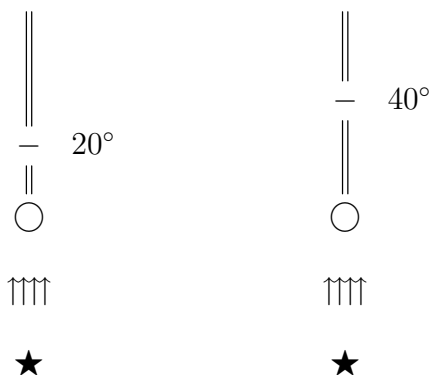
Of course, things are not over here, because if looking for troubles, we can still talk about tides, affecting what we call sea level, or seas and oceans shamelessly spilling into each other, for no clear reason, again affecting what we call sea level, and so on. The solution to all this comes from the notion of pressure, with the more precise formulation of Answer 1.3 saying at the end “calibrated at 1 atm”. But more on pressure later.

All this sounds good, looks like we have a beginning of theory here. So, let us get now to the main point, namely understanding how our main scientific device for measuring temperature, the thermometer, works. Unfortunately there are all sorts of thermometers available, and while all seem to indicate the same temperature, unless too old, too cheap, or with various defects, this is certainly something that we will have to understand. So, we are faced with the following question, which does not look trivial:

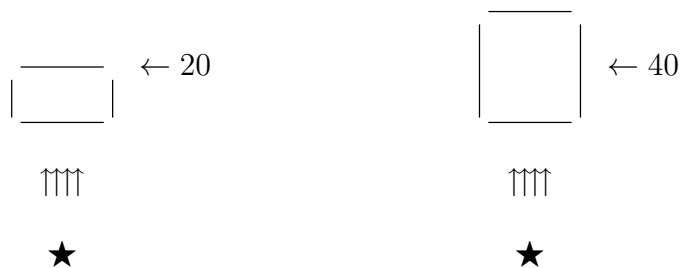
QUESTION 1.4. How to thermometers work? And, in fact, what exactly is temperature, the quantity that thermometers measure?

In answer, let us look at a basic thermometer. This is made of colored alcohol in a glass bulb, and when you move it to a warmer room, the environment manages to interact with the alcohol, despite the glass in between, and dilates that alcohol, leading to a higher reading on the scale. Inversely, when you move it to a colder room, the alcohol contracts, and leads to a lower reading on the scale. And the same trick works when putting the thermometer in contact with whatever material, this time the thermometer measures the

temperature of the material, instead of that of the ambient room:

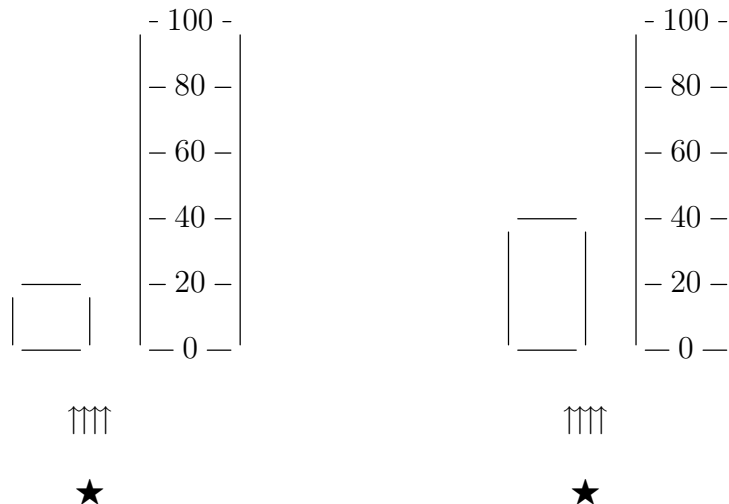


By going now a bit abstract, alcohol is not really needed in all this, and the same thermometer can function as well with mercury, or more generally with any liquid, or even gas, and even solid, of your choice. Needless to say, nor is the glass bulb really needed. And finally, the scale is not needed either, we just need a volume measuring device, for recording the dilation or contraction of our material:



It is actually interesting, as a thought experiment, to try to design the simplest thermometer ever. Starting with the usual alcohol thermometer, obviously we don't want to bother with the liquid enclosed in a glass container, which is something too complicated, so will replace these by a simple metal bar. But then for measuring the length of this metal bar, when influenced by heat, we need another metal bar, with a scale on it, and with this second metal chosen to be more stable than the first one, under the influence of

heat. Thus, we end up with a sort of bi-metal device, which looks like this:



But, getting now to engineering matters, in order to implement our discovery, go find in the real life such metals, which dilate so differently under small temperature changes that we can see the difference with the naked eye, that won't be an easy task. In practice, although bi-metal thermometers do exist, based on various designs appearing as variations of the above one, the good old alcohol thermometer remains the best one.

In any case, we have now a beginning of an answer to Question 1.4. This answer, which counts as well as supplementary piece of answer to Question 1.2, is as follows:

ANSWER 1.5. Thermometers measure temperature, which measures the heat present in the environment, and can be computed by exposing various materials to the environment, and measuring their volume, based on the following general facts:

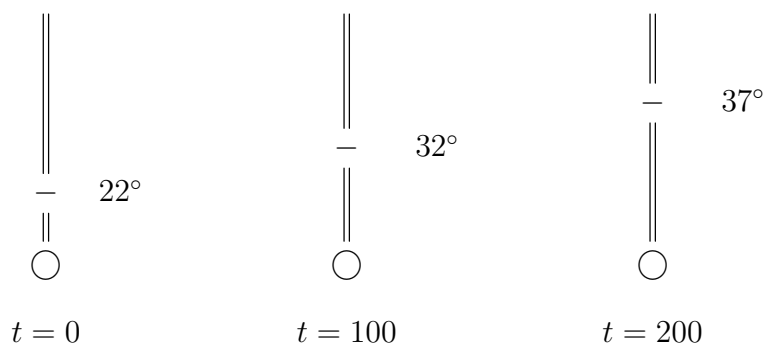
- (1) *Heat dilates the material, and cold contracts the material.*
- (2) *Heat flows from warm to cold, aiming at equalizing temperature.*
- (3) *The heat flow needs some perceptible time $t > 0$, to fully happen.*
- (4) *Temperature can be regulated, as to be independent of the material used.*

All this looks quite reasonable, but we insist however on the word “general”, referring to the above facts. Indeed, there are several bugs with the above, as follows:

(1) This principle does certainly not apply to things like cold water, which dilates when freezing. However, water is something quite special, and more on this later in this book, and for the vast majority of materials, our principle applies well.

(2) You would probably say here that this is not the case for the wind, blowing from cold to warm. However, in this situation, it is also true that wind blows from higher pressure to lower pressure. We will be back to this, with a full discussion.

(3) This is certainly true, thermometers being not instantaneous, and with this being a quite mysterious thing. Remember for instance that when measuring your body temperature with an alcohol thermometer, readings evolve as follows:



Thus, what we have here is something of main concern, because we certainly don't want to mix up temperature T with time t . We will be back to this issue, later.

(4) These are engineering matters, and we have already talked in Answer 1.3 about several precautions when calibrating a thermometer, and that is probably just the tip of the iceberg, with all sorts of other concerns being most likely involved.

This being said, even with the above flaws, which remain to be further investigated, Answer 1.5 does not really solve our question regarding the nature of temperature, because we still need to know what exactly is heat. So, our question becomes:

QUESTION 1.6. *What is heat?*

As a first comment, yes I know, all this starts becoming a bit tiring, looks like thermodynamics plays a sort of cat and mouse game with us, with temperature, pressure and heat being like paws, claws and teeth, applied in a playful, cyclic way to our patience.

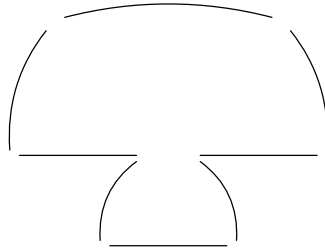
This being said, we are making progresses with our physics, so let us try to answer our latest question, as formulated above. Getting to experiments, we have:

FACT 1.7. *Increases in overall heat, and so in temperature, are produced by:*

- (1) *Friction or drag, acting on a moving object.*
- (2) *Letting electricity fight with a resistor, via the Joule law.*
- (3) *Lighting gas, or doing other chemical reactions which release heat.*
- (4) *Microbes and viruses in your body, producing illness and fever.*

Here (1,2) are something that we know well from everyday life, but their understanding via physics is certainly no simple business. As for (3,4), taking us into chemistry and biology, which means chemistry for short, these are even more concerning. Of course,

things are not over here, and in case you need a sudden and substantial increase in overall heat, more advanced technologies, such as atomic fission or fusion, are available:



Tsar Bomba (CCCP)

Time now to conclude this opening section. We have certainly learned many things, but in what concerns laying some solid foundations for thermodynamics, which was our initial objective, we are stuck more than ever with understanding what temperature T is. So, want it or not, we are probably aiming too high, the overall conclusion being:

CONCLUSION 1.8. *Thermodynamics is no easy business, the precise understanding of the temperature T most likely requiring a good knowledge of matter, and so of:*

- (1) *Classical mechanics.*
- (2) *Fluid mechanics.*
- (3) *Electrostatics.*
- (4) *Electrodynamics.*
- (5) *Relativity theory.*
- (6) *Quantum mechanics.*
- (7) *Atomic theory.*
- (8) *Basic chemistry.*

So, shall we give up? Certainly not. The word that bothers us in the above is “precise”, but finally who cares about that, so we will just keep developing thermodynamics, based on our everyday knowledge of the temperature T , which is after all not that bad. And, as good news coming in advance, our method will work more than fine, because:

– We will end up in precisely understanding what temperature T is, and this even without mastering well the disciplines (1-8) mentioned above.

– Ironically, the temperature T will turn to be a statistical quantity, that no scientist or thermometer in this world can precisely measure.

So long for preliminaries, now that we studied the problem, and have our plan, we’ll just go for it. Of course, if you’re looking for more rigor, alternative texts are available, but none really escapes from the truths formulated in Conclusion 1.8. A good idea here is to have a look at the books of Landau and Lifshitz [56], [57], [58], [59], [60], [61],

[62], [63], [64], [65]. To my knowledge at least, this series of 10 books is closest to what we could call a rigorous, or at least logical, treatment of physics, and the simple contemplation of their titles can be a source of joy, here they are:

1. Mechanics.
2. The classical theory of fields.
3. Quantum mechanics: non-relativistic theory.
4. Quantum electrodynamics.
5. Statistical physics I.
6. Fluid mechanics.
7. Theory of elasticity.
8. Electrodynamics of continuous media.
9. Statistical physics II: theory of the condensed state.
10. Physical kinetics.

Observe that thermodynamics in particular, which at the advanced level is part of statistical physics, comes quite late into the series, as it should. So, very nice. This being said, be aware that these Landau-Lifshitz books are of graduate level, and so unless you decently know some basic physics, learned from here, or from any other place of your choice, chances are slim that you will understand. So, good luck with reading Landau-Lifshitz, or an equivalent treatise, and in the hope to see you back soon.

1b. Physics, matter

Welcome to thermodynamics, take two. Armed with some modesty, coming from what we discussed so far, let us attempt to axiomatize thermodynamics, as decently as we can. According to Conclusion 1.8, we need, at least a little bit, to have some knowledge of matter, to which our theory, thermodynamics, is supposed to apply.

So, let us follow the list from Conclusion 1.6. In what regards the first item, classical mechanics, the basics here, that you know well, can be summarized as follows:

FACT 1.9 (Classical mechanics). *The force of attraction between two bodies of masses m_1, m_2 , having distance $d > 0$ between them, is given by*

$$\|F\| = G \cdot \frac{m_1 m_2}{d^2}$$

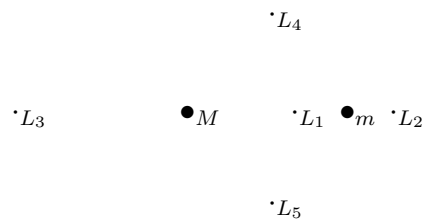
where $G = 6.674 \times 10^{-11}$ is a constant. *This force alters the trajectory of one body with respect to the other according to the following formula, a being the acceleration:*

$$F = ma$$

This trajectory is a curve of degree 2, called conic, which can be an ellipsis, parabola, or hyperbola. However, for 3 or more objects, all this can lead to order, or chaos.

Here you surely know all this, with perhaps some gaps in the mathematics at the end, regarding conics and their classification. As an advice, learn this too from somewhere, this is all beautiful and useful mathematics, going back to the ancient Greeks. Also, in what regards the last sentence, that is a very short summary of what happens for the N -body problem with $N \geq 3$, and as a piece of advice here, have a look at Earth scientific satellites and Lagrange points, in relation with $N = 3$, and also go on internet for more about $N = 3$, including weird solutions, all this is very interesting, and worth a look.

As a piece of advertisement here, the interesting problem at $N = 3$ is how to position a specialized scientific satellite, deep in space, and away from the dust and radiation of the usual orbits around the Earth, as to stay there, under the joint influence of the gravity of the Sun M and of the Earth m . And there are 5 possible solutions here, called Lagrange points L1-L5, whose positions with respect to M, m are as follows:



Moreover, and here comes another interesting point, L4, L5 are stable, in the sense that a satellite installed there will really stay there, regardless of the various tiny little things that might happen, like an asteroid passing by, while L1, L2, L3 are unstable, in the sense that a satellite installed there will need constant tiny adjustments, in order to really stay there. So, which one would you choose for installing your satellite?

You would probably say L4, L5, but this is precisely the wrong answer, because due to their stability, these points attract a lot of asteroids and space garbage, and our satellite will certainly not perform well there, in that crowd. So, with L4, L5 ruled out, and with L1 ruled out too, being too far, the correct choices are L1, L2. But here, you still need to learn a lot more mechanics, for understanding how to do this, in practice.

But probably enough advertisement for classical mechanics, again, learn as much as possible. Regarding now fluid mechanics, this is quite tricky, with the mathematics being quite involved. We will not really need this here, and so, just some very basics:

FACT 1.10 (Fluid mechanics). *Fluids can be thought of as being formed by very slippery particles, soil liquefaction being a good example. As in the case of classical mechanics, this can lead to order, such as laminar flows, or to chaos, turbulent flows.*

In what regards now electrostatics, this is again something very fundamental, that you know well, the basics here being summarized as follows:

FACT 1.11 (Electrostatics). *Ordinary matter is made of electrons $-$, protons $+$ and neutrons 0 , with the number of $+$, $-$ being roughly equal. We set*

$$q = \#\{+\} - \#\{-\}$$

and if $q \neq 0$, we call this a charge. Any pair of charges $q_1, q_2 \in \mathbb{R}$ is then subject to a force as follows, which is attractive if $q_1 q_2 < 0$ and repulsive if $q_1 q_2 > 0$,

$$\|F\| = K \cdot \frac{|q_1 q_2|}{d^2}$$

where $K = 8.988 \times 10^9$. However, unlike in classical mechanics, $q_1 < 0$ will not spin around $q_2 > 0$ on an ellipsis, due to magnetism, relativity, and quantum mechanics.

Here you are certainly familiar with the Coulomb law formula in the statement, which is very similar to the Newton law formula from Fact 1.9. This normally suggests that when the force is attractive, $q_1 q_2 < 0$, the negative charge, say an electron $-$, will spin around the positive charge, say a proton $+$, on an ellipsis. But this is well-known to be wrong, with the solution of this 2-body problem, which corresponds to the hydrogen atom, being far more complicated, due to the numerous reasons mentioned in the statement.

Regarding now electrodynamics, this comes as a continuation of electrostatics, with the aim of fixing some of the obvious bugs there, the basics being as follows:

FACT 1.12 (Electrodynamics). *Moving charges produce magnetic fields, and the dynamics of the electric fields E and magnetic fields B is governed by the formulae*

$$\langle \nabla, E \rangle = \frac{\rho}{\varepsilon_0}$$

$$\langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B}$$

$$\nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \dot{E}$$

called Maxwell equations. Also, accelerating or decelerating charges produce electromagnetic radiation, of various wavelengths, called light, of various colors.

Obviously, we are now into serious science here, with the Maxwell equations being something quite complicated, and the pride of 19th century physics. Regarding the math, \langle, \rangle and \times are the usual scalar and vector products on \mathbb{R}^3 , the dots denote derivatives with respect to time, and ∇ is the gradient operator, or space derivative, given by:

$$\nabla = \begin{pmatrix} \frac{d}{dx} \\ \frac{d}{dy} \\ \frac{d}{dz} \end{pmatrix}$$

As for the physics, the first formula is the Gauss law, ρ being the charge, and ε_0 being a constant, and with this Gauss law more or less replacing the Coulomb law from electrostatics. The second formula is something basic, and anonymous. The third formula is the Faraday law. As for the fourth formula, this is the Ampère law, as modified by Maxwell, with J being the volume current density, and μ_0 being a constant.

In what regards now the last sentence, this is something fundamental too, putting an end to centuries or even millenia of discussions, regarding the nature of light. Speaking light, here is the table coming from Fact 1.12, which is a must-know:

Frequency	Type	Wavelength
	—	
$10^{18} - 10^{20}$	γ rays	$10^{-12} - 10^{-10}$
$10^{16} - 10^{18}$	X – rays	$10^{-10} - 10^{-8}$
$10^{15} - 10^{16}$	UV	$10^{-8} - 10^{-7}$
	—	
$10^{14} - 10^{15}$	blue	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	yellow	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	red	$10^{-7} - 10^{-6}$
	—	
$10^{11} - 10^{14}$	IR	$10^{-6} - 10^{-3}$
$10^9 - 10^{11}$	microwave	$10^{-3} - 10^{-1}$
$1 - 10^9$	radio	$10^{-1} - 10^8$

Observe the tiny space occupied by the visible light, all colors there, and the many more missing, being squeezed under the $10^{14} - 10^{15}$ frequency banner. Here is a zoom on that part, with of course the remark that all this, colors, is something subjective:

Frequency THz = 10^{12} Hz	Color	Wavelength nm = 10^{-9} m
	—	
670 – 790	violet	380 – 450
620 – 670	blue	450 – 485
600 – 620	cyan	485 – 500
530 – 600	green	500 – 565
510 – 530	yellow	565 – 590
480 – 510	orange	590 – 625
400 – 480	red	625 – 750

Hang on, we are not done yet with the Maxwell equations, and their consequences. Yet another feature of these equations is that these can be regarded as well as a precursor of Einstein's relativity theory, which can be summarized as follows:

FACT 1.13 (Relativity theory). *The speeds are bounded, $v < c$, by the speed of light in vacuum, which is the same for all inertial observers, given by:*

$$c = 299\,792\,458 \text{ m/s}$$

In view of this, classical mechanics must be fixed, and the correct formula for the addition of speeds, guaranteeing $v < c$ for the sum, is Einstein's formula

$$v_{AC} = \frac{v_{AB} + v_{BC}}{1 + v_{AB}v_{BC}/c^2}$$

which at small speeds reduces to the usual Galileo formula $v_{AC} = v_{AB} + v_{BC}$. Moreover, the improved theory is invariant under the space-time Lorentz transformation

$$x' = \gamma(x - vt)$$

$$y' = y$$

$$z' = z$$

$$t' = \gamma(t - vx/c^2)$$

where $\gamma = 1/\sqrt{1 - v^2/c^2}$, exactly as the Maxwell equations. Gravity can be added, too.

Obviously, many deep things going on here, and many other things can be said, for instance $E = mc^2$ comes from this too. This being said, the idea of Einstein is very simple, based only on $v < c$. Indeed, by rescaling things as to have $c = 1$, we are looking for a speed addition formula $(u, v) \rightarrow u +_e v$ satisfying the following condition:

$$u, v \leq 1 \implies u +_e v \leq 1$$

But here, thinking at the math, not many choices, with the obvious choice being:

$$u +_e v = \frac{u + v}{1 + uv}$$

And the miracle is that this formula, which is the one in the statement after rescaling by c , is indeed the correct one. With everything coming afterwards, namely Lorentz transformation, and gravity added, being more or less straightforward mathematics.

Finally, no discussion of relativity would be complete without a proof of $E = mc^2$. The idea here is that the relativistic energy of an object of rest mass $m > 0$ is as follows, making it clear that at speed $v = 0$, the energy should be $E = mc^2$:

$$\mathcal{E} = \frac{mc^2}{\sqrt{1 - v^2/c^2}} = mc^2 \left(1 + \frac{v^2}{2c^2} + \dots \right) = mc^2 + \frac{mv^2}{2} + \dots$$

Now still speaking deep things, and going back to the Maxwell equations, although almighty, and compatible with relativity too, via the mathematics of the Lorentz transformation, these still do not solve the 2-body problem in electrodynamics, which is the

functioning problem for the hydrogen atom. The problem comes from quantum mechanics, whose basic philosophy can be summarized as:

FACT 1.14 (Quantum mechanics). *Small particles like electrons and protons do not have clear positions and speeds. This is how things are, at that scale, and it is all about the probability of finding the particle here or there, and with this or that speed.*

This might seem overly vague, but sometimes a totally new and weird thought, of course in the hands of someone having the technical know-how, is enough to make science advance. Besides the above fact, which is something mathematical and theoretical, of key importance was the discovery, by Balmer, Rydberg and others, of the mechanism of the spectral lines of hydrogen H. These lines, depending on integer parameters $n_1 \leq n_2$, are given by the Rydberg formula, which is as follows, with $R = 1.096\,775\,83 \times 10^7$:

$$\frac{1}{\lambda_{n_1 n_2}} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Interestingly, and perhaps reminding a bit speed addition in relativity, these spectral lines combine according to the Ritz-Rydberg principle, which is as follows:

$$\frac{1}{\lambda_{n_1 n_2}} + \frac{1}{\lambda_{n_2 n_3}} = \frac{1}{\lambda_{n_1 n_3}}$$

In practice, all these lines came from the efforts of several people, namely Balmer in 1885, in the visible range, then Lyman in 1906 in UV, Paschen in 1908 in IR, and later Brackett in 1922, Pfund in 1924, Humphreys in 1953, and others afterwards, with all the extra lines being in far IR. The simplified complete table is as follows:

n_1	n_2	Series name	Wavelength $n_2 = \infty$	Color $n_2 = \infty$
1	2 – ∞	Lyman	91.13 nm	UV
2	3 – ∞	Balmer	364.51 nm	UV
3	4 – ∞	Paschen	820.14 nm	IR
4	5 – ∞	Brackett	1458.03 nm	far IR
5	6 – ∞	Pfund	2278.17 nm	far IR
6	7 – ∞	Humphreys	3280.56 nm	far IR
...

Now back to the Ritz-Rydberg principle, which is the main theoretical result in all this, this reminds the following multiplication formula for the usual matrix units $e_{ij} : e_j \rightarrow e_i$, perhaps taken in infinite dimensions, as to allow infinite-ranging indices:

$$e_{n_1 n_2} e_{n_2 n_3} = e_{n_1 n_3}$$

But this is very interesting, suggesting that the observables of the hydrogen atom should be some sort of infinite matrices, making the link with Fact 1.14.

Obviously, what we have here is a first-class scientific puzzle. Based on all this, and on some earlier predictions of Bohr, who was the initiator of the whole program, Heisenberg and Schrödinger, and then De Broglie, Dirac, Pauli and others were able to solve this puzzle, and develop a quantum mechanics theory starting from Fact 1.14, with the main applications, to the functioning of hydrogen and of other atoms, being as follows:

FACT 1.15 (Atomic theory). *The atoms are formed by a core of protons and neutrons, surrounded by a cloud of electrons, basically obeying to a modified version of electromagnetism. And with a fine mechanism involved, as follows:*

- (1) *The electrons are free to move only on certain specified elliptic orbits, labelled $1, 2, 3, \dots$, situated at certain specific heights.*
- (2) *The electrons can jump or fall between orbits $n_1 < n_2$, absorbing or emitting light and heat, that is, electromagnetic waves, as accelerating charges.*
- (3) *The energy of such a wave, coming from $n_1 \rightarrow n_2$ or $n_2 \rightarrow n_1$, is given, via the Planck viewpoint, by the Rydberg formula, applied with $n_1 < n_2$.*
- (4) *The simplest such jumps are those observed by Lyman, Balmer, Paschen. And multiple jumps explain the Ritz-Rydberg formula.*

Still with me, I hope? We are certainly now into complicated physics, and even seem to be somewhere towards the end of science, as understandable by humans. But, thinking well, we are in fact only at the beginning, because Fact 1.15 is not that useful as such, for the simple reason that atoms usually don't come alone, but rather tend to attach to each other, and form molecules. So, with physics understood, welcome to chemistry:

FACT 1.16 (Basic chemistry). *Atoms can be labeled according to their atomic number, which is the number of protons in their nucleus, in practice*

$$Z = 1, \dots, 118$$

and tend to attach to each other, and form molecules, with the electron distribution on the orbitals being responsible for this mechanism.

All this is very interesting, and truly corresponding to what happens in the real life, meaning at our scale, our usual temperature, our usual pressure, and so on. More precisely now, there are two assertions here. First is a continuation of Fact 1.15, namely more atomic physics, which leads to the conclusion that the known atoms, also called chemical elements, basically depend only on their atomic number $Z = 1, \dots, 118$. These chemical

elements can be arranged in a table, called periodic table, as follows:

	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	$\frac{\text{H}}{1}$																		$\frac{\text{He}}{2}$
2	$\frac{\text{Li}}{3}$	$\frac{\text{Be}}{4}$												$\frac{\text{B}}{5}$	$\frac{\text{C}}{6}$	$\frac{\text{N}}{7}$	$\frac{\text{O}}{8}$	$\frac{\text{F}}{9}$	$\frac{\text{Ne}}{10}$
3	$\frac{\text{Na}}{11}$	$\frac{\text{Mg}}{12}$												$\frac{\text{Al}}{13}$	$\frac{\text{Si}}{14}$	$\frac{\text{P}}{15}$	$\frac{\text{S}}{16}$	$\frac{\text{Cl}}{17}$	$\frac{\text{Ar}}{18}$
4	$\frac{\text{K}}{19}$	$\frac{\text{Ca}}{20}$		$\frac{\text{Sc}}{21}$	$\frac{\text{Ti}}{22}$	$\frac{\text{V}}{23}$	$\frac{\text{Cr}}{24}$	$\frac{\text{Mn}}{25}$	$\frac{\text{Fe}}{26}$	$\frac{\text{Co}}{27}$	$\frac{\text{Ni}}{28}$	$\frac{\text{Cu}}{29}$	$\frac{\text{Zn}}{30}$	$\frac{\text{Ga}}{31}$	$\frac{\text{Ge}}{32}$	$\frac{\text{As}}{33}$	$\frac{\text{Se}}{34}$	$\frac{\text{Br}}{35}$	$\frac{\text{Kr}}{36}$
5	$\frac{\text{Rb}}{37}$	$\frac{\text{Sr}}{38}$		$\frac{\text{Y}}{39}$	$\frac{\text{Zr}}{40}$	$\frac{\text{Nb}}{41}$	$\frac{\text{Mo}}{42}$	$\frac{\text{Tc}}{43}$	$\frac{\text{Ru}}{44}$	$\frac{\text{Rh}}{45}$	$\frac{\text{Pd}}{46}$	$\frac{\text{Ag}}{47}$	$\frac{\text{Cd}}{48}$	$\frac{\text{In}}{49}$	$\frac{\text{Sn}}{50}$	$\frac{\text{Sb}}{51}$	$\frac{\text{Te}}{52}$	$\frac{\text{I}}{53}$	$\frac{\text{Xe}}{54}$
6	$\frac{\text{Cs}}{55}$	$\frac{\text{Ba}}{56}$	<i>l</i>	$\frac{\text{Lu}}{71}$	$\frac{\text{Hf}}{72}$	$\frac{\text{Ta}}{73}$	$\frac{\text{W}}{74}$	$\frac{\text{Re}}{75}$	$\frac{\text{Os}}{76}$	$\frac{\text{Ir}}{77}$	$\frac{\text{Pt}}{78}$	$\frac{\text{Au}}{79}$	$\frac{\text{Hg}}{80}$	$\frac{\text{Tl}}{81}$	$\frac{\text{Pb}}{82}$	$\frac{\text{Bi}}{83}$	$\frac{\text{Po}}{84}$	$\frac{\text{At}}{85}$	$\frac{\text{Rn}}{86}$
7	$\frac{\text{Fr}}{87}$	$\frac{\text{Ra}}{88}$	<i>a</i>	$\frac{\text{Lr}}{103}$	$\frac{\text{Rf}}{104}$	$\frac{\text{Db}}{105}$	$\frac{\text{Sg}}{106}$	$\frac{\text{Bh}}{107}$	$\frac{\text{Hs}}{108}$	$\frac{\text{Mt}}{109}$	$\frac{\text{Ds}}{110}$	$\frac{\text{Rg}}{111}$	$\frac{\text{Cn}}{112}$	$\frac{\text{Nh}}{113}$	$\frac{\text{Fl}}{114}$	$\frac{\text{Mc}}{115}$	$\frac{\text{Lv}}{116}$	$\frac{\text{Ts}}{117}$	$\frac{\text{Og}}{118}$
			<i>l</i> :	$\frac{\text{La}}{57}$	$\frac{\text{Ce}}{58}$	$\frac{\text{Pr}}{59}$	$\frac{\text{Nd}}{60}$	$\frac{\text{Pm}}{61}$	$\frac{\text{Sm}}{62}$	$\frac{\text{Eu}}{63}$	$\frac{\text{Gd}}{64}$	$\frac{\text{Tb}}{65}$	$\frac{\text{Dy}}{66}$	$\frac{\text{Ho}}{67}$	$\frac{\text{Er}}{68}$	$\frac{\text{Tm}}{69}$	$\frac{\text{Yb}}{70}$		
			<i>a</i> :	$\frac{\text{Ac}}{89}$	$\frac{\text{Th}}{90}$	$\frac{\text{Pa}}{91}$	$\frac{\text{U}}{92}$	$\frac{\text{Np}}{93}$	$\frac{\text{Pu}}{94}$	$\frac{\text{Am}}{95}$	$\frac{\text{Cm}}{96}$	$\frac{\text{Bk}}{97}$	$\frac{\text{Cf}}{98}$	$\frac{\text{Es}}{99}$	$\frac{\text{Fm}}{100}$	$\frac{\text{Md}}{101}$	$\frac{\text{No}}{102}$		

Here the horizontal parameter $1, \dots, 18$ is called the group, and the vertical parameter $1, \dots, 7$ is called the period. The two rows on the bottom consist of lanthanum $_{57}\text{La}$ and its followers, called lanthanides, and of actinium $_{89}\text{Ac}$ and its followers, called actinides. These are to be inserted in the main table, where indicated, lanthanides between barium $_{56}\text{Ba}$ and lutetium $_{71}\text{Lu}$, and actinides between radium $_{88}\text{Ra}$ and lawrencium $_{103}\text{Lr}$.

Regarding now the second assertion in Fact 1.16, regarding the formation of molecules, this again comes from Fact 1.15, but via a more complicated mechanism. The idea here is that given two or several atoms, which can have the same atomic number Z or not, what happens is that, depending on their respective Z , these atoms might choose to share some electrons, with this coming somehow from less energy needed for functioning, in this new configuration. And so, we are led to clusters of atoms, called molecules.

As an example here, or rather counterexample, let us look at the group 18 elements, helium $_{2}\text{He}$, neon $_{10}\text{Ne}$, argon $_{18}\text{Ar}$, krypton $_{36}\text{Kr}$, xenon $_{54}\text{Xe}$ and radon $_{86}\text{Rn}$. These are called noble gases, and are allergic to chemistry, because the group 18 elements are precisely those with all possible electron positions fully occupied, up to a certain $n \in \mathbb{N}$, which makes them very unfriendly to any chemistry proposition from the outside.

So long for the story and basics of material science, and we will regularly talk about molecules, in what follows. In fact, remembering what we wanted to do, namely axiomatize thermodynamics, we can now formulate a sort of definition, as follows:

DEFINITION 1.17. *Thermodynamics is the science concerned with the behavior of molecules, under the influence of heat.*

Finally, before going ahead with some theory, and as a reminder that we should be always modest, things do not end of course with chemistry, because we have:

FACT 1.18 (Biology). *Advanced molecules, called organic, which are typically long and contain lots of carbon ${}_6\text{C}$ and hydrogen ${}_1\text{H}$, tend to team together, and form cells.*

So, we can now better understand what thermodynamics is about. This is about advanced forms of matter, like the neurons in our brains, trying to understand more vulgar forms of matter, not necessarily of organic type. Said like this, this looks easy, and it remains to be seen if thermodynamics is as simple as this might suggest.

1c. Basic principles

With matter understood, let us try now to axiomatize thermodynamics, based on the various things that we know from the beginning of this chapter. As a first principle, that we can formulate without even thinking, we have, and no surprise here:

LAW 1.19 (First law of thermodynamics). *Energy is conserved.*

In practice, this requires of course some discussion about how heat gets converted to work and vice versa. But this looks quite routine, with energy conservation matters being usually quite routine in physics, and with everyday devices like gas engines or refrigerators witnessing for the functioning of all this. So, we will leave this for later.

Getting now into the real thing, here is one remarkable thing about thermodynamics, that we already met in the beginning of this book, and which waits to be understood:

LAW 1.20 (Second law of thermodynamics). *Heat flows from warm to cold.*

As an important remark, this is just one of the possible formulations of the second law, due to Clausius, and there are many more, with basically all the thermodynamics greats having made contributions to the matter. Let us just record here a well-known equivalent formulation, due to Lord Kelvin, which is very instructive, as follows:

LAW 1.21 (Second law, Kelvin's formulation). *It is impossible to extract heat from a source staying at constant temperature T , and convert it into work.*

In other words, this tells us that we cannot make money by cooling the land, and converting that heat into work, then electricity, that we can sell afterwards. This won't work, due to the second law. But of course, you are welcome to try this at home.

In practice now, looking at Law 1.20 and Law 1.21, it is quite clear that these are about the same thing. However, the equivalence is not trivial, so let us state:

FACT 1.22. The second law in Clausius' formulation, Law 1.20, is equivalent to the second law in Lord Kelvin's formulation, Law 1.21.

We will see later, in chapter 4, a proof for the equivalence, with mathematics and everything. This proof will be actually quite exciting, with even a heat engine working for us, in order to do the math, a bit like a computer does. More on this later.

Finally, let us mention that there is a third law of thermodynamics too, but this is something more specialized, involving a quantity called entropy, that we cannot even state at this stage of things. More on this later, in Part II of the present book.

So far, so good, thermodynamics axiomatized, so what is next? Obviously, some math and formulae. But here, what we have in Law 1.19 and Law 1.20 is far too general, so in order to reach to something concrete, we must go back to material science, and select from there, among the many beasts available, some materials which can be used in order to modelize our problems, and more specifically, the heat flows from Law 1.20.

In our context, the gases are the simplest materials, and in any case, far simpler than liquids or solids. To be more precise, based on our usual life knowledge, we have:

GUESS 1.23. The pressure, volume and temperature of a given amount of gas should be related, at least approximately, by a formula of type

$$PV \sim T$$

with the proportionality constant related to the nature of the gas, the precise amount of gas, and also the shape of that amount of gas.

This is surely something intuitive, coming from the fact that heating the gas in a given volume increases the pressure, that compressing the gas at constant temperature increases the pressure too, and so on. What is really amazing is that, upon measuring, all these changing quantities vary linearly with each other, and we have indeed:

FACT 1.24. The formula guessed above holds indeed, under the circumstances there,

$$PV \sim T$$

with P being measured by usual means, and T being measured as in Answer 1.5.

To be more precise here, in order to measure the pressure P , we can put the gas in a container with a piston, and measure the pressure exerted by the gas on that piston:

$$\begin{array}{cccccc} = & = & = & = & = & = \\ || & \circ & \circ & \circ & | & \\ || & \circ & \circ & \circ & | & \rightarrow P \\ || & \circ & \circ & \circ & | & \\ = & = & = & = & = & = \end{array}$$

This is already quite nice, and as a new answer to Question 1.4, which is far more precise than what we know from Answer 1.5, we can formulate:

ANSWER 1.25. *The temperature of gases is given by the following formula, adjusted for different gases by constants found by using Answer 1.5,*

$$T \sim PV$$

and the temperature of various liquids and solids can be afterwards computed too, based on these gas standards, again by using Answer 1.5.

So far so good, but there is still a bit of mystery in all this. What is the pressure P on that piston due to? Or, more simply put, what is the reason for gas pressure? And also, importantly, why the phenomena (1,2,3,4) in Answer 1.5 hold indeed for gases?

Obviously, we're here into some kind of mechanics, with all the above questions requiring, more specifically, some basic understanding of the mechanics of gases. And here, fortunately, a look through a good microscope reveals:

FACT 1.26. *Gases are formed of free molecules, moving around with certain speeds, and colliding from time to time. This movement produces the pressure P of the gas, say as mechanical force on a measuring piston, and so the temperature T too, via:*

$$T \sim PV$$

Moreover, both the pressure P and the temperature T are proportional to the average molecular speed v , and so temperature can be defined equivalently as

$$T \sim v$$

with of course all these formulae being approximative, and subject to certain rescaling factors, coming from the nature, amount and shape of the gas.

This certainly looks simple, good and quite final, so time now to put everything together, and nicely answer Question 1.4. By putting together our findings from Answer 1.5, Answer 1.25 and Fact 1.26, and then making a bit of cleanup, first by forgetting about liquids and solids, to be discussed later, and also by forgetting the formula $T \sim PV$, which is certainly lower technology than $T \sim v$, we are led to the following answer:

ANSWER 1.27. *Temperature T of a gas is its average molecular speed v , up to a scaling factor, which corresponds to the amount of heat present in the gas. Moreover:*

- (1) *Heat dilates the gas, and cold contracts it.*
- (2) *Heat flows from warm to cold, aiming at equalizing temperature.*
- (3) *That heat flow needs some perceptible time $t > 0$, to fully happen.*
- (4) *Temperature can be regulated, as to be independent of the gas used.*

Armed with this answer, let us get now into the underlying math and physics, trying to understand how v and T exactly work, for gases as above. We are particularly interested in knowing more about (2,3) above, which look quite mysterious, so as a first piece of work, let us separate these two items from the rest, by formulating:

PRINCIPLE 1.28. *Heats flows from warm to cold, aiming at equalizing temperature, and with the flow needing some perceptible time $t > 0$, in order to fully happen.*

Note in passing that, in view of Answer 1.5, which was a correct statement too, but not fully satisfactory as answer to Question 1.4, this principle holds for liquids and solids as well. Thus, we have here a general principle of thermodynamics, that we have to understand, first for the gases, and then for other materials like liquids or solids.

Generally speaking, Principle 1.28 is something quite intuitive for gases. Imagine indeed a box containing two gases, or two samples of the same gas, with a separation between them, with the gas on the left being hotter than the gas on the right:



Obviously the pressure is higher on the left, so when removing the separation, there will be a warm wind from left to right, in agreement with Principle 1.28. And also, this warm wind will take some time $t > 0$ to happen, because each fast particle \oplus is just a free particle, not knowing about the separation, and the other gas, consisting of slower moving particles \ominus , and it will take this particle \oplus some time, in order to discover all this, and perhaps decide to join the warm wind. As predicted, again, by Principle 1.28.

1d. Maxwell demon

So far so good, we have a beginning of theory here. This being said, there is still a bit of a bug with Principle 1.28, because that is something of statistical nature. Imagine for instance that our two gases in a box, as above, consist of one molecule each:



In this case, what Principle 1.28 says will obviously not work, and who really knows that will happen. And there is even worse, along these lines, as follows:

FACT 1.29 (Maxwell demon). *There might be a demon \star out there, who one day will start playing with our nice, uniformly arranged gases*

$$\begin{array}{ccccc} \oplus & \ominus & \star & \ominus & \oplus \\ \ominus & \oplus & & \oplus & \ominus \end{array}$$

by staying somewhere in the middle, and sorting out fast and slow molecules, as to rearrange everything into a hot gas and a cold gas, as follows,

$$\begin{array}{ccccc} \oplus & \oplus & \star & \ominus & \ominus \\ \oplus & \oplus & & \ominus & \ominus \end{array}$$

thereby violating Principle 1.28, and pushing our whole universe on a path of destruction.

As a first observation, the Maxwell demon exists indeed, because for a gas made of 2 molecules there are 50% chances for things to evolve exactly as the demon wants, and this even without the demon having to move a single finger:

$$\oplus \qquad \ominus$$

As for the remaining 50%, these are obviously not any good either. What can happen here is either the demon to intervene, making things as above, or the demon not to intervene, in which case the gas will be separated again into hot and cold, as follows, not exactly in the sense desired by the demon, but still violating Principle 1.28:

$$\ominus \qquad \oplus$$

Welcome to probability. In real life such things never happen, because gases are made of tons of molecules, say 1 billion for having a figure, and the probability for things to happen like the demon wants, with the fate of each single molecule sealed, is:

$$P = \frac{1}{2^{1,000,000,000}} = 0$$

This being said, let us record however, as a complement to Principle 1.28, coming from this discussion, and for the sake of correct science, the following:

WARNING 1.30 (Demon's advice). *Principle 1.28 is something of statistical nature, but shall we really trust statistics.*

Of course, we are a bit into personal things here, and you might agree with all this or not. What if things happening with probability 0 will indeed happen? But wait, isn't everything that happens, happening with probability 0? And so on.

Usually the solution to such things, and in particular to the possible existence of the Maxwell demon, is to have a good meal, or some drinks, or go to a party, lift some weights, cut some wood, and so on. Sometimes science can be quite abstract, temporarily taking you away from reality, but it does not take much to get back to real life, and realize, time and again, that this world was certainly not built with bad intentions.

Excuse me for interrupting, but cat is here, meowing for something, so let's ask him too, what he thinks about all this. And cat says:

FACT 1.31 (Cat's take). *I ate the Maxwell demon.*

Wow, that's quite something. It surely arranges our physics, and surely sounds plausible too. Knowing the fate of small birds and other mice, when meeting cat when in shape, I can hardly imagine how a small demon like Maxwell's could have escaped from his claws. So no more demon, and we will now develop our physics with optimism.

So, getting back now to serious physics, our theory above starts taking shape, but there are still a number of mysteries in regards with temperature, as follows:

QUESTIONS 1.32. *Regarding the temperature T , as defined above, besides fixing all the theory, with details, constants, and correction terms where needed:*

- (1) *Is T quantized?*
- (2) *Is T bounded from above?*
- (3) *Is T bounded from below?*
- (4) *Does measuring T affect T ?*

These are all difficult questions, that we will discuss later on, once the basic theory of T clarified. To be more precise, anticipating a bit, the situation is as follows:

(1) We will see that, passed the thermodynamics basics, one interesting problem is that of determining the radiation of a black body. And here, surprise, not only we will reach to the conclusion that T is quantized, but also that any theory with T non-quantized spectacularly fails. We will discuss this later, following Max Planck and others.

(2) This is a bit of a philosophical question, because at the $T \gg 0$ end things are no longer solid, liquid or gaseous, but rather plasma, or worse, and it takes some skill in order to talk about the temperature of such things, and to measure it. We will talk a bit about this, the idea being that there should be indeed an upper bound.

(3) This is, quite surprisingly, the easiest question in the list, as opposed to the difficulties of bounding other things like time $t \in \mathbb{R}$ or distance $d > 0$ from below. We will see that, with suitable conventions, we have $T > 0$, as a theorem.

(4) This is another philosophical question, coming by looking carefully at Answer 1.5, and also at the method used for measuring the pressure P , and so on. We will talk a bit about this later, towards the end of the book, in relation with quantum mechanics.

And with this, we will end this preliminary chapter. We certainly have many things to do, in order to understand what temperature T exactly is, and how basic thermodynamics works. But no worries, we will manage to have all this worked out. In the remainder of this

Part I we will get familiar first with pressure P , then with temperature T , and then based on this knowledge, we will do some engineering, in relation with engines, refrigerators, and other thermodynamical devices. Then in Part II we will further build on all this, with more thermodynamics, culminating with a first discussion about the states of matter, namely solid, liquid, gaseous, and beyond. And finally, in Part III and Part IV, we will go full throttle with advanced mathematics and physics, as to transform thermodynamics into a powerful theory of “statistical mechanics”, which explains everything, or almost.

1e. Exercises

Exercises.

CHAPTER 2

Pistons, pressure

2a. Collision basics

We have seen so far that the study of thermodynamics, or rather the attempt to start a study of thermodynamics, leads us into gases. These are indeed the simplest forms of matter to which thermodynamics applies, and we already have an interesting equation here, coming from common life experience, and waiting to be understood, namely:

$$PV = kT$$

To be more precise, here V is the volume of the gas, P is its pressure, read with a manometer, and T is the temperature, read with a thermometer. Real life tells us that we have an interesting proportionality happening, $PV \sim T$, so that we can expect to have an equation as above, with the constant $k \in \mathbb{R}$ most likely depending on the gas.

Of course, and as always in physics, and science in general, we must be careful with all this. Simple equations as the above one are usually just the tip of the iceberg, and the truth is probably that we only have an approximate formula, as follows, with lots of further theory needed, in order to understand the correction terms:

$$PV \simeq kT$$

Thus, in order to formulate our question, more generally, our guess is that any gas should be subject to an “equation of state”, which is a formula as follows, relating the variables P, V, T , and with the function $f \simeq PV - kT$ in need to be found:

$$f(P, V, T) = 0$$

To start with, let us improve our previous general knowledge about gases. We know that ordinary matter is made of molecules, and that in the case of gases, these molecules are free to move. Let us axiomatize this situation as follows:

DEFINITION 2.1. *A gas is made of molecules which are free to move, in a certain volume $B \subset \mathbb{R}^3$, with each molecule moving with its own speed. These molecules have perceptible size, and are subject to elastic collisions, when they meet.*

Obviously, this is something quite general. A first simplification is by assuming that the volume $B \subset \mathbb{R}^3$ is something standard, such as a sphere, or a cube, with this allowing

us to forget about B , and talk instead about the volume of the gas, $V = \text{vol}(B) > 0$. With this assumption made, the problem is that of finding the equation of state:

$$f(P, V, T) = 0$$

Another problem appears at the level of speeds. Molecules are of course, by definition, free to move in any direction, but if the speed is assumed to have the same magnitude $\|v\| > 0$ for all molecules, this will bring of course some simplifications.

Finally, the big problem appears in connection with collisions. We know from classical mechanics that elastic collisions in 3D, even between bodies of the same mass, and in fact even between bodies of same mass arriving with the same speed, are uniquely determined up to a scattering angle θ . Thus, in order to clarify our collision formalism, we would need to know more about the chemical structure of the gas, telling us about θ .

Summarizing, many questions to be discussed, potentially leading into quite complicated mathematics. Getting started now, speaking collisions, we will need:

FACT 2.2. *In the context of general linear motion, in the case of a collision between two particles, m_1, m_2 travelling at speeds v_1, v_2 , the total momentum of the system*

$$p = m_1 v_1 + m_2 v_2$$

is conserved. The same happens of course without collision either, and also for systems of N bodies, with $N \in \mathbb{N}$ arbitrary, with all sorts of collisions allowed between them.

In order to understand now what is going on, consider two objects as above, travelling first in 1D, for simplifying, and bound for collision:

$$\circ_{m_1} \rightarrow_{v_1} \quad \leftarrow_{v_2} \circ_{m_2}$$

We know from real life that two things can happen, in this situation. The first case is that of an inelastic, also called plastic collision, where m_1, m_2 decide when meeting that they love each other, and pursue their journey as a couple, $m = m_1 + m_2$:

$$\bullet_m \rightarrow_v$$

Of course, who really knows what really happens during a plastic collision, at the microscopic level, but assuming somehow that no energy or something is dissipated, during that hot encounter, Fact 2.2 holds indeed, and allows us to do the math.

To be more precise, the math is quite simple, so let us upgrade right away our discussion, to the case where we have two bodies colliding, in arbitrary N dimensions:

$$\begin{array}{cc} \circ_{m_1} & \circ_{m_2} \\ \searrow_{v_1} & \swarrow_{v_2} \end{array}$$

As a result of our collision, we have a new body $m = m_1 + m_2$, with speed v :

$$\begin{array}{c} \bullet_m \\ \downarrow v \end{array}$$

The math, coming from the conservation of momentum, is very simple, as follows:

PROPOSITION 2.3. *In the context of a plastic collision between two bodies,*

$$m = m_1 + m_2 \quad , \quad v = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

are the mass and speed of the resulting body.

PROOF. This follows straight from Fact 2.2, because the momentum of $m = m_1 + m_2$ equals the sum of the initial momenta of m_1, m_2 , and is therefore given by:

$$mv = m_1 v_1 + m_2 v_2$$

Thus, we are led to the speed formula in the statement. \square

The second case now, that can happen as well, is that of an elastic collision. This is something more complicated, so let us go back to 1D, the situation being:

$$\circ_{m_1} \rightarrow_{v_1} \quad \leftarrow_{v_2} \circ_{m_2}$$

The elastic collision is then the case opposed to love, with our two bodies meeting, comparing their m_i, v_i , then exchanging some speed depending on that, via a few quick fists, and then either keeping travelling forward, but slower, or going backwards:

$$\begin{array}{cc} \bullet_{m_1} \rightarrow_{v'_1} & \circ_{m_2} \rightarrow_{v'_2} \\ \leftarrow_{v'_1} \circ_{m_1} & \leftarrow_{v'_2} \bullet_{m_2} \\ \leftarrow_{v'_1} \circ_{m_1} & \circ_{m_2} \rightarrow_{v'_2} \end{array}$$

In the above pictures, the winner, which was m_1 in the first case, and m_2 in the second case, was awarded a black belt. As for the third case, that is some sort of draw.

Getting back now to the conservation of momentum, from Fact 2.2, it is pretty much clear that what we have there won't allow us to do the math. To be more precise, we can get from there only 1 equation, which is not enough for computing the output data. Fortunately, in the case of elastic collisions, Fact 2.2 can be complemented with:

FACT 2.4. *In the context of general linear motion, in the case of an elastic collision between two bodies, m_1, m_2 travelling at speeds v_1, v_2 , the total energy of the system*

$$E = \frac{m_1 \|v_1\|^2}{2} + \frac{m_2 \|v_2\|^2}{2}$$

is conserved. The same happens of course without collision either, and also for systems of N bodies, with $N \in \mathbb{N}$ arbitrary, with multi-elastic collisions allowed between them.

Again, as in the case of the plastic collisions, who really knows what really happens during an elastic collision, at the microscopic level, but again, assuming that no things are lost, during that event, Fact 2.4 holds indeed, and allows us to do the math.

As another comment, while the formula of the momentum $p = mv$ from Fact 2.1 was something quite simple and intuitive, the above formula of the energy $E = m||v||^2/2$ is obviously something more subtle. We will be back to this, later.

Going ahead now, let us first investigate, just out of curiosity, what happens to the energy during a plastic collision. The result here, contradicting our previous guess that the moment conservation comes somehow from “no energy lost”, is as follows:

THEOREM 2.5. *In the context of a plastic collision between two bodies, we have:*

$$E < E_1 + E_2$$

That is, some of the initial energy gets dissipated during the collision.

PROOF. We use the equations found in Proposition 2.3, namely:

$$m = m_1 + m_2 \quad , \quad v = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

According to our definition of energy, from Fact 2.3, the initial energy is:

$$E_1 + E_2 = \frac{m_1 ||v_1||^2 + m_2 ||v_2||^2}{2}$$

As for the final energy, this is given by the following formula:

$$E = \frac{m ||v||^2}{2} = \frac{||m_1 v_1 + m_2 v_2||^2}{2(m_1 + m_2)}$$

So, let us compute now the difference between these two quantities. We obtain:

$$\begin{aligned} E_1 + E_2 - E &= \frac{(m_1 + m_2)(m_1 ||v_1||^2 + m_2 ||v_2||^2) - ||m_1 v_1 + m_2 v_2||^2}{2(m_1 + m_2)} \\ &= \frac{m_1 m_2 (||v_1||^2 + ||v_2||^2) - 2 \langle m_1 v_1, m_2 v_2 \rangle}{2(m_1 + m_2)} \\ &= \frac{m_1 m_2 (||v_1||^2 + ||v_2||^2 - 2 \langle v_1, v_2 \rangle)}{2(m_1 + m_2)} \end{aligned}$$

But the quantity on top right is subject to the following inequality, valid for any two vectors $v_1, v_2 \in \mathbb{R}^N$, and with the equality case happening precisely when $v_1 = v_2$:

$$||v_1||^2 + ||v_2||^2 \geq 2 \langle v_1, v_2 \rangle$$

Thus $E_1 + E_2 \geq E$, and since a collision cannot happen when the initial speeds are the same, $v_1 = v_2$, the equality case cannot happen, and so $E_1 + E_2 > E$, as stated. \square

As already mentioned, the above result might seem quite surprising, contradicting our previous guess that the momentum conservation principle comes from something of type “no energy lost”. Let us record this finding in the form of an informal statement:

CONCLUSION 2.6. *Momentum ain't the same thing as energy.*

Moving ahead now, and back to the elastic collisions, the two conservation principles that we have, namely Fact 2.2 and Fact 2.4, allow us to do the math. Let us first work out the case of an elastic collision in 1D, the initial picture being as follows:

$$\circ_{m_1} \rightarrow_{v_1} \qquad \leftarrow_{v_2} \circ_{m_2}$$

Depending on the resulting fight, we can have either a win or m_1 or m_2 , or a draw. Abstractly however, we can simply say that we are in a draw situation, the picture being as follows, with the convention that we do not know yet the directions of v'_1, v'_2 :

$$\leftarrow_{v'_1} \circ_{m_1} \qquad \circ_{m_2} \rightarrow_{v'_2}$$

With these conventions made, the precise 1D result is as follows:

PROPOSITION 2.7. *In the context of a 1D elastic collision between two bodies,*

$$v'_1 = \frac{(m_1 - m_2)v_1 + 2m_2v_2}{m_1 + m_2}$$

$$v'_2 = \frac{(m_2 - m_1)v_2 + 2m_1v_1}{m_1 + m_2}$$

are the resulting speeds of the two bodies.

PROOF. According to our momentum and energy conservation principles from Fact 2.2 and Fact 2.4, the resulting speeds v'_1, v'_2 satisfy the following two equations:

$$m_1v_1 + m_2v_2 = m_1v'_1 + m_2v'_2$$

$$m_1v_1^2 + m_2v_2^2 = m_1v'^2_1 + m_2v'^2_2$$

Now observe that these equations can be written as follows:

$$m_1(v_1 - v'_1) = m_2(v'_2 - v_2)$$

$$m_1(v_1^2 - v'^2_1) = m_2(v'^2_2 - v_2^2)$$

By dividing the second equation by the first one, our system becomes:

$$m_1(v_1 - v'_1) = m_2(v'_2 - v_2)$$

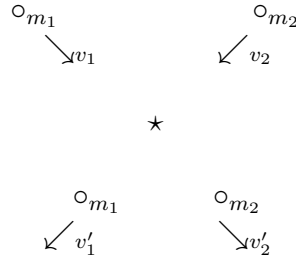
$$v_1 + v'_1 = v'_2 + v_2$$

And by doing now the math, we are led to the formulae in the statement. \square

Getting now to arbitrary N dimensions, things here become more complicated, due to a number of reasons. As a first observation, which is actually very good news, we are in fact in 2 dimensions, and more specifically in the following plane:

$$E = \text{span}(v_1, v_2)$$

Thus we may assume $E = \mathbb{R}^2$, with the collision point being the origin $0 \in \mathbb{R}^2$, and do our computations here. Schematically, we can represent the collision as follows:



Let us quickly do the math. We have to compute two vectors v'_1, v'_2 , accounting for a total of 4 numbers. But what we have is one vector equation, coming from momentum, and one scalar equation, coming from energy, so a total of 3 equations. Thus, we won't be able to do the math, unless we know something more on the collision mechanism.

To be more precise here, as already mentioned on numerous occasions, we don't really know what happens, at the microscopic level, when collisions take place, be them plastic or elastic, or of any other kind. And in the case of elastic collisions in $N \geq 2$ dimensions, there are several possible mechanisms, which in practice each correspond to a different way in which the original angles of v_1, v_2 get transformed into the output angles of v'_1, v'_2 . More specifically, the extra parameter that we need is some sort of "scattering angle" θ , coming from the precise mechanism of collision that we are investigating.

But this is something quite complicated, that we won't get into, at this stage. So long story short, and getting back now to math, in the absence of more data, and physical knowledge in general, our tools will be Fact 2.2 and Fact 2.4, and we will be able to solve the problem up to 1 degree of freedom. So, let us do this. The result is as follows:

THEOREM 2.8. *In the context of an elastic collision between two bodies, assumed without loss of generality to happen in \mathbb{R}^2 , the output speeds are*

$$v'_1 = v_1 + \frac{q}{m_1} \quad , \quad v'_2 = v_2 - \frac{q}{m_2}$$

with the vector parameter $q \in \mathbb{R}^2$ being subject to the following equation:

$$2 \langle v_2 - v_1, q \rangle = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \|q\|^2$$

Thus, the collision problem is solved, up to an angle $\theta \in \mathbb{R}$.

PROOF. We can solve this by using Fact 2.2 and Fact 2.4, as follows:

(1) According to our general momentum and energy conservation principles, the output speeds v'_1, v'_2 are subject to the following two equations:

$$\begin{aligned} m_1 v_1 + m_2 v_2 &= m_1 v'_1 + m_2 v'_2 \\ m_1 \|v_1\|^2 + m_2 \|v_2\|^2 &= m_1 \|v'_1\|^2 + m_2 \|v'_2\|^2 \end{aligned}$$

Let us first look at the first equation. This equation can be written as follows:

$$m_1(v'_1 - v_1) = m_2(v_2 - v'_2)$$

Now if we call q this quantity, which is the individual change of momentum, from the perspective of m_1 , and from the opposite perspective of m_2 , we have:

$$v'_1 = v_1 + \frac{q}{m_1} \quad , \quad v'_2 = v_2 - \frac{q}{m_2}$$

(2) Now let us plug these values into the second equation above. We obtain:

$$m_1 \|v_1\|^2 + m_2 \|v_2\|^2 = m_1 \left\| v_1 + \frac{q}{m_1} \right\|^2 + m_2 \left\| v_2 - \frac{q}{m_2} \right\|^2$$

By expanding the scalar products and then simplifying, we obtain:

$$\frac{\|q\|^2}{m_1} + \frac{\|q\|^2}{m_2} + 2 \langle v_1, q \rangle - 2 \langle v_2, q \rangle = 0$$

Thus, we are led to the formulae in the statement.

(3) As for the last assertion, this is something rather philosophical. To be more precise, we know that our parameter $q \in \mathbb{R}^2$ is subject to an equation of the following type:

$$\langle v, q \rangle = \lambda \|q\|^2$$

Now if we denote by $\theta \in \mathbb{R}$ the oriented angle between v, q , this equation reads:

$$\|v\| \cos \theta = \lambda \|q\|$$

Thus we can recover $\|q\|$, and so also $q \in \mathbb{R}^2$ itself, out of this angle $\theta \in \mathbb{R}$, and this leads to the conclusion that our problem is indeed solved up to an angle $\theta \in \mathbb{R}$. \square

As an illustration for Theorem 2.8, let us work out what happens in the case of a 1D collision. Here we already know the answer, from Proposition 2.7, but wait for it. So, let us get back to our usual 1D scheme, with m_1, m_2 about to collide, on a line:

$$\circ_{m_1} \rightarrow_{v_1} \quad \leftarrow_{v_2} \circ_{m_2}$$

In the context of Theorem 2.8, the fact that we are now in 1D simply tells us that the speed vectors $v_1, v_2 \in \mathbb{R}^2$ are proportional, $v_1 = \lambda v_2$. But this does not force in any way the vector $q \in \mathbb{R}^2$ there to be aligned with v_1, v_2 , or if you prefer, the angle $\theta \in \mathbb{R}$ there to be 0. Thus, we are led to the peculiar conclusion that our general elastic collision formalism, leading to Theorem 2.8, theoretically allows escapes from 1D to 2D.

What to do? Modesty as usual, this is what we have, and it's after all not that bad. And for closing this 1D discussion, let us however formulate, as a consequence of our new knowledge from Theorem 2.8, a better formulation of Proposition 2.7, as follows:

THEOREM 2.9. *In the context of a 1D elastic collision between two bodies, staying as normal in 1D, the resulting speeds of the two bodies are*

$$v'_1 = v_1 + \frac{q}{m_1} \quad , \quad v'_2 = v_2 - \frac{q}{m_2}$$

where $q \in \mathbb{R}$ is the individual change of momentum, given by

$$\left(\frac{1}{m_1} + \frac{1}{m_2} \right) q = 2(v_2 - v_1)$$

from the perspective of m_1 , and from the opposite perspective of m_2 .

PROOF. This follows either from Proposition 2.7, or from Theorem 2.8:

(1) From the perspective of Proposition 2.7, we have done some quick algebra there, without really knowing what we're doing, leading to the following formulae:

$$v'_1 = \frac{(m_1 - m_2)v_1 + 2m_2v_2}{m_1 + m_2} \quad , \quad v'_2 = \frac{(m_2 - m_1)v_2 + 2m_1v_1}{m_1 + m_2}$$

Now observe that these two formulae can be alternatively written as follows:

$$v'_1 = v_1 + \frac{2m_2(v_2 - v_1)}{m_1 + m_2} \quad , \quad v'_2 = v_2 + \frac{2m_1(v_1 - v_2)}{m_1 + m_2}$$

But this leads to the formulae in the statement, and to that conclusion about q .

(2) From the perspective of Theorem 2.8, we have indeed the formulae of v'_1, v'_2 in the statement, and with q being the change of momentum, as stated. Thus, it remains to establish the precise formula of q . In the context of Theorem 2.8, the equation is:

$$2 \langle v_2 - v_1, q \rangle = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \|q\|^2$$

Now since everything happens, by assumption, in 1D, the vectors v_1, v_2, q are pairwise proportional. Thus the above scalar product becomes a usual product, and also the squared norm becomes a usual square, and so our equation simply reads:

$$2(v_2 - v_1)q = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) q^2$$

But this gives the formula of q in the statement, and we are done. \square

Moving ahead towards gases, we must review here the collision formulae, in the case where the colliding masses are equal. We have here the following result:

THEOREM 2.10. *In the context of an elastic 2D collision between particles having the same mass m , the output speeds are given by the formulae*

$$v'_1 = v_1 + u \quad , \quad v'_2 = v_2 - u$$

or alternatively, by the following equivalent formulae

$$v'_1 = v_2 - w \quad , \quad v'_2 = v_1 + w$$

where u, w with $u + w = v_2 - v_1$ form with $v_2 - v_1$ a right triangle, $u \perp w$.

PROOF. This follows from our general collision formulae, as follows:

(1) We recall that the general output speeds are $v'_1 = v_1 + q/m_1$ and $v'_2 = v_2 - q/m_2$, with the parameter $q \in \mathbb{R}^2$ being subject to the following equation:

$$2 \langle v_2 - v_1, q \rangle = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \|q\|^2$$

(2) In the case of equal masses, $m_1 = m_2 = m$, if we set $u = q/m$ then we have the first formulae in the statement, $v'_1 = v_1 + u$ and $v'_2 = v_2 - u$, with $u \in \mathbb{R}^2$ satisfying:

$$\langle v_2 - v_1, u \rangle = \|u\|^2$$

(3) Now by setting $w = v_2 - v_1 - u$, the first formulae in the statement transform into the second ones, namely $v'_1 = v_2 - w$ and $v'_2 = v_1 + w$, and we have:

$$\langle u, w \rangle = \langle u, v_2 - v_1 - u \rangle = 0$$

(4) Thus, we are led to the conclusion in the statement, and with the remark that everything depends, equivalently, on the angle $\theta \in \mathbb{R}$ between $(u, v_2 - v_1)$, which fully determines the right triangle $(u, w, v_2 - v_1)$ in the statement.

(5) To be more precise, when this angle is $\theta = 0$ we have $w = 0$ and so, as in the 1D case, the collision simply amounts in an exchange of particles. However, for $\theta \neq 0$ this exchange is perturbed, by the vector w , having magnitude $\|w\| = \|v_2 - v_1\| \sin \theta$. \square

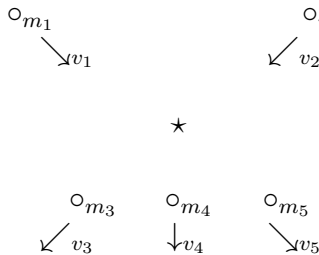
In the general 3D case, the situation becomes even more complicated, because the output speeds v'_1, v'_2 consist of $3 + 3 = 6$ unknowns, and conservation of energy and momentum give us only $1 + 3 = 4$ equations. Thus, we have here 2 free parameters, unless of course we want to declare that the collision stays in the 2D plane (v_1, v_2) , in which case the problem is fully solved by Theorem 2.10, with just 1 parameter.

However, in practice, this latter assumption is not very realistic, due to the usually complex 3D shape of the gas molecules. As an example here, you can go to your chemistry lab, pick two big plastic H_2O molecules, and make them collide on a table. And, even if you always throw them with the same speeds v_1, v_2 , what happens at the moment of the impact can vary, depending on which side of the first H_2O will hit which side of the second H_2O . To be more precise, you can observe in this way the above-mentioned angle

θ , and if you throw hard enough, one of the two H_2O might even take off upon impact, making it clear that there is as well a 2nd parameter involved there.

So long for elastic collisions. We will be back to them later on in this book, and to some related scattering questions too, once we'll decide what exact types of particles we are dealing with, as to be able to come up, via some more phenomenology and physics, with answers to some of the above questions, not to say weird mysteries.

Finally, again speaking generalities about collisions, remember that our first example was that of two trains colliding. But that type of collision, which is somewhat generic in real-life problems, is not elastic, neither plastic, but rather something in between, with the generic, 2D picture being something quite frightening, of the following type:



Again, this is something complicated, that we will not discuss at this stage. Let us point out, however, that the conservation of momentum, from Fact 2.2, does apply to such situations, and can be used in order to get information. More on this later.

2b. Pressure models

Now back to thermodynamics and gases, in order to deal with the various problems that might appear, it is convenient to relax a bit our formalism, as follows:

DEFINITION 2.11. *We call 1D, 2D or 3D gas a gas as in Definition 2.1, with the molecules allowed to move in 1, 2 or all 3 directions.*

This is of course something purely mathematical, but the 1D and 2D gases will prove to be useful, as toy examples to be worked out before getting into the usual, 3D gas problems. As a first result now, dealing with the non-collision case, we have:

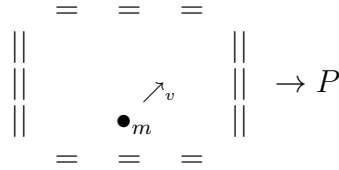
THEOREM 2.12. *The pressure P , volume V and total kinetic energy K of a gas, having point molecules, with no collisions between them, satisfy*

$$PV = \frac{2K}{d}$$

where $d = 1, 2, 3$ is the dimensionality of the gas, $d = 3$ for usual 3D gases.

PROOF. We can do this in several steps, as follows:

(1) Let us first assume that the gas is enclosed in a cubic volume, $V = L^3$. We want to compute the pressure P on the right wall. Since there are no collisions, we can assume by linearity that our gas has 1 molecule, having mass m and travelling at speed v . We must compute the pressure P exerted by this molecule on the right wall:



(2) We first look at a 1D gas. Our molecule hits the right wall at every $\Delta t = 2L/v$ interval, with its change of momentum being $\Delta p = 2mv$. We obtain, as desired:

$$P = \frac{F}{L^2} = \frac{\Delta p}{L^2 \Delta t} = \frac{2mv}{L^2 \cdot 2L/v} = \frac{mv^2}{L^3} = \frac{2K}{V}$$

(3) In the case of a d -dimensional gas, exactly the same computation takes place, but this time with v being replaced by its horizontal component v_1 . Thus, we have:

$$P = \frac{mv_1^2}{V}$$

But, we have the following formula, with the equality on the right being understood in a statistical sense, our molecule being assumed to follow a random direction:

$$\|v\|^2 = v_1^2 + \dots + v_d^2 = dv_1^2$$

Thus, the pressure in this case is given by the following formula, as desired:

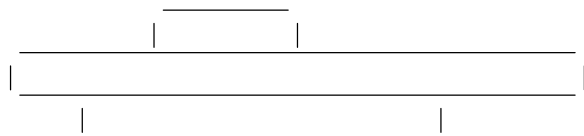
$$P = \frac{m\|v\|^2}{dV} = \frac{2K}{dV}$$

(4) It remains to extend our result to arbitrary volume shapes. For this purpose, let us first redo the above computations for a parallelepiped, $V = L_1L_2L_3$. Here the above 1D gas computation carries on, and gives the same result, as follows:

$$P = \frac{F}{L_2L_3} = \frac{\Delta p}{L_2L_3 \Delta t} = \frac{2mv}{L_2L_3 \cdot 2L_1/v} = \frac{mv^2}{L_1L_2L_3} = \frac{2K}{V}$$

Thus the d -dimensional computation carries on too, and gives the result.

(5) In order now to reach to arbitrary shapes, the idea will be that of stacking thin parallelepipeds, best approximating the shape that we have in mind, as follows:



(6) But for this purpose it is better to drop our assumption that the gas has 1 molecule, and use N molecules instead. With $\rho = N/V$ being the molecular density, and K_0 being the kinetic energy of a single molecule, our computation in (4) for the parallelepiped, with now N molecules instead of 1, reformulates as follows:

$$P = \frac{2K}{dV} = \frac{2NK_0}{dV} = \frac{2\rho VK_0}{dV} = \frac{2\rho K_0}{d}$$

(7) But this latter formula shows that the pressure has nothing to do with the precise volume V , but just with the molecular density $\rho = N/V$. Thus, we can stack indeed parallelepipeds, with of course the assumption that ρ is constant over these parallelepipeds, and we obtain that the above formula holds for an arbitrary volume shape V :

$$P = \frac{2\rho K_0}{d}$$

Now by getting back to the volume V , we obtain the following formula:

$$P = \frac{2\rho K_0}{d} = \frac{2NK_0}{dV} = \frac{2K}{dV}$$

Thus, we are led to the conclusion in the statement. \square

The above result is something quite interesting, so for future reference, let us record its $d = 3$ particular case, which is the one that we are mainly interested in:

THEOREM 2.13. *The pressure P , volume V and total kinetic energy K of a gas, having point molecules, with no collisions between them, satisfy:*

$$PV = \frac{2K}{3}$$

Thus, when formally defining the temperature of such a gas as being $T = 2K/3k$, with $k \in \mathbb{R}$ being a constant of our choice, the formula $PV = kT$ works.

PROOF. Here the first assertion follows from Theorem 2.12, and the second assertion is, obviously, just some wild speculation based on that. Observe however that we are entitled to do such speculations, because gases as in the statement, with point molecules, and no collisions between them, do not exist in real life. So, we are free to talk about the temperature of a gas which does not exist, at the level of abstractions, so to say. \square

What is have in Theorem 2.13 is something quite interesting, obviously we are on the good way on understanding the master equation of gases, $PV = kT$. To be more precise, as dream, we can wish to further include in our study the collisions between molecules, via some further mathematics, as for that formula to eventually become $PV = kT$.

This being said, there is a bit of a problem here, because the temperature T , while certainly being related to the total kinetic energy of the gas K , in the sense for instance that the smaller K is, the smaller T should be too, is something that we can expect to be rather coming from collisions, and so to be, ultimately, quite unrelated to Theorem 2.13. Indeed, remembering how thermometers work, via exchange of heat, it is quite clear that we need collisions there, in order for that exchange of heat to happen.

Thus, as a conclusion now, Theorem 2.13, while certainly nice, misses all the point with the temperature T . What we have there is something regarding the pressure P , and so this is the way to be followed, next, further understanding the pressure P . And in what regards the temperature T , and the formula $PV = kT$, we will leave this for later.

So, pressure. What we know so far is that the pressure P comes from the mechanical pressure of the gas on a piston, that is, from the force of the gas molecules colliding with the piston. In view of this, we would first like to better understand the physics of the measuring piston. And we have plenty of interesting questions here, as follows:

QUESTIONS 2.14. *In a context of a gas enclosed in a cylinder with a piston, assumed to be formed of point molecules, with no collisions between them:*

- (1) *What is the correct modelling of the elastic collisions between the molecules and the piston, instantaneous, $\Delta t = 0$, or in nonzero time, $\Delta t > 0$?*
- (2) *How will the piston exactly move, depending on the chosen model? Will equilibrium lead to some special distribution of the molecular speeds?*
- (3) *How does measured pressure P_t evolve with time $t > 0$? What is the correct time $t_f > 0$ for reading the correct, final pressure, $P_f = 2K/dV$?*

These are certainly all good questions, in view of the fact that our only way of knowing more about the gas is via its interaction with the piston. In practice now:

(1) This is obviously a quite complicated question, and contemplating a good soup cooking, in a pot with a cover, with the cover jiggling under the effect of the steam, will certainly give you a taste of the complexity and chaos involved there.

(2) This is a question which looks more mathematical, and obviously of prime theoretical importance, but in order to have some fun with it, and do some computations there, we will need a model for it, to start with, as in (1).

(3) Again this looks like mathematics, where we can have some theory and computations running, and again this is of importance, physically speaking, but again we need a model for it, as in (1), in order to get started, in our computations.

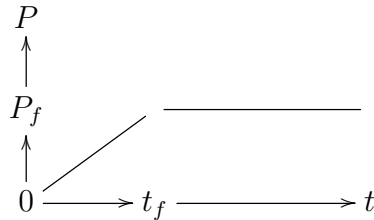
So, these are our problems, and this even before getting to the real-life gases, made of molecules having perceptible size, with collisions between them. We will attempt now to solve these questions, with our main focus being on (2), try to have something done there, that can afterwards evolve into the Maxwell-Boltzmann distribution, which is the correct distribution of the molecular speeds for a real-life gas, with collisions.

Let us start with discussing (3). Obviously this question is in need of a model, say with a spring for the piston, exactly as in the case of the usual manometers, functioning with a spring. However, we can actually say something, to start with, purely mathematical, even without a spring or other model for the piston involved, as follows:

THEOREM 2.15. *In the context of a gas consisting of point molecules, with no collisions between them, the correct time for reading the correct pressure is*

$$t_f = \frac{2\sqrt{d}V^{1/3}}{\|v\|} \quad : \quad P_f = \frac{2K}{dV}$$

with $\|v\|$ being the average molecular speed, with the precise pressure reading being



and with this being taken in an approximate, statistical sense.

PROOF. We can do this in two steps, as follows:

(1) Let us first look at a 1D gas. We can assume that we are in a cubic container, $V = L^3$, and we know that each molecule i hits the right wall, where P is measured, at $\Delta t_i = 2L/|v_i|$ intervals. But with this picture in hand, it is quite clear that, on average, the pressure reading process will be linear, starting from $P = 0$, up to time $t_f = 2L/|v|$, with $|v|$ being the average molecular speed, where the correct pressure $P_f = 2K/V$ will be read, and constant at P_f afterwards. Now since $L = V^{1/3}$, this gives, as desired:

$$t_f = \frac{2V^{1/3}}{|v|} \quad : \quad P_f = \frac{2K}{V}$$

(2) In the general case now, that of a d -dimensional gas, with $d = 1, 2, 3$, the same argument carries on, with the only change being that each molecular speed $v_i \in \mathbb{R}^d$ is now

replaced by its horizontal component $v_{i1} \in \mathbb{R}$, which by statistical reasons has squared magnitude as follows, as explained in the proof of Theorem 2.12:

$$v_{i1}^2 = \|v_i\|^2/d$$

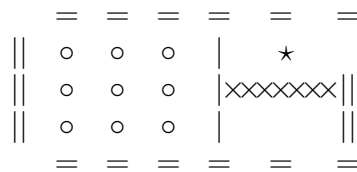
Thus, with respect to (1), the correct final pressure must be adjusted by a d factor, and becomes $P_f = 2K/dV$, as in Theorem 2.12. As for the correct reading time, this must be adjusted by a \sqrt{d} factor, and becomes $t_f = 2\sqrt{d} V^{1/3}/\|v\|$, as claimed. \square

All the above is quite interesting, but remains something theoretical, because our gas is not a real gas, with collisions between molecules. We will be back to this.

Going ahead now with the real problem, namely finding models for the piston, and then doing some math afterwards, we have several choices here. First we have:

MODEL 2.16 (Spring model). *The piston has a spring on its back, with the energy $E = mv^2/2$ of each incoming molecule being converted, over a certain period of time $\Delta t > 0$, into internal energy E_s of the spring, until the molecule comes to a stop, and then released back as identical kinetic energy $E = mv^2/2$, over the same period of time $\Delta t > 0$, of that molecule bouncing back, with speed of same magnitude $\|v\|$.*

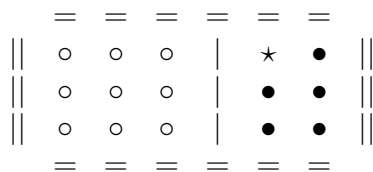
In other words, we are proposing here a model for the piston which is similar to the one which can be found inside the usual, real-life manometers. The functioning is as follows, with \star standing for our displacement measuring devices:



This model surely stands, and certainly brings some fresh air into our physics. Indeed, what we have been doing so far assumes that the collisions with the piston are elastic and instantaneous, $\Delta t = 0$, and the problem now is about fine-tuning our theory using collision times $\Delta t > 0$, as above. In addition, the model can be further complicated afterwards, say allowing for some friction on the vertical, which amounts in allowing heat diffusion at the piston, having something to do with the temperature T of the gas.

As a variation of this model, again inspired by usual manometers, the spring used above is just a flexible solid, so why not using instead a liquid, or even a gas. We are led in this way to the following scheme, with \bullet standing our favorite lab fluid, and with

★ standing as usual for our measurement devices, now floating inside this fluid:



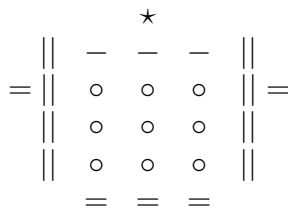
To be more precise, assuming for instance that \bullet is another gas, initially at lower pressure than the gas to be studied \circ , the piston will certainly start moving to the right, and then after some time, start to stabilize, with an interesting jiggling to be studied.

But do we really have some lab gas \bullet , that we know well. Not really, at this point of our story. So we are led into liquids, which are a bit more similar to the solid springs in Model 2.16, but do we really know about compression of liquids, and the answer here is not either. So, we will not use such fluid models, and keep them in mind for later.

As a third model now, which is intuitive and viable as well, we have:

MODEL 2.17 (Cooking pot model). *The cylinder and piston, functioning now vertically, work as a cooking pot with cover. That is, the gas is cooking inside the pot, the cover has a certain weight $M \gg m$ and is subject to an acceleration $g > 0$, not affecting the gas itself, and the molecules m collide elastically with the cover M , assumed to travel frictionless on the vertical only, making it jiggle, around an average height L .*

This model looks quite interesting, and here is the picture, with handles attached, for easy transportation inside the lab, and with \star standing for our measuring devices:



The same general comments as for the spring model apply, with this model being something preliminary, which can be subject to further improvements. However, there are two notable differences with the spring model. First, in this cooking model the collisions are still assumed to be instantaneous, $\Delta t = 0$, and so we have less physics to care about. And also, speaking simplicity, our cooking pot model is purely gravitational, and so no need to go into springs and their functioning, we're just ready to go.

As another comment, if the fact that $g > 0$ acts by definition on the cover M , but not on the gas molecules m , bothers you, you can assume for instance that the cover M and the acceleration $g > 0$ are something more modern, say of magnetic nature. But, in what

follows, we will refer to what happens as being gravitational, nothing being better in life than a good soup or stew, cooking in an old pot, with old-style gravitational cover.

2c. Cooking molecules

Here is now our result, regarding the cooking pot model:

THEOREM 2.18. *The following happen, for a gas having N point molecules, with no collisions between them, cooking in a pot with cover, as in Model 2.17:*

- (1) *In the usual regime, $N \gg 0$, the cover mass M and the acceleration g must be subject to the formula $dLMg = 2K$, with d, L, K being as before.*
- (2) *At $N = 1$, that is to say, when cooking a single molecule, the cover will bounce up and fall, perfectly in tune with the molecule, which keeps its speed $\|v\|$.*
- (3) *At $N = 2$ however, when cooking two molecules, the initial speeds v_1, v_2 of these molecules, even when taken equal, will change over time, due to the cover.*
- (4) *Even worse, at $N = 2$ the system will exhibit chaotic behavior, and this for all choices of the initial data. And the same will happen at any $N \geq 2$.*

PROOF. There are many things to be done here, the idea being as follows:

(1) Let us first assume that we have a 1D gas. The molecular force acting on the cover, upwards, is given by the following formula, A being the area of the cover:

$$F = PA = \frac{2KA}{V} = \frac{2K}{L}$$

But this force must cancel $F' = Mg$, pointing downwards, so we have:

$$\frac{2K}{L} = Mg \implies LMg = 2K$$

In general, the computation is identical, with the parameter $d = 1, 2, 3$ appearing attached to the volume V , and so to the length L , leading to $dLMg = 2K$, as stated.

(2) Let us cook now a single molecule, $N = 1$. Again, by assuming first that we deal with a 1D gas, the process here will take place in 4 steps, as follows:

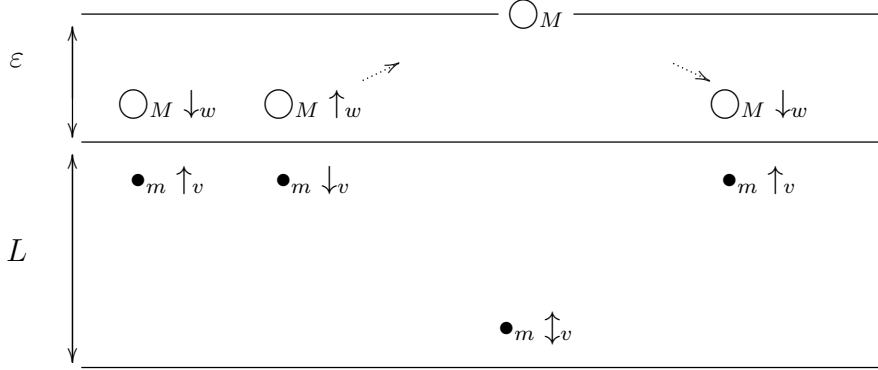
– The molecule, with mass m and upwards speed v , meets the cover, with mass M and downwards speed w , and has an elastic collision with it. Since we want our molecule to simply switch its speed after the collision, $v \rightarrow -v$, we must assume $Mw = mv$.

– In the second step, which is also infinitesimal, our molecule is now travelling downwards with speed v , and the cover is now travelling upwards with speed w .

– In the third step, the cover travels upwards during some time t_e , until getting to a halt, under the influence of g . As for the molecule, this travels downwards, during some time t_m , until reaching the bottom of the pot, for an elastic collision there.

– Finally, in the fourth step, the cover falls during time t_c , under the influence of g , until reaching its initial height L , with its initial downwards speed w . As for the molecule, this reaches to the initial height L , with its upwards speed v , in time t_m .

(3) In order now to have a cycle, we must have $t_c = t_m$, as for the whole picture of our cycle to look as follows, over this common travelling time $t_c = t_m$:



(4) But travelling times are easy to compute. In what regards the molecule, its travelling time during half of the full cycle is given by:

$$t_m = \frac{L}{v}$$

As for the cover, its equation of movement, with respect to the origin taken at height L , is $x = wt - gt^2/2$. We have $x = 0$ at $t = 0$, of course, and then again at $t = 2w/g$, and so the travelling time of the cover during half of the full cycle is given by:

$$t_c = \frac{w}{g}$$

Thus, our cycle condition $t_c = t_m$ amounts in saying that we must have $gL = vw$, and so to conclude, our machinery works well when the following conditions are satisfied:

$$Mw = mv \quad , \quad Lg = vw$$

Observe that when multiplying these two equations, as to get rid of the initial cover speed w , we obtain the following equation, which is the one found in (1) above:

$$LMg = mv^2 = 2K$$

(5) In the general case now, that of a d -dimensional gas, formed as before by 1 molecule, the analysis is similar. To be more precise, let us get back to Model 2.17, and to the exact prescriptions there, namely that the collisions between the molecule and the cover should be elastic, but with the cover travelling on the vertical only, in a frictionless manner, and managing somehow to absorb the lost horizontal momentum of the molecule, at each collision. Under these assumptions, the above computations carry over, with the

only thing that changes being that the molecule speed v must be replaced by its vertical component v_1 . Thus, the equations found in (4) become:

$$Mw = mv_1 \quad , \quad Lg = v_1w$$

Also as before, when multiplying these two equations, as to get rid of the initial cover speed w , we obtain the following equation, which is the one found in (1) above:

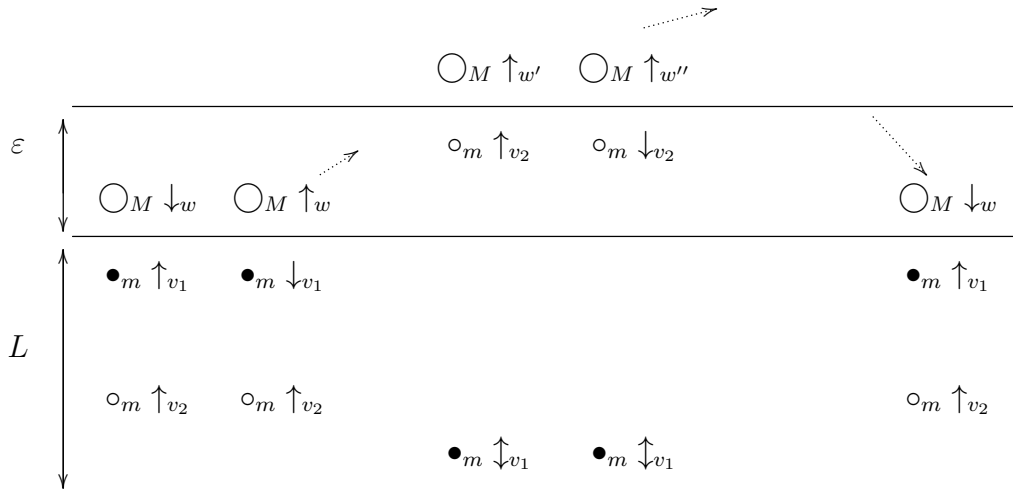
$$LMg = mv_1^2 = \frac{m\|v\|^2}{d} = \frac{2K}{d}$$

Here, as in the proof of Theorem 2.12, we have used the formula $\|v\|^2 = dv_1^2$, which is something of statistical nature, coming from the fact that our molecule is assumed to move in a random direction, inside its allowed d -dimensional space.

(6) At $N = 2$ now, when cooking two molecules, some interesting things happen. To be more precise, our claim is that the initial speeds v_1, v_2 of these two molecules, even when taken equal in magnitude initially, will change over time, due to the cover.

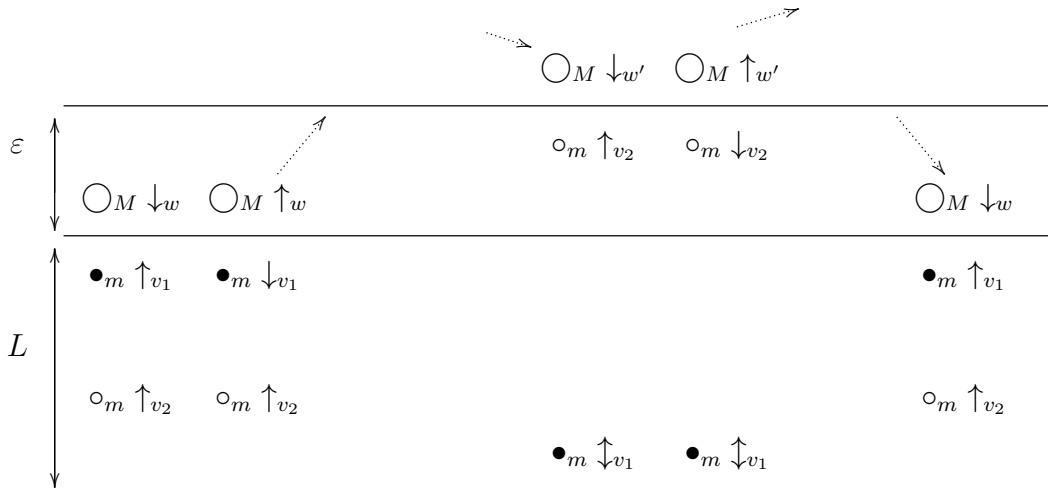
Indeed, in the context of the analysis done in (2-4), a second molecule, hitting the cover after the first one, will hit this cover travelling either upwards or downwards, and in both cases at a speed of different magnitude, $w' \neq w$. Thus, when assuming for instance $v_1 = v_2$ initially, this second collision will be no longer between objects having equal, opposite momenta, and so the speed v_2 , instead of simply getting reversed, $v_2 \rightarrow -v_2$, will get modified, into something of type $v_2 \rightarrow -v'_2$ with $v'_2 < v_2$. And so on.

(7) To be more precise, let us show now that there is no possible configuration of the initial parameters as to have a perfect cycle. There are two possible cases. The first case is where the second coming molecule hits the cover during its upwards travel:



But this certainly won't work, because the collision between the cover and the second molecule cannot happen as indicated, on top, due to obvious momentum reasons.

(8) The other case, which is perhaps more realistic, is that when the second coming molecule hits the cover during its downwards travel, as follows:



Here both the collisions will perform fine, as indicated, provided that the equal and opposite momenta conditions for them are satisfied, namely:

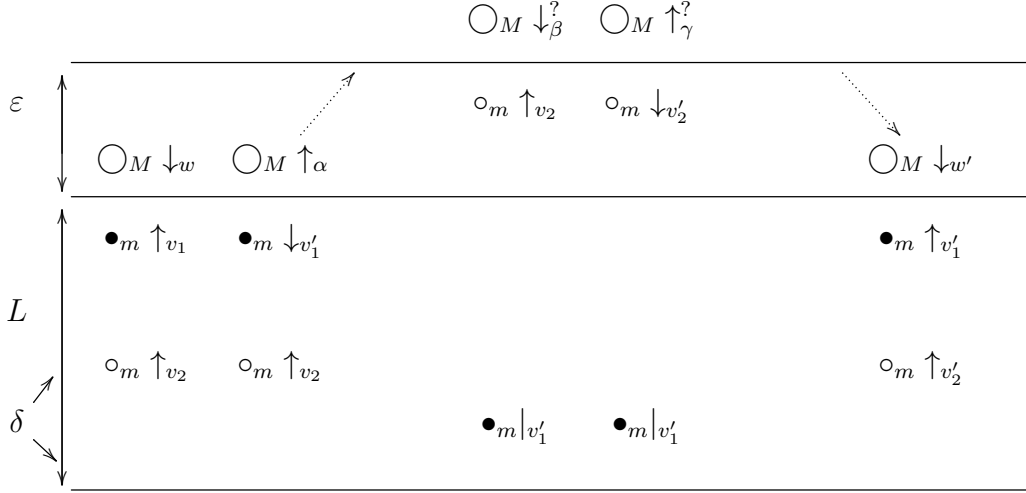
$$Mw = mv_1 \quad , \quad Mw' = mv_2$$

However, there is a bug at the level of time. On one hand we must have $v_2 > v_1$, since the second molecule has to travel 2ε more than the first one, during the whole cycle. And on the other hand we must have $v_2 < v_1$ due to the above collision equations, since $w' < w$. Thus, contradiction, and this second configuration is ruled out too.

(9) In short, complicated, but as a comment however, frankly, who would have guessed that we can get into such interesting math, just by cooking 2 molecules in a pot.

(10) Moving ahead now, the next problem is that of understanding how the speeds w, v_1, v_2 will modify over the time. Assuming, to start with, that we still want to have some sort of cycle, with the positions of the two molecules and of the cover being unchanged

after the cycle, but with the speeds modified, the picture of the problem as follows:



To be more precise, things evolve as indicated, with the upper question marks standing for the fact that we want to deal with all possible orientations there, but we have chosen some orientations, as indicated, for doing our computations, with the convention $\beta, \gamma \in \mathbb{R}$. As for the $|$ signs on the bottom, near the speeds v'_1 , these stand for the orientations of these speeds $v'_1 > 0$, which are irrelevant at that exact moment. And finally, as new parameter we have the distance $\delta > 0$ between the second molecule and the bottom.

(11) Getting now to equations, there are many of them. First we have the two collision equations, momentum and energy, which after simplification for energy are:

$$\begin{aligned} M(w - \alpha) &= m(v'_1 - v_1) \quad , \quad M(\beta - \gamma) = m(v'_2 - v_2) \\ w + \alpha &= v_1 + v'_1 \quad , \quad \beta + \gamma = v_2 + v'_2 \end{aligned}$$

We have then two equations relating the speeds of M , left to middle, and middle to right, which can be obtained by conservation of energy, and are as follows:

$$\alpha^2 - \beta^2 = w^2 - \gamma^2 = 2g\varepsilon$$

We have then equations regarding the partial times t_1, t_2 of our two-step cycle, viewed from the perspective of the second molecule, and of the first molecule, as follows:

$$t_1 = \frac{L - \delta + \varepsilon}{v_2} \quad , \quad t_2 = \frac{L + \delta + \varepsilon}{v'_2} \quad , \quad t_1 + t_2 = \frac{2L}{v'_1}$$

And finally we have degree 2 equations for t_1, t_2 from the perspective of the cover, which are as follows, with the \pm sign standing for upwards vs downwards collision:

$$t_1 = \frac{\alpha \pm \sqrt{\alpha^2 - 2\varepsilon g}}{g} \quad , \quad t_2 = \frac{\gamma + \sqrt{\gamma^2 + 2\varepsilon g}}{g}$$

(12) Looking at these equations, they don't look that bad. The first 6 equations, all regarding speeds, can be used in order to compute α, β, γ and w', v'_1, v'_2 in terms of w, v_1, v_2 . And then we have 5 equations for t_1, t_2 , which can be used for computing t_1, t_2 , and then for finding what exact conditions must the initial data $m, M, g, L, \delta, w, v_1, v_2$ satisfy, as for the positions of our 3 objects to be the same in the end as in the beginning.

(13) Summarizing, the math for some sort of cycle seems to be here, but this must be taken with care. First, because we have seen in (8) above that things can fail due to positivity reasons, which are invisible from the linear algebra viewpoint. And second, importantly, because nothing guarantees that the final data of a first cycle can run well as initial data for a second cycle, and such kind of thing must be checked too.

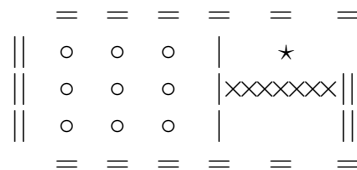
(14) We can only conclude from all this that things are quite chaotic at $N = 2$, and consequently, at $N \geq 3$ too. With the comment however that with $N \gg 0$ something interesting must certainly happen, because after all at $N = \infty$ we have equilibrium, as explained in (1). But we are here with our math on the thin edge between equilibrium and chaos, and such things are reputed to be difficult, so we will just stop here. \square

2d. Manometers

Let us discuss now the spring model, which is something quite familiar, as follows:

MODEL 2.19 (Spring model). *The piston has a spring on its back, with the energy $E = mv^2/2$ of each incoming molecule being converted, over a certain period of time $\Delta t > 0$, into internal energy E_s of the spring, until the molecule comes to a stop, and then released back as identical kinetic energy $E = mv^2/2$, over the same period of time $\Delta t > 0$, of that molecule bouncing back, with speed of same magnitude $\|v\|$.*

The scheme is as follows, with \star standing for our displacement measuring devices:



In practice, however, a bit like it was the case for the cooking pot model, the spring model leads to some order, at the level of some simple computations that can be done, but in general, this rather leads to chaos. So, as a conclusion to all this, we must rethink our methods, forget a bit about classical mechanics, and rather go towards probability. And also, importantly, perhaps start to include collisions in our gas formalism.

2e. Exercises

Exercises.

CHAPTER 3

Energy and heat

3a. Energy, work

We already know a bit about temperature and heat, and about pressure too, but time now to take things seriously, and formulate some precise definitions. As usual when starting a new physical theory, as it was already the case with classical mechanics and electromagnetism, we must approximate a bit what we know, take some things for granted, and be modest in general. So, let us start with something modest, as follows:

DEFINITION 3.1. *We are interested in gases, described by their equation of state*

$$f(P, V, T) = 0$$

relating their pressure P , volume V and temperature T .

Here the parameters P, V, T should be taken in an intuitive sense, at least to start with. The pressure $P > 0$ is measured by using a cylinder with a piston, as explained before. The volume $V > 0$ is the usual 3D volume, and with the remark here that our theory, as formulated above, neglects the precise shape of this volume. As for the temperature $T \in \mathbb{R}$, this is measured by using a thermometer, as explained before, with this thermometer being for the moment arbitrarily calibrated, meaning that T is well-determined up to $T \rightarrow aT + b$, but that we chose some $a, b \in \mathbb{R}$, as to be able to talk about $T \in \mathbb{R}$, and write our equation of state $f(P, V, T) = 0$.

Regarding the equation of state $f(P, V, T) = 0$ itself, we already know that $PV = kT$ with $k \in \mathbb{R}$ is something quite reasonable, to start with, but we will not make this assumption. First because our thermometer is for the moment arbitrarily calibrated, but then also because we will need later, when talking corrections to it, some of the general theory to be developed right next. Let us record however, for future reference:

DEFINITION 3.2. *An ideal gas is described by the equation of state*

$$PV = kT$$

or rather $PV = k(T + e)$, our thermometer being so far arbitrarily calibrated.

This is, of course, something quite theoretical, and we will be using such gases in what follows, for illustrations for our computations. Later on, after calibrating our thermometer, we will back to them, explaining who these ideal gases are, and what their constants k are, with numerics and everything. And we will talk about corrections too.

So, getting back now to Definition 3.1, our equation of state $f(P, V, T) = 0$ there is for the moment assumed to be arbitrary. Geometrically, this means that we are on a certain surface in \mathbb{R}^3 , defined by the equation $f(P, V, T) = 0$, with the parameters P, V, T being of course the coordinates. We will also tacitly assume that the equation of state $f(P, V, T) = 0$ is something non-degenerate, say appearing as a perturbation of $PV = kT$, allowing us to recover any of the parameters P, V, T , once two of them are given.

As an important observation, note the radical change with respect to mechanics, where the 3D coordinates x, y, z used to refer to the ambient space. Gone all that, the 3D space from now on will be for us that of all possible (P, V, T) points, with $P, V, T \in \mathbb{R}$, and with of course the regions $P < 0$ and $V < 0$ being excluded by obvious reasons.

As a first piece of math now, let us take a look at P , measured with a piston:

$$\begin{array}{cccccc} = & = & = & = & = & = \\ || & \circ & \circ & \circ & | & \\ || & \circ & \circ & \circ & | & \rightarrow P \\ || & \circ & \circ & \circ & | & \\ = & = & = & = & = & = \end{array}$$

When performing this measurement, the gas does some mechanical work W . This work is quite easy to compute, and we are led to the following statement:

PROPOSITION 3.3. *The mechanical work done by a gas pushing a piston is*

$$W = \int_a^b P dV$$

where $[a, b]$ is the interval where the piston has travelled.

PROOF. In order to compute mechanical work W done by the gas, observe that, infinitesimally, if we denote by dl the distance travelled by the piston in time dt , we have the following formula, with S being the area of the piston:

$$dW = F dl = P S dl = P d(Sl) = P dV$$

Now assuming that the piston has travelled from a to b , we obtain:

$$W = \int_a^b dW = \int_a^b P dV$$

Thus, we are led to the formula in the statement. \square

Obviously what we have above is a general formula, which will hold in more general situations, not necessarily involving a container with a piston. So, let us formulate:

THEOREM 3.4. *The mechanical work done by a gas evolving on a path γ , in the state space $f(P, V, T) = 0$, is given by:*

$$W_\gamma = \int_\gamma P dV$$

When representing the transformation γ as a one-variable function $P = \varphi(V)$, with T being determined at each moment by $f(P, V, T) = 0$, this formula reads

$$W_\gamma = \int_{V_0}^{V_1} \varphi(V) dV$$

with V_0 being the initial volume, and V_1 being the final volume.

PROOF. This is quite clear from the previous discussion, involving the cylinder with a piston, the argument there carrying on to the general case without problems, and giving the first formula. As for the second formula, this follows from it, with again the case of the cylinder with a piston being a good illustration, φ being there linear. \square

In order to discuss now examples, let us introduce as well the following notions:

DEFINITION 3.5. *A transformation of a gas is called:*

- (1) *Isobaric, if P is constant.*
- (2) *Isochoric, if V is constant.*
- (3) *Isothermal, if T is constant.*

Here all terminology comes from Greek, with isos meaning equal, baros meaning weight, chora meaning space, and therme meaning heat. In what regards the isochoric transformations, some authors, including Fermi [27], use the convention that this means $W = 0$, which is not the same as V being constant. Finally, there is as well a 4th class of transformations, the adiabatic ones, coming from the Greek adiabatos, meaning impassable. These latter transformations are the scary ones, and more on them later.

As an illustration for Theorem 3.4, for an ideal gas, we have the following result:

PROPOSITION 3.6. *For an ideal gas, $PV = kT$, isothermally expanding, we have*

$$W = T \log \frac{V_1}{V_0}$$

where V_0 is the initial volume, and V_1 is the final volume.

PROOF. This follows indeed from Theorem 3.4, in either formulation:

(1) With the first formula the work is readily computed, as follows:

$$W = \int_{\gamma} P dV = kT \int_{\gamma} \frac{dV}{V} = T \log \frac{V_1}{V_0}$$

(2) With the second formulation, since we have $PV = kT$ by the equation of state, and T constant by assumption, the transformation is given by $\varphi(V) = kT/V$, and so:

$$W = \int_{V_0}^{V_1} \frac{kT}{V} dV = kT \int_{V_0}^{V_1} \frac{dV}{V} = T \log \frac{V_1}{V_0}$$

(3) Finally, there is a discussion to be made too in connection with the calibration of the thermometer. As explained in Definition 3.2, in the lack of a precise calibration, the equation of state of ideal gases is rather $PV = k(T + e)$, with $k, e \in \mathbb{R}$. But this leads to exactly the same final answer, with T being now replaced by $T + e$. \square

We know from classical mechanics that work is intimately related to energy. So, let us discuss now energy, in the context of thermodynamics. In analogy with what happens in classical mechanics, we will have two guiding principles, as follows:

PRINCIPLES 3.7. *In the context of thermodynamics:*

- (1) *Energy E comes in two flavors, namely work W and heat Q .*
- (2) *We will talk about variations ΔE of the energy, instead of E itself.*

To be more precise, here (1) is in analogy with what we know from classical mechanics, where energy E comes in two flavors too, namely kinetic energy T and potential energy V , and with our excuses here for the conflicting T, V notations, but the alphabet is not long enough for all our physics in this book. As for (2), this is again in analogy with classical mechanics, where the potential energy V is defined only up to an additive constant, which makes $E = T + V$ itself be to defined only up to an additive constant too.

In what regards now the physics of Q , this is heat as we know it, related to the temperature T . To be more precise here, its main properties are as follows:

PRINCIPLE 3.8. *The amount of heat Q received during a transformation is a thermodynamical quantity, in relation with temperature, and which normally depends on the chosen path in the state space. However, we usually have*

$$Q = C\Delta T$$

with $C > 0$ being a constant, called heat capacity of the material, independently on the chosen path in the state space, between the unital and the final point.

With the above principles in hand, we can now talk about energy, or rather about energy variation, and formulate the first law of thermodynamics, as follows:

LAW 3.9 (First law of thermodynamics). *During a transformation of a gas, along a path in the state space $f(P, V, T) = 0$, we have the formula*

$$\Delta E = Q - W$$

where Q is the amount of heat received, and W is the work performed, with ΔE not depending on the precise path chosen between the initial and the final point.

This first law of thermodynamics, which will replace in what follows Principles 3.7 and Principle 3.8, for most of our practical purposes, might seem a bit head-scratching. You would say that this is just the definition of ΔE , or if you want the definition of E up to a constant. But, more is true. The whole point lies in the last words, stating that ΔE is independent of precise path chosen between the initial and the final point.

So, to reformulate. The first law of thermodynamics states two things:

(1) First we have a true law of physics, which is something non-trivial, stating that, while both the quantities Q and W generally depend on the chosen path in the state space, between the initial and the final point, their difference $Q - W$ does not.

(2) And then we have a definition based on this, namely $\Delta E = Q - W$, which tells us that the independence of $Q - W$ on the chosen path comes in fact from the existence of an internal energy function E of the system, well-defined up to a scalar.

But perhaps most illustrating for all this are some simple examples, as follows:

PROPOSITION 3.10. *The following happen:*

- (1) *For a cyclic transformation we have $Q = W$, regardless of the chosen path in the state space, between the initial and the final point.*
- (2) *Assuming that the heat received is subject to $Q = C\Delta T$, with $C > 0$, for a thermally insulated system we have $\Delta E = -W$.*

PROOF. Both these assertions are clear from definitions, as follows:

- (1) For a cyclic transformation we have $\Delta E = 0$, and so $Q = W$, as claimed.
- (2) Our combined assumptions mean $Q = C\Delta T = 0$, so $\Delta E = -W$, as claimed. \square

Finally, the first law of thermodynamics invites us to introduce, as a complement to the various elementary notions from Definition 3.5:

DEFINITION 3.11. *A transformation is called adiabatic if:*

$$Q = 0$$

Equivalently, we must have the energy conservation law $\Delta E = -W$.

Obviously, this is something a bit complicated. As basic examples here we have the transformations in Proposition 3.10 (2), namely those of the thermally insulated systems obeying to $Q = C\Delta T$, with $C > 0$. More on adiabatic transformations later.

3b. Heat equations

Let us do now some math, based on all this. We have here the following result:

THEOREM 3.12. *We have the following heat equations,*

$$\begin{aligned} dQ &= \left(\frac{dE}{dP}\right)_V dP + \left[\left(\frac{dE}{dV}\right)_P + P\right] dV \\ dQ &= \left[\left(\frac{dE}{dP}\right)_T + P\left(\frac{dV}{dP}\right)_T\right] dP + \left(\frac{dH}{dT}\right)_P dT \\ dQ &= \left[\left(\frac{dE}{dV}\right)_T + P\right] dV + \left(\frac{dE}{dT}\right)_V dT \end{aligned}$$

where $H = E + PV$, called *enthalpy of the system*.

PROOF. This follows indeed by doing some computations, as follows:

(1) We first have the following formulae, coming from definitions:

$$\begin{aligned} dE(P, V) &= \left(\frac{dE}{dP}\right)_V dP + \left(\frac{dE}{dV}\right)_P dV \\ dE(P, T) &= \left(\frac{dE}{dP}\right)_T dP + \left(\frac{dE}{dT}\right)_P dT \\ dE(V, T) &= \left(\frac{dE}{dV}\right)_T dV + \left(\frac{dE}{dT}\right)_V dT \end{aligned}$$

(2) In order to advance, we use the work formula in Theorem 3.4, rewritten as:

$$dW = PdV$$

By plugging into formula into the first law, the first law becomes:

$$dQ = dE + dW = dE + PdV$$

(3) Now by using this latter formula, the equations found in (1) become:

$$\begin{aligned} dQ &= \left(\frac{dE}{dP}\right)_V dP + \left[\left(\frac{dE}{dV}\right)_P + P\right] dV \\ dQ &= \left(\frac{dE}{dP}\right)_T dP + \left(\frac{dE}{dT}\right)_P dT + PdV \\ dQ &= \left[\left(\frac{dE}{dV}\right)_T + P\right] dV + \left(\frac{dE}{dT}\right)_V dT \end{aligned}$$

(4) In what regards the first and third equations, these are those in the statement. In what regards the second equation, we can work a bit more on it, and make it look better. Indeed, we can use here the following formula, coming from definitions:

$$dV = \left(\frac{dV}{dP}\right)_T dP + \left(\frac{dV}{dT}\right)_P dT$$

With this formula in hand, the second equation can be rewritten as:

$$dQ = \left[\left(\frac{dE}{dP}\right)_T + P \left(\frac{dV}{dP}\right)_T\right] dP + \left(\frac{d(E + PV)}{dT}\right)_P dT$$

(5) Still in regards with this second equation, with the aim of making it even better, let us introduce a new state function of the system, called enthalpy, as follows:

$$H = E + PV$$

In terms of this function, the second equation as modified in (4) becomes:

$$dQ = \left[\left(\frac{dE}{dP}\right)_T + P \left(\frac{dV}{dP}\right)_T\right] dP + \left(\frac{dH}{dT}\right)_P dT$$

Thus, we have as well the second equation in the statement, and we are done. \square

As an immediate consequence of the above result, we have:

PROPOSITION 3.13. *The heat capacities at constant V and P are*

$$C_V = \left(\frac{dE}{dT}\right)_V$$

$$C_P = \left(\frac{dE}{dT}\right)_P$$

with the derivatives being taken as usual, as above.

PROOF. This follows indeed from the formulae in Theorem 3.12. \square

Before going ahead, let us comment on the enthalpy function $H = E + PV$ appearing in Theorem 3.12. We came upon this function via some math, but we have:

COMMENT 3.14. *The enthalpy function of a system, given by*

$$H = E + PV$$

is what's needed for creating the system out of nothing, and putting it into environment.

To be more precise, assume that you are a magician, and want to create a rabbit. You first need energy E for creating the rabbit. But then you also need energy for putting it into environment, with this meaning pushing out the atmosphere, for creating space for the rabbit. And assuming that we are at 1 atm, this extra energy needed is PV .

Due to this, enthalpy is an important quantity in chemistry computations, and this even for simple reactions like $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, because the basic quantum chemistry formulae for them, involving electrons and so on, do not take into account the energy needed for putting the output into environment, and must be therefore fine-tuned.

For more on all this, including a picture of the magician and rabbit, we refer to the lovely book of Schroeder [73]. By the way, speaking books, an excellent reference for thermodynamics is the old, small red book by Fermi [27].

3c. Joule law

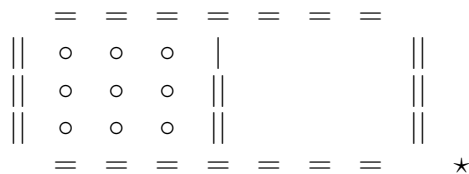
Back to work now, let us try to understand what the theory that we have so far says for the ideal gases. And here, we first have the following important finding:

FACT 3.15 (Joule). *For an ideal gas we have the formula*

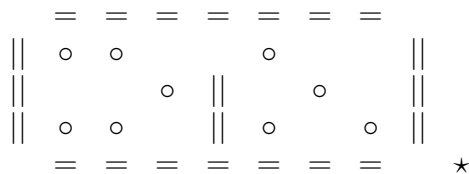
$$E = E(T)$$

meaning that the total energy depends only on the temperature.

Joule came upon this via a simple experiment, namely an adiabatic expansion of a gas. His experiment used a double gas chamber with a separation, as follows, with the left side being initially filled with gas, and with the right side being empty:



Everything was talking place inside a calorimeter, which is a device preventing heat from entering or escaping. The calorimeter was containing as well a thermometer \star . Joule opened the separation, and the gas distended, occupying the whole double chamber:



What Joule noticed is that the thermometer reading did not change much, $\Delta T \simeq 0$. And his conclusion came from here, the reasoning being as follows:

- (1) With an ideal gas, $\Delta T \simeq 0$ could only have meant $\Delta T = 0$.
- (2) Due to the calorimeter, the transformation was adiabatic, $Q = 0$.
- (3) Equivalently, $\Delta E = -W$. But $W = 0$, clearly, and so $\Delta E = 0$.
- (4) Thus $\Delta T = 0$ corresponds to $\Delta E = 0$, so we must have $E = E(T)$.

So, this was the story of the Joule finding. There is actually more to be said here, because Fact 3.15 eventually became a theorem, being possible to be proved by using the second law of thermodynamics, that we have not learned yet. More on this later.

As another comment, our E, T are defined so far up to a scalar, but this is not an issue for stating $E = E(T)$. For a discussion here we refer to our favorite books, Fermi [27] or Schroeder [73]. Now with Fact 3.15 in hand, we can go ahead, as follows:

THEOREM 3.16. *For an ideal gas, $PV = kT$, we have the equation*

$$C_V dT + PdV = dE$$

called first law thermodynamics for ideal gases, in Joule formulation.

PROOF. We know from Joule that the following quantity is constant:

$$C_V = \frac{dE}{dT}$$

By integrating, we obtain a formula as follows, with $\lambda \in \mathbb{R}$ being a constant:

$$E = C_V T + \lambda$$

But with this in hand, the first law becomes the first formula in the statement. \square

Next in line, we have the following key result:

THEOREM 3.17. *For an ideal gas, $PV = kT$, we have the equation*

$$C_P = C_V + k = \left(\frac{dE}{dT} \right)_P$$

relating the molecular heats at constant pressure, and constant volume.

PROOF. By using $PV = kT$ and Theorem 3.16, we obtain:

$$\begin{aligned} PV = kT &\implies PdV + VdP = kdT \\ &\implies (C_V + k)dT - VdP = dE \end{aligned}$$

With $dP = 0$, we are led to the second formula in the statement. \square

3d. Adiabatics

As a third important result now, regarding the ideal gases, we have:

THEOREM 3.18. *The adiabatic transformations of an ideal gas, $PV = kT$, satisfy*

$$TV^{K-1} = \text{constant}$$

where K is a modified version of k , appearing as follows:

$$K = \frac{C_P}{C_V} = 1 + \frac{k}{C_V}$$

Together with $PV = kT$, the above equation produces certain curves, called adiabatics.

PROOF. Since for an adiabatic transformation we have $dE = 0$, the Joule formula in Theorem 3.16 becomes:

$$C_V dT + PdV = 0$$

Now by using $PV = kT$, we successively obtain:

$$\begin{aligned} PV = kT &\implies C_V dT + \frac{kT}{V} dV = 0 \\ &\implies \frac{dT}{T} + \frac{k}{C_V} \cdot \frac{dV}{V} = 0 \\ &\implies \log T + \frac{k}{C_V} \log V = \text{constant} \\ &\implies TV^{k/C_V} = \text{constant} \end{aligned}$$

Thus, we are led to the conclusion in the statement. \square

All the above is very interesting, theoretically speaking, and the only thing that is still missing is a discussion about the ideal gases themselves, not necessarily thermodynamic. To be more precisely, given a certain gas G , that is to say, a chemical substance in gaseous form, we would like to know which number $k > 0$ makes the ideal gas equation $PV = kT$ best approximate the equation of state of G itself, and also to which extent is this approximation reliable, what about correction terms, and so on.

This is obviously more chemistry than physics, and we will talk about this later. In the meantime, just believe me, we are dealing here with usual, real-life gases, up to our silence on $k > 0$, and up to some $\varepsilon \simeq 0$ in the final formulae. More on this later.

3e. Exercises

Exercises.

CHAPTER 4

Engines, refrigerators

4a. Carnot engines

Good news, we already know enough thermodynamics in order to do some engineering. So, let us step into this, discussion of the various heat engines that can be constructed, and of refrigerators too, because as we will soon discover, these are just some sort of reverse heat engines. All this will be very exciting. And finally, in case you're only interested in abstractions, sorry for you, but please don't skip this chapter, because the Carnot engines that we will construct here will be used later on, in Part II, a bit like computers can be used in mathematics or physics, for proving interesting abstract things.

So, making money out of physics. Before anything, in order to avoid wrong paths that can be taken, let us recall the second law of thermodynamics, both in the Clausius and the Lord Kelvin formulation. In the Clausius formulation, this is as follows:

LAW 4.1 (Second law, Clausius' formulation). *Heat flows from warm to cold.*

At the first glance, this might seem like a rather purely scientific, non-profit statement. However, the point is that this law is in fact equivalent to the following statement, due to Lord Kelvin, which is suddenly something very instructive:

LAW 4.2 (Second law, Kelvin's formulation). *It is impossible to extract heat from a source staying at constant temperature T , and convert it into work.*

In other words, this tells us that we cannot make money by cooling the land, and converting that heat into work, then electricity, that we can sell afterwards. It also tells us that, no matter how much fuel we are willing to burn, unless we have some special device, called heat engine, and that remains to be discovered, we cannot extract work, then electricity and money, out of that fuel. In that case, say when having an unlimited source of fuel, we either have to hire some engineers, or sell the fuel.

Before getting forward, let us mention that Law 4.1 and Law 4.2 are equivalent:

FACT 4.3. *The second law in Clausius' formulation, Law 4.1, is equivalent to the second law in Lord Kelvin's formulation, Law 4.2.*

Of course, while quite intuitive, when thinking a bit, this remains something which is not obvious. However, this fact is true, and is even a theorem. We will prove this theorem in a moment, after knowing a bit more about engines, which are needed in the proof.

Finally, as one more piece of abstract discussion, remember from chapter 1 the Maxwell demon, and all the damage that demon can do. In relation with this, let us record:

FACT 4.4. *The second law is something of statistical nature.*

For more on this, we refer to the discussion in chapter 1, namely probability theory, and its practical and philosophical consequences, the idea being that, a bit in analogy with the fact that there is a chance $P > 0$ for you to step in a casino and exit a few hours after with a few millions in cash, there is as well a chance $P > 0$ for the engines that we will construct here to not work. But this should not be a source of worries, at least for engineers, where fighting with small probabilities $P \sim 0$ is part of everyday life.

Getting started now, our workhorses for exploiting the second law will be the Carnot engines, which are somewhat mathematical objects, constructed as follows:

DEFINITION 4.5. *A Carnot engine is a 4-cycle engine, functioning between temperatures $T_1 < T_2$, consisting of:*

- (1) *An isothermal expansion at T_2 , absorbing heat.*
- (2) *An adiabatic expansion, down to temperature T_1 .*
- (3) *An isothermal compression at T_1 , expelling heat.*
- (4) *An adiabatic compression, back to temperature T_2 .*

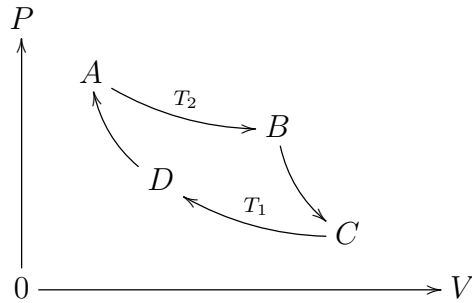
So, what kind of engine is this. In a nutshell, these are the best possible engines, and quite fascinating objects, no one really knowing to which area of science they belong. We will see that, from the perspective of physics, such things rather belong to mathematics. From the perspective of a mathematician, such things look more as engineering. And from the perspective of an engineer, such things look more like theoretical physics.

In short, and by anticipating a bit, we have:

ADVERTISEMENT 4.6. *Carnot engines are creatures from the outer space, having a deep meaning, and bringing a certain order in the universe.*

In order to get familiar with such engines, let us discuss their functioning. We can represent a Carnot engine on a (P, V) diagram, as follows, with the horizontals AB, CD

being the isothermals, and the verticals BC, DA being the adiabatics:



Regarding now the engineering, the Carnot engines can be implemented as 1-cylinder, 4-stroke engines, with the functioning of one full cycle being as follows:

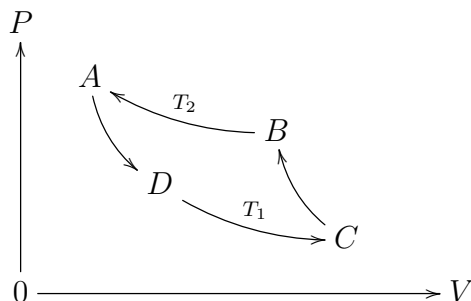
	A	B	C	D	A'
V_C			\perp		
V_B		\perp			
V_D				\perp	
V_A	\perp				\perp
	T_2	T_2	\equiv	T_1	\equiv

To be more precise, pictured here is the height of the piston \perp at every step, with the lower data corresponding to the transformations made, T_1, T_2 standing for the temperatures of the isothermals, and \equiv standing for an insulator, needed for the adiabatics.

Obviously, a Carnot engine is an engine as we know them, converting heat into work. To be more precise, an amount of heat Q_2 is absorbed during the upper isotherm AB , and is transformed into an amount of work W during the lower isotherm CD , with an amount of heat Q_1 expelled as well during this lower isotherm CD . And with the adiabatics being there for adjusting the machine, as to make it work as a cycle, in the $[T_1, T_2]$ regime.

As an interesting theoretical remark about the Carnot engines, that we will need in what follows, for theoretical purposes, but which is of practical use as well, we have:

REMARK 4.7. *When running a Carnot engine in the other sense, namely*



what we have is a refrigerator, absorbing heat Q_1 on the isotherm DC, helped by some input work W , and expelling it as heat Q_2 during the isotherm BA.

We will be back to this later, when systematically discussing refrigerators. At the theoretical level, however, observe in passing that due to $Q_2 > Q_1$, using a refrigerator for cooling the room during the Summer, with the door wide open, is not a good idea.

4b. Engine efficiency

We have seen that a Carnot engine converts heat into work, $Q_2 \rightarrow W$, with a loss Q_1 . Based on this, let us formulate the following definition:

DEFINITION 4.8. *The efficiency of a cyclic engine functioning between temperatures $T_1 < T_2$ is the quantity $\eta \in (0, 1)$ given by*

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

where Q_2 is the heat absorbed at T_2 , from the heat source of the engine, W is the work done, and Q_1 is the loss in the process $Q_2 \rightarrow W$, appearing as heat expelled at T_1 .

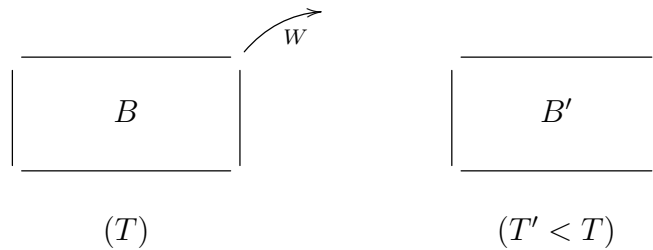
Since we are a bit abstract here, we must comment on the fact that we have indeed $W > 0$ and $Q_2 > Q_1 > 0$. First, we will take $W > 0$ by definition, with the above word “engine” standing for that, that is, “useful engine”. So we are left with $W = Q_2 - Q_1 > 0$, and the problem is whether this really must come from $Q_2 > Q_1 > 0$.

This question might seem a bit futile, but it is not. The second law has certainly something to do with this, because that’s the only principle that we have, preventing heat from flowing from cold to warm, and producing weird things like $Q_1 < 0$, or $Q_2 < 0$. So, let us try now to clarify all this, as our first application of the second law. We have:

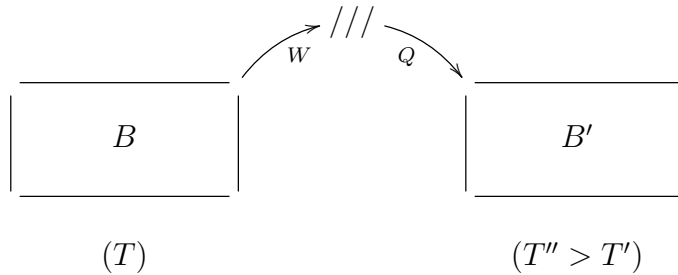
THEOREM 4.9. *The second law in Clausius’ formulation, Law 4.1, is equivalent to the second law in Lord Kelvin’s formulation, Law 4.2.*

PROOF. Following Fermi [27], we will do this as mathematicians do, via double implication, and cherry on the cake, by reasoning via negation too:

“ \implies ” Assume that Kelvin is wrong, so that we can extract heat from a body B at temperature T , and convert it into work W . In order to reach to a contradiction with what Clausius says, consider as well a body B' , lying nearby, at temperature $T' < T$:

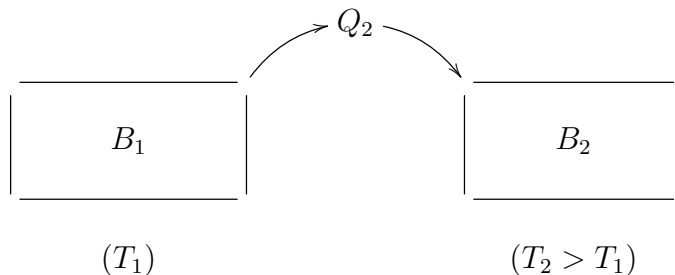


By friction we can convert W into heat, and then heat B' with this heat Q :



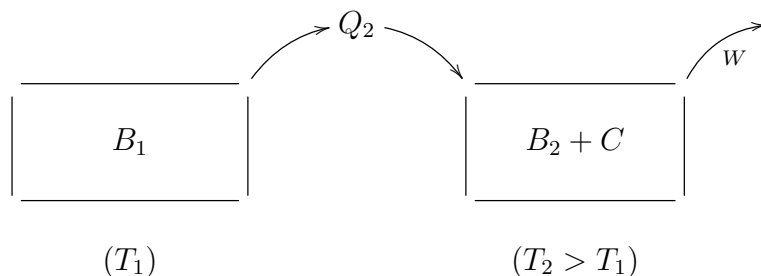
Thus heat has flown from B to B' , so Clausius was wrong too. As a conclusion, our assumption that Kelvin is wrong makes no sense, so Kelvin is right, as desired.

“ \impliedby ” Assume now that Clausius is wrong, so that heat Q_2 can flow from a body B_1 at temperature T_1 to a body B_2 of temperature $T_2 > T_1$:



With the help of a Carnot engine C installed on B_2 and functioning in the $[T_1, T_2]$ regime we can convert this heat Q_2 into work W , and with the expelled heat Q_1 , at

temperature $T_1 < T_2$, not affecting the body B_2 :



Thus B_2 has in fact nothing to do with the whole process, which ultimately consists in extracting heat from B_1 and converting it into work W . So Kelvin was wrong too. \square

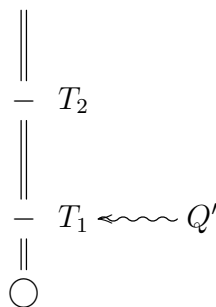
Still following [27], we can now fix the bug in Definition 4.8, as follows:

PROPOSITION 4.10. *In the context of Definition 4.8, assuming that the engine there is a true, useful engine, $W > 0$, we have indeed $Q_2 > Q_1 > 0$.*

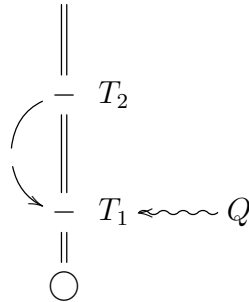
PROOF. Since we know that we have $W = Q_2 - Q_1 > 0$, in order to prove the result, we just need to show that we have the following inequality:

$$Q_1 > 0$$

So, assume by contradiction that we have $Q_1 < 0$, say $Q_1 = -Q$ with $Q > 0$. In the context of Definition 4.8, this means that our heat engine functioning in the $[T_1, T_2]$ regime manages to absorb positive heat, $Q' < Q$, at the low temperature T_1 :



But then we can install an extra device, letting heat flow from status T_2 to status T_1 , during each cycle, as for our machine at status T_1 to absorb exactly $Q > 0$ heat:



And what we have here, in the end, is a machine leaving things at T_1 status unchanged, and making work $W > 0$ out of the source at constant temperature T_2 , contradicting Kelvin. Thus, our assumption $Q_1 < 0$ is wrong, and we are done. \square

Summarizing, everything fine with Definition 4.8, we know now what the efficiency of an engine is. So, let us compare now these engines. We have here:

THEOREM 4.11. *Among the engines functioning in a given $[T_1, T_2]$ regime, the maximum efficiency*

$$\eta = 1 - \frac{Q_1}{Q_2}$$

is achieved by the reversible engines, including the Carnot ones, and with all these reversible engines having the same efficiency.

PROOF. This is something quite tricky, requiring the use of some clever mathematics. Following as before Fermi [27], the proof goes as follows:

(1) Our first claim is that is enough to prove the following inequality, for any two engines M, M' , with the first engine M being assumed to be reversible:

$$\frac{Q_1}{Q_2} \leq \frac{Q'_1}{Q'_2}$$

Indeed, this certainly proves the first assertion, regarding the maximum efficiency of M . It also proves the last assertion, because assuming that M' was reversible too, we can interchange $M \leftrightarrow M'$, and by double inequality we obtain equality of the above quotients, and so of efficiencies. Finally, the fact that the Carnot engines are reversible is something that we know well, their inverses being refrigerators, as explained in Remark 4.7.

(2) Some math first. We want to prove that we have the following inequality:

$$\frac{Q_1}{Q'_1} \leq \frac{Q_2}{Q'_2}$$

So, assume that this is wrong, and pick a rational number in between:

$$\frac{Q_1}{Q'_1} > \frac{N'}{N} > \frac{Q_2}{Q'_2}$$

We must come up with a contradiction, out of these inequalities.

(3) In order to do so, we use a trick. Consider the engine \mathcal{M} consisting of N' cycles of M' , and N reverse cycles of M . The data for this new, complex engine \mathcal{M} is:

$$Q_1 = N'Q'_1 - NQ_1$$

$$Q_2 = N'Q'_2 - NQ_2$$

$$W = N'W' - NW$$

We have then $W = Q_2 - Q_1$. On the other hand, the inequalities in (2) read:

$$Q_1 < 0 \quad , \quad Q_2 > 0$$

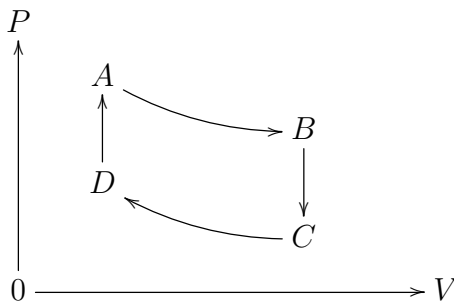
Thus, the total work is positive, $W > 0$, so we have here a true engine, in the sense of Proposition 4.10. But the point now is that, as explained in Proposition 4.10, this should imply $Q_2 > Q_1 > 0$. Thus, we have our contradiction, and we are done. \square

So long for Carnot engines and other theoretical heat engines, and their efficiency. We will see in Part II that by using the same kind of techniques as in the proof of Theorem 4.11, namely Carnot engines and refrigerators, skilfully combined, we will be able to say something general about temperature T itself, namely the surprising fact that T is bounded from below. Thus, with a suitable rescaling, $T > 0$.

4c. Otto, Diesel, Rankine

As explained above, the Carnot engine is the most efficient engine of them all. However, this does not mean that this type of engine is the best, for practical uses, and in the case of the Carnot engine, we can see that this is indeed the case, the engine being hard to implement, and very slow. For powering a car we have much better, as follows:

DEFINITION 4.12. *The Otto engine is the 4-stroke engine working as*

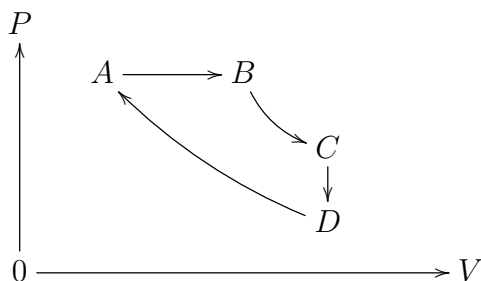


with isochores on the vertical, and adiabatics on the horizontal.

To be more precise, during a cycle $C \rightarrow D \rightarrow A \rightarrow B$ the gas gets compressed on CD , ignites on DA , moves the piston on AB , and gets exhausted on BC . This cycle was invented by Otto, shortly after Carnot, and is still used nowadays, for powering cars.

Yet another popular engine, invented by Diesel shortly after Otto, is the Diesel one. This makes a bit of a compromise between Carnot and Otto, being certainly less funny to drive than Otto, but a bit more efficient. The functioning is as follows:

DEFINITION 4.13. *The Diesel engine is the 4-stroke engine working as*



consisting of an isobaric, an isochore, and two adiabatics.

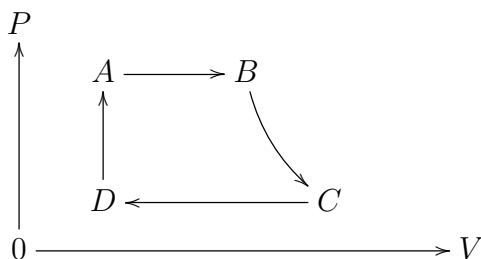
Here during a cycle $D \rightarrow A \rightarrow B \rightarrow C$ the gas gets compressed on DA , heated on AB , ignites and moves the piston on BC , and gets cooled on CD . This cycle is very useful for powering heavy machinery like 20-ton trucks, or big ships of any size.

There are of course many other heat engines, starting of course with the venerable steam engine, that we will talk about in a moment. However, in what regards real-life, modern engines, the two main schemes are those above, due to Otto and Diesel.

Of course, regarding these Otto and Diesel engines, there are many further things that can be said, regarding the precise configuration and geometry of the engine. All this is of course very interesting, and there is even a bit of mathematics here, for us.

Finally, let us discuss the steam engine. This is a different type of beast, because steam is obviously not an ideal gas. The functioning is as follows:

DEFINITION 4.14. *The steam, or Rankine engine is the 4-stroke engine working as*



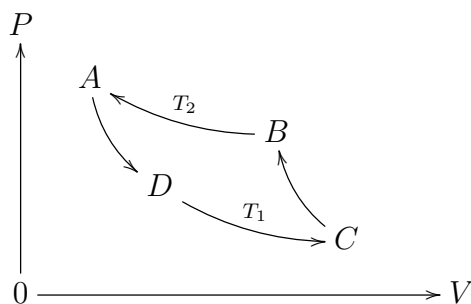
with a boiler on AB , a turbine on BC , a condenser on CD , and a pump on DA .

Here the pump on DA takes its power from the excess power produced by the turbine on BC. Such engines are a bit outdated, but in comparison with the Otto and Diesel engines, they still have some advantages, when it comes to looking at torque.

4d. Refrigerators, heaters

Going ahead with more thermodynamics engineering, let us discuss now refrigerators and heaters. Let us start with something that we already know, namely:

DEFINITION 4.15. *The Carnot refrigerator is the inverse engine working as*

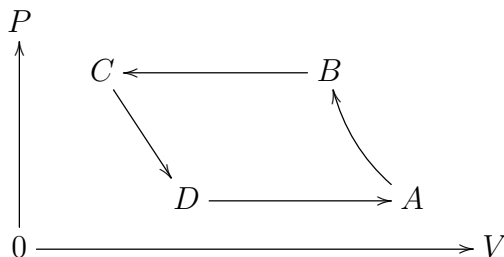


with AD and CB being adiabatics, and DC and BA being isothermals.

Observe that we have indeed a refrigerator, absorbing heat Q_1 on the isothermal DC , helped by some input work W , and expelling it as heat Q_2 during the isothermal BA .

In practice now, although the Carnot refrigerators can be theoretically implemented, they suffer from the same problems as the Carnot engines, and the real life refrigerators are built by using a sort of inverse Rankine cycle, as follows:

DEFINITION 4.16. *The usual refrigerator, or inverse Rankine engine, works as*



with a compressor on AB , condenser on BC , expander on CD , and evaporator on DA .

Here, as in the case of the Rankine cycle, things are quite complex to evaluate, due to the fact that this device functions with both the liquid and gas phases of the same material, typically $\text{F}_3\text{C}_2\text{FH}_2$ in modern refrigerators. Also, the expansion, or throttling process on CD , also called Joule-Thomson process, is something quite complex.

Finally, now that we talked about refrigerators, let us talk as well about heaters. Normally burning some wood will do, and with this being known since the Stone Age. Modern heaters however use electricity, and we will discuss now this.

In order to understand how electricity can produce heat, we will need some electricity preliminaries. The first question is that of understanding the current density J flowing through a given material. The answer here is given by Ohm's law, which is as follows:

FACT 4.17 (Ohm's law). *The current density J is given by*

$$J = \sigma E$$

where σ is a constant, called conductivity of the material.

We are already a bit familiar with this, with our notion of ideal conductor corresponding to $\sigma = \infty$, and our notion of ideal insulator corresponding to $\sigma = 0$. In real life, however, we have of course $\sigma \in (0, \infty)$. Here are 3 + 3 + 3 basic examples, at 20° C and 1 atm, consisting of 3 conductors, 3 semiconductors and 3 insulators, and with σ being replaced by its inverse $\rho = 1/\sigma$, called resistivity, more employed in engineering:

Silver	:	1.59×10^{-8}
Iron	:	9.61×10^{-8}
Graphite	:	1.6×10^{-5}
—		
Seawater	:	0.2
Diamond	:	2.7
Silicon	:	2500
—		
Water	:	8300
Glass	:	$10^9 - 10^{14}$
Teflon	:	$10^{22} - 10^{24}$

Getting back now to Ohm's law, a more familiar version of it is as follows, expressing the total current flowing from one electrode to the other in terms of the potential difference between them, or rather vice versa, and with $R \sim \rho$ being the resistance, which depends, besides on ρ , on the precise configuration of the resistor to be crossed:

$$V = IR$$

With this second formulation of the Ohm law in hand, we can now formulate as well, following Joule, a formula in regards with energy, as follows:

FACT 4.18 (Joule heating law). *The work done by the electric force is*

$$P = VI = I^2R$$

with this being understood as corresponding to heating the resistor.

Summarizing, we know that letting electricity fight with a resistor will produce heat, and we have as well explicit formulae for computing everything that happens. As an interesting statement here, which can only be a source of theoretical joy, we have:

FACT 4.19. *Electric heaters, or any kind of heaters, work at efficiency 100%.*

And isn't this good to know, when going to the supermarket for buying a new heater, and being puzzled by all sorts of claims made by manufacturers. This being said, of course pay some money, so many things that can break, if the heater is really very cheap.

4e. Exercises

Exercises.

Part II

Thermodynamics

*I'll never be Maria Magdalena
You're a creature of the night
Maria Magdalena
You're a victim of the fight*

CHAPTER 5

Absolute temperature

5a. Absolute temperature

Welcome to advanced thermodynamics. As our first result, we will have something truly amazing, one of the most beautiful findings in mathematics, physics and engineering combined. You have probably witnessed some episodes of cold, say -5°C or -10°C , why not -20°C , or even -30°C , depending on where you live, where you have travelled to, and so on. Things can be sometimes freezing cold, but, in all honesty, in such a situation, have you ever said to yourself “things cannot be colder than that”?

I bet not. I’m sure your thought was something of type “hope tomorrow will be not -10° colder than today”. We are just so used, intuitively, for temperature to be like so many other quantities, like space and time, unbounded from above and from below.

So here comes our point. Not only temperature is bounded from below, $T > 0$, after a rescaling, which is something itself quite crazy, as a fact. But you can prove this just armed with your brain, with no need for any weird experiments and scientific machinery. And in addition, the proof is something truly amazing, mixing all the bizarre mathematics, physics and engineering that we have been doing so far, in this book.

But perhaps enough advertisement. Here is the claim:

CLAIM 5.1. *The temperature as measured before, with an arbitrarily calibrated thermometer, can be linearly rescaled into an absolute temperature, which is positive,*

$$T > 0$$

and is given by the following equation, valid for any $T_1 < T_2$,

$$\frac{T_1}{T_2} = 1 - \eta$$

where η is the efficiency of a reversible engine operating in the regime $[T_1, T_2]$.

In order to prove this claim, we will use engine techniques from chapter 4. Let us first review the material there, with abstract applications in mind. First, we have:

DEFINITION 5.2. *The efficiency of an arbitrary cyclic engine functioning between temperatures $T_1 < T_2$ is the quantity $\eta \in (0, 1)$ given by*

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

where Q_2 is the heat absorbed at T_2 , from the heat source of the engine, W is the work done, and Q_1 is the loss in the process $Q_2 \rightarrow W$, appearing as heat expelled at T_1 .

We have seen in chapter 4 that, while all sorts of useful heat engines, with variable efficiencies, can be designed, for practical use in the real life, the efficiency is the same, and is maximal, for the reversible engines running at $[T_1, T_2]$, and with these reversible engines including the Carnot ones, the precise result being as follows:

PROPOSITION 5.3. *Among the engines functioning in a given $[T_1, T_2]$ regime, the maximum efficiency*

$$\eta = 1 - \frac{Q_1}{Q_2}$$

is achieved by the reversible engines, including the Carnot ones, and with all these reversible engines having the same efficiency.

PROOF. This is something that we know from chapter 4, but since we will be heavily using all this, we will review the proof, with more details. This goes as follows:

(1) Our first claim is that is enough to prove the following inequality, for any two engines M, M' , with the first engine M being assumed to be reversible:

$$\frac{Q_1}{Q_2} \leq \frac{Q'_1}{Q'_2}$$

Indeed, this certainly proves the first assertion, regarding the maximum efficiency of M . It also proves the last assertion, because assuming that M' was reversible too, we can interchange $M \leftrightarrow M'$, and by double inequality we obtain equality of the above quotients, and so of efficiencies. Finally, the fact that the Carnot engines are reversible is something that we know well, their inverses being refrigerators, as explained in chapter 4.

(2) Some math first. We want to prove that we have the following inequality:

$$\frac{Q_1}{Q'_1} \leq \frac{Q_2}{Q'_2}$$

So, assume that this is wrong, and pick a rational number in between:

$$\frac{Q_1}{Q'_1} > \frac{N'}{N} > \frac{Q_2}{Q'_2}$$

We must come up with a contradiction, out of these inequalities.

(3) In order to do so, we use a trick. Consider the engine \mathcal{M} consisting of N' cycles of M' , and N reverse cycles of M . The data for this new, complex engine \mathcal{M} is:

$$\mathcal{Q}_1 = N'Q'_1 - NQ_1$$

$$\mathcal{Q}_2 = N'Q'_2 - NQ_2$$

$$\mathcal{W} = N'W' - NW$$

We have then $\mathcal{W} = \mathcal{Q}_2 - \mathcal{Q}_1$. On the other hand, the inequalities in (2) read:

$$\mathcal{Q}_1 < 0 \quad , \quad \mathcal{Q}_2 > 0$$

Thus, the total work is positive, $\mathcal{W} > 0$, so we have here a true, usual engine. But the point now is that, as explained in chapter 4, this would imply via the second law that we have $\mathcal{Q}_2 > \mathcal{Q}_1 > 0$. Thus, we have our contradiction, and we are done. \square

As a consequence of Proposition 5.3, we can now fine-tune our definition of efficiency, for the reversible engines, that we will use exclusively in this chapter, as follows:

DEFINITION 5.4. *The efficiency of a reversible engine operating in the regime $[T_1, T_2]$ is the number $\eta = \eta(T_1, T_2)$ defined as follows,*

$$\eta(T_1, T_2) = 1 - \frac{Q_1}{Q_2}$$

known to depend only on the temperatures T_1, T_2 .

To be more precise here, the formula for η is the previous one, from Definition 5.2, and the fact that this number η depends only on T_1, T_2 comes from Proposition 5.3.

We have now all the ingredients for stating our main result, as follows:

THEOREM 5.5. *The temperature as measured before, with an arbitrarily calibrated thermometer, can be linearly rescaled into an absolute temperature, which is positive,*

$$T > 0$$

and is given by the following equation, valid for any $T_1 < T_2$,

$$\frac{T_1}{T_2} = 1 - \eta$$

where η is the efficiency of a reversible engine operating in the regime $[T_1, T_2]$.

PROOF. This follows from the theory developed above, the idea being as follows:

(1) Consider the following function, defined for any temperatures $T_1 < T_2$:

$$f(T_1, T_2) = \frac{1}{1 - \eta(T_1, T_2)} = \frac{Q_2}{Q_1}$$

Our claim, which will basically lead to the result, via some elementary mathematics, is that we have the following formula, valid for any temperatures $T_0 < T_1 < T_2$:

$$f(T_0, T_2) = f(T_0, T_1)f(T_1, T_2)$$

(2) In order to prove this claim, consider a reversible engine E_1 running in the regime $[T_0, T_1]$, and a reversible engine E_2 running in the regime $[T_0, T_2]$. We denote by Q_0, Q_1 the amount of heat expelled/absorbed by E_1 at T_0/T_1 , and, after suitably normalizing E_2 , we denote by Q_0, Q_2 the amount of heat expelled/absorbed by E_2 at T_0/T_2 . According to our definition of efficiency, we have the following formulae:

$$f(T_0, T_1) = \frac{Q_1}{Q_0} \quad , \quad f(T_0, T_2) = \frac{Q_2}{Q_0}$$

(3) Consider now an engine E , obtained by running a cycle of A_1 , and then a reverse cycle of A_2 . Let us analyze how E works at the temperatures T_0, T_1, T_2 :

- At T_0 , no heat is exchanged, Q_0 being absorbed by the reverse A_2 .
- At T_1 , what happens is that an amount of Q_1 is expelled by E_1 .
- At T_2 , what happens is that an amount of Q_2 is absorbed by E_2 .

(4) We conclude from this that E is a reversible engine running in the regime $[T_1, T_2]$, and so, by our definition of efficiency, we have the following formula:

$$f(T_1, T_2) = \frac{Q_2}{Q_1}$$

Now by comparing with the two formulae obtained at (2), we get, as claimed:

$$f(T_0, T_2) = f(T_0, T_1)f(T_1, T_2)$$

(5) But this tells us that we can find a certain function $\theta = \theta(T)$ such that:

$$f(T_1, T_2) = \frac{\theta(T_2)}{\theta(T_1)}$$

Moreover, this function $\theta = \theta(T)$ must be strictly positive, and increasing.

(6) Getting back now to efficiencies, we have the following formula:

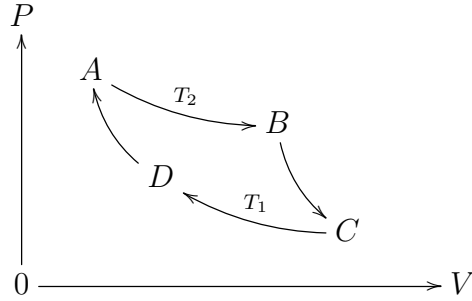
$$\eta(T_1, T_2) = 1 - \frac{1}{f(T_1, T_2)} = 1 - \frac{\theta(T_1)}{\theta(T_2)}$$

The point now is that, for computing θ , we can use this formula, and any reversible engine, of our choice. And by choosing here the Carnot engine operating on $[T_1, T_2]$, and doing the computation, based on the adiabatics for the ideal gases, we obtain:

$$\eta(T_1, T_2) = 1 - \frac{T_1}{T_2}$$

Thus the absolute temperature $\theta = \theta(T) \in (0, \infty)$ constructed in (5) is given by $\theta(T) = \lambda T$, for some $\lambda \in \mathbb{R}$, and we are led to the conclusion in the statement.

(7) To be more precise here, let us first recall from chapter 4 the general functioning scheme of the Carnot engines. This is as follows, with the horizontals AB, CD being the isothermals, and the verticals BC, DA being the adiabatics:



(8) Assuming now that our Carnot engine runs with an ideal gas, and by using the fact, that we know from chapter 3, that the energy of such an ideal gas depends only on the temperature, we have, by looking what happens on the above AB isothermal:

$$Q_2 = L_{AB} = RT_2 \log \frac{V_B}{V_A}$$

Similarly, by looking what happens on the CD isothermal, we have:

$$Q_1 = L_{CD} = RT_1 \log \frac{V_C}{V_D}$$

(9) As a second ingredient now, also as a consequence of the results from chapter 3, since the points A, D lie on an adiabatic, we have the following formula:

$$T_1 V_D^{k-1} = T_2 V_A^{k-1}$$

Similarly, since the points B, C lie on an adiabatic, we have:

$$T_1 V_C^{k-1} = T_2 V_B^{k-1}$$

Now by taking the quotients of these two formulae, we obtain:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

(10) But with this in hand, we can go back to the two formulae obtained in (8). Since the logarithms on the right are the same, by dividing these formulae, we obtain:

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Thus, we are led to the conclusions in the statement. \square

So, that was it, and truly amazing, isn't it. Obviously, having $T > 0$ is something of similar impact to Einstein's $v < c$. And, not only this discovery came before Einstein's, but its proof, explained above, was via a sort of enormous Gedankenexperiment, far more technically involved than the trains and clocks needed for special relativity.

Hommage to the thermodynamics greats, Boyle, Gay-Lussac, Celsius, Joule, Carnot, Otto, Diesel, Clapeyron, Clausius, Lord Kelvin and the others, for this remarkable discovery. More homage to follow later, to Maxwell, Boltzmann and others, for further discoveries. And even more homage later, to Max Planck and then Bose, Fermi and others, for even further discoveries, such as the difference between bosons and fermions. And finally, with a special thought for Fermi, and his wonderful book [27], where all the basic thermodynamics, and much more, is explained, much better than here.

5b. Kelvin degrees

In practice now, with Theorem 5.5 in hand, we can do several useful things. First, we can eventually calibrate our thermometer, now after 100 pages of thermodynamics, a practical definition here, based on the same philosophy as Celsius, being as follows:

DEFINITION 5.6. *We can calibrate our thermometer, as follows:*

- (1) *Celsius: $T = 0$ is where water freezes, and $T = 100$ is where water boils.*
- (2) *Kelvin: $T = 0$ is the absolute minimum, and the degrees are as in Celsius.*

In practice, this means $0^\circ \text{K} = -273.15^\circ \text{C}$. We will use in what follows the Kelvin scale for abstract physics, and Celsius for various engineering matters. We will be also back to all this later on, with various refinements and finer numerics.

Getting back now to the Kelvin degrees, as constructed in Definition 5.6, these are for the moment quite abstract things, and some numerics would certainly help. To start

with, here is a table with the melting points of various common materials:

material	melting point
—	—
water	273
mercury	234
radon	202
fluorine	200
chlorine	171
xenon	161
krypton	116
argon	83
oxygen	54
nitrogen	63
neon	25
hydrogen	14
helium	1

Many interesting things happen around 0 – 1K, and we will be back to this exciting topic, on regular occasions, in this book. Let us also mention that engineers nowadays are quite advanced in producing extreme cold, the world record, established in 2021 through matter-wave lensing of rubidium Bose-Einstein condensates, being 38 picokelvin:

$$T = 0.000\ 000\ 000\ 038\ K$$

Finally, as an important remark, all this extreme cold physics is not as fringe as it seems. Indeed, while the universe is mostly known for all sorts of bright and very hot stars, its average temperature is 2.73 K. So, extreme cold is in fact the norm.

5c. Low temperatures

There are many interesting things happening at low temperatures, including:

- (1) Liquid helium.
- (2) Bose-Einstein condensates.
- (3) Superconductivity.
- (4) And many more.

5d. Interstellar space

Interstellar space, whose temperature is close to 0° K too. Many interesting things happen here, often in conjunction with gravity, and with electromagnetism too, and with, thermodynamically, the Maxwell demon roaming around.

5e. Exercises

Exercises.

CHAPTER 6

Entropy

6a. Entropy

As a continuation of what we did in the last chapter, we can now talk about an important and frightening thermodynamic quantity, having both practical and philosophical consequences, called entropy. This quantity, that we will denote here by a Gothic \mathfrak{E} , as a matter of never forgetting what all this is about, is constructed as follows:

THEOREM 6.1. *Given a gas, with states denoted $S = (P, V, T) \in \mathbb{R}^3$, subject to the equation of state $f(S) = 0$, define the entropy of a state by the formula*

$$\mathfrak{E}(S) = \int_{S_0}^S \frac{dQ}{T}$$

where S_0 is a chosen state, and the integral is over a reversible transformation from S_0 to S . Then \mathfrak{E} is well-defined up to an additive scalar, and we have the inequality

$$\mathfrak{E}(S_1) \leq \mathfrak{E}(S_2)$$

for any transformation $S_1 \rightarrow S_2$, with equality when this transformation is reversible.

PROOF. This comes as a continuation of the material from chapter 5, and we will use the same methods as there, namely calculus, and Carnot machines:

(1) Our first claim is that for any cycle $\circ : S \rightarrow S$ we have:

$$\int_{\circ} \frac{dQ}{T} \leq 0$$

In order to prove this, we approximate the cycle \circ by a sequence of isothermals $\gamma_1, \dots, \gamma_k$, at temperatures T_1, \dots, T_k . Now let us fix $T_0 > T_i$, and for each i consider a Carnot machine C_i , refrigerator or engine, which functions in the range $[T_i, T_0]$, by absorbing at T_i the positive or negative heat dQ_i emitted by our gas during γ_i .

(2) Let us see how our machinery, consisting of our gas and of the Carnot machines C_1, \dots, C_k , works, over the full cycle \circ . At each T_i nothing happens, because what is absorbed or expelled by the gas is expelled or absorbed by C_i , due to our conventions above. So, if there is something that our machinery does, that happens at T_0 .

(3) But at T_0 the gas does nothing, and the system of our Carnot machines C_1, \dots, C_k extracts or absorbs work, of total quantity, positive or negative, given by:

$$W = T_0 \int_{\circ} \frac{dQ}{T}$$

But we know from the second law of thermodynamics, in Lord Kelvin's formulation, that you cannot extract work from a given temperature T_0 . Thus, our system of Carnot machines C_1, \dots, C_k works overall as a refrigerator, $W \leq 0$, as desired.

(4) Thus our claim in (1) is proved, and all the rest is trivial, just by gluing paths. Indeed, by using (1), we first conclude that $\mathfrak{E}(S)$ is not dependent on the choice of a reversible path $S_0 \rightarrow S$. Moreover, also by using (1), we conclude afterwards that $\mathfrak{E}(S)$ is well-defined up to an additive scalar, independently of the choice of S_0 . And finally, again by using (1), we conclude that the equality in the statement $\mathfrak{E}(S_1) \leq \mathfrak{E}(S_2)$ holds indeed, with equality when the transformation $S_1 \rightarrow S_2$ is reversible. \square

6b. Consequences

As a first consequence of Theorem 6.1, that you have surely already met, by reading popular physics books, but which now comes with mathematical proof, we have:

CONSEQUENCE 6.2. *Entropy increases, and there is nothing much that you can do about it.*

To be more precise, this comes from the inequality $\mathfrak{E}(S_1) \leq \mathfrak{E}(S_2)$ in Theorem 6.1, which is not at all something speculative and philosophical, but rather something rock-solid, definitely true, and of course annoying, regarding our universe. To put it squarely, our universe is slowly dying, over the long term, because of entropy increasing, and so basically because the heat flowing from warm to cold never comes back.

And isn't this frightening. Personally I first learned about this when I was 12-13, having at that time the bad idea of reading a popular physics book too, in parallel to my usual kids readings at that time. On the day I read about entropy, I had a serious nightmare the night after. In order to calm me down, my parents, both scientists, tricked me with something of type "later you'll learn math and physics, and understand that things are more complicated than this". But as you can see, learning math and physics does not help much, quite the opposite, the more you know, the more entropy is there.

Now with the age, I care less about such things, busy with science and other. But since cat is passing by, let us ask him too about this, right. Hope he will reply with a gentle piece of advice, instead of one of these raw cat facts. And cat says:

FACT 6.3. *Good scientists will watch the fate of the universe from Heaven. Bad scientists will watch it from Hell.*

Which sounds good to me, for one time we are on the same wavelength. So, with the scare passed, we can now move ahead, and do some more mathematics and physics, in relation with the entropy. Perhaps even try to beat it, by trying to imagine better worlds, where thermodynamics as we know it is not the Queen. But more on this later.

6c. Some mathematics

Let us do now some more mathematics for the entropy, for a gas, or whatever other system, represented on a (P, V) diagram. We know from chapter 3 that the amount of heat dQ received by the system during an infinitesimal transformation is given by:

$$dQ = \left(\frac{dU}{dT}\right)_V dT + \left[\left(\frac{dU}{dV}\right)_T + P\right] dV$$

Now since $dS = dQ/T$, we obtain from this, by dividing by T :

$$dS = \frac{1}{T} \left(\frac{dU}{dT}\right)_V dT + \frac{1}{T} \left[\left(\frac{dU}{dV}\right)_T + P\right] dV$$

As an example for this, let us consider an ideal gas. Here we have:

$$\begin{aligned} dQ &= C_V dT + P dV \\ &= C_V dT + \frac{RT}{V} dV \end{aligned}$$

By using this, we obtain as well the following formula:

$$\begin{aligned} dS &= \frac{d}{T} \left(C_V dT + \frac{RT}{V} dV \right) \\ &= \frac{C_V}{T} dT + \frac{R}{V} dV \end{aligned}$$

Now by integrating, we obtain from this a formula as follows, with $a \in \mathbb{R}$ being a constant, whose indeterminacy comes from our definition of the entropy:

$$S = C_V \log T + R \log V + a$$

Moreover, by using the formula $C_P = C_V + R$, that we know from chapter 3, and the equation of state $PV = RT$, this further reads:

$$\begin{aligned} S &= (C_P - R) \log T + R \log \frac{RT}{P} + a \\ &= (C_P - R) \log T + R(\log R + \log T - \log P) + a \\ &= C_P \log T + R \log R - R \log P + a \end{aligned}$$

Now back to the general case, our claim is that we have:

THEOREM 6.4. *We have the following formula,*

$$\left(\frac{dU}{dV}\right)_T = T \left(\frac{dP}{dT}\right)_V - P$$

for any system represented on a (P, V) diagram.

PROOF. We recall from the above that we have:

$$dS = \frac{1}{T} \left(\frac{dU}{dT}\right)_V dT + \frac{1}{T} \left[\left(\frac{dU}{dV}\right)_T + P\right] dV$$

But this expression is a perfect differential with respect to T, V , in a multivariable calculus sense, and by taking derivatives, we obtain from this:

$$\frac{d}{dV} \left(\frac{1}{T} \cdot \frac{dU}{dT}\right) = \frac{d}{dT} \left[\frac{1}{T} \left(\frac{dU}{dV}\right) + P\right]$$

Thus, we are led to the formula in the statement. \square

As an illustration for this result, let us go back to the ideal gases, satisfying $PV = RT$. For such a gas, the formula in Theorem 6.4 becomes:

$$\left(\frac{dU}{dV}\right)_T = T \frac{d}{dT} \left(\frac{RT}{V}\right) - \frac{RT}{V} = 0$$

Thus, as a consequence, the energy U of the gas does not depend on V .

6d. Clapeyron equation

In the case of a saturated vapor, with this meaning equilibrium between liquid and gaseous state, Theorem 6.4 becomes the Clapeyron equation, which is as follows, with λ being a constant, depending on the substance, called latent heat of vaporization:

$$\frac{dP}{dT} = \frac{\lambda}{T(v_2 - v_1)}$$

We will be back to critical state physics in chapter 8 below, when talking about Van der Waals gases, then to entropy in chapter 10, when doing statistical mechanics, with a number of important findings, due to Boltzmann and others, and then again to states of matter in chapter 12, and all over Part IV of the present book.

6e. Exercises

Exercises.

CHAPTER 7

Heat diffusion

7a. Heat diffusion

We have seen so far, over 150 pages, the basics of thermodynamics. As already said, on numerous occasions, it is possible to improve all this, following ideas of Boltzmann, and more specifically his “kinetic theory” of gases, which provides a conceptual and mathematical approach to the whole theory of gases. However, no hurry with this, and in this remainder of Part II of the present book, we will do some more thermodynamics.

As a first question, that we would like to investigate in this chapter, we have:

QUESTION 7.1. *How does heat propagate, in the context of two of several materials put in contact, or even in the case of a single material, not uniformly heated?*

As a first observation, this is a quite wide-ranging and tricky question, and even in the case of gases, assuming the Boltzmann theory developed, talking about such things will full mathematical rigor will be no easy task. In short, we are here deep into physics, or very physical type, and of material science flavor, so modesty, and time to discuss all this, with a mixture of general laws, experimental findings, and some math too.

Regarding several materials put in contact, we already has a flavor of that at the end of the previous chapter, when talking about the Clapeyron equation, with the “materials” in that case being the liquid and gaseous form of the same material.

However, all this is rather something quite advanced. The simplest diffusion problems appear in fact when putting several gases, at different temperatures, in contact, and with these several gases being allowed to be actually samples of the same gas, but at different temperatures. And there are countless things that can be said here, both at the level of basic thermodynamics, and at the level of more advanced theory.

7b. Heat equation

As a second question that we would like to investigate in this chapter, we have the problem of understanding how heat will get diffused over time $t > 0$ inside a piece of a material, which is unevenly heated, initially. This is something quite tricky, and suggests modelling first a “heat wave”. So, let us start with the waves. We have here:

THEOREM 7.2. *The wave equation is*

$$\ddot{\varphi} = v^2 \Delta \varphi$$

where $v > 0$ is the propagation speed, and

$$\Delta = \sum_i \frac{d}{dx_i^2}$$

is the Laplace operator.

PROOF. There are several proofs here, a nice one, by discretizing, being as follows:

(1) Let us first consider the 1D case. In order to understand the propagation of waves, we will model \mathbb{R} as a network of balls, with springs between them, as follows:

$$\cdots \times \times \times \bullet \times \times \times \bullet \times \times \times \bullet \times \times \times \bullet \times \times \times \bullet \times \times \times \bullet \times \times \times \cdots$$

Now let us send an impulse, and see how balls will be moving. For this purpose, we zoom on one ball. The situation here is as follows, l being the spring length:

$$\cdots \cdots \cdots \bullet_{\varphi(x-l)} \times \times \times \bullet_{\varphi(x)} \times \times \times \bullet_{\varphi(x+l)} \cdots \cdots \cdots$$

We have two forces acting at x . First is the Newton motion force, mass times acceleration, which is as follows, with m being the mass of each ball:

$$F_n = m \cdot \ddot{\varphi}(x)$$

And second is the Hooke force, displacement of the spring, times spring constant. Since we have two springs at x , this is as follows, k being the spring constant:

$$\begin{aligned} F_h &= F_h^r - F_h^l \\ &= k(\varphi(x+l) - \varphi(x)) - k(\varphi(x) - \varphi(x-l)) \\ &= k(\varphi(x+l) - 2\varphi(x) + \varphi(x-l)) \end{aligned}$$

We conclude that the equation of motion, in our model, is as follows:

$$m \cdot \ddot{\varphi}(x) = k(\varphi(x+l) - 2\varphi(x) + \varphi(x-l))$$

(2) Now let us take the limit of our model, as to reach to continuum. For this purpose we will assume that our system consists of $N \gg 0$ balls, having a total mass M , and spanning a total distance L . Thus, our previous infinitesimal parameters are as follows, with K being the spring constant of the total system, which is of course lower than k :

$$m = \frac{M}{N} \quad , \quad k = KN \quad , \quad l = \frac{L}{N}$$

With these changes, our equation of motion found in (1) reads:

$$\ddot{\varphi}(x) = \frac{KN^2}{M}(\varphi(x+l) - 2\varphi(x) + \varphi(x-l))$$

Now observe that this equation can be written, more conveniently, as follows:

$$\ddot{\varphi}(x) = \frac{KL^2}{M} \cdot \frac{\varphi(x+l) - 2\varphi(x) + \varphi(x-l)}{l^2}$$

With $N \rightarrow \infty$, and therefore $l \rightarrow 0$, we obtain in this way:

$$\ddot{\varphi}(x) = \frac{KL^2}{M} \cdot \frac{d^2\varphi}{dx^2}(x)$$

(3) In arbitrary N dimensions now, the same argument carries on, and we are led to the following equation, with $v = \sqrt{K/M} \cdot L$ being the propagation speed:

$$\ddot{\varphi}(x) = v^2 \sum_i \frac{d^2\varphi}{dx_i^2}(x)$$

But we recognize at right the Laplace operator, and we are done. There is of course some more discussion to be made here, arguing that our spring model in (1) is indeed the correct one, for modelling such wave propagation questions. But hey, we're doing theoretical physics here. And don't worry, experiments confirm our findings. \square

Getting now to heat diffusion, as a kind of miracle, we have here a simple and beautiful equation, which looks quite similar to the wave equation, as follows:

FACT 7.3. *Heat diffusion is described by the heat equation*

$$\dot{\varphi} = \alpha \Delta \varphi$$

where $\alpha > 0$ is a constant, called thermal diffusivity of the medium, and

$$\Delta = \sum_i \frac{d}{dx_i^2}$$

is the Laplace operator.

Observe the amazing similarity with the wave equation $\ddot{\varphi} = v^2 \Delta \varphi$. This similarity is quite interesting, because remember that the wave equation can be fully justified just by doing some mechanics. In what regards the heat equation, however, things are more complicated, and the modelling question is more subtle than for the waves.

7c. Heavy calculus

In order to study the heat equation, we will need some multivariable calculus. Let us start with a straightforward definition, as follows:

DEFINITION 7.4. *We say that a map $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$ is differentiable at $x \in \mathbb{R}^N$ if*

$$f(x+t) \simeq f(x) + f'(x)t$$

for some linear map $f'(x) : \mathbb{R}^N \rightarrow \mathbb{R}^M$, called derivative of f at the point $x \in \mathbb{R}^N$.

But is this the correct definition. I can hear you screaming that we are probably going the wrong way, because for functions $f : \mathbb{R} \rightarrow \mathbb{R}$ the derivative is something much simpler, as follows, and that we should try to imitate, in our higher dimensional setting:

$$f'(x) = \lim_{t \rightarrow 0} \frac{f(x+t) - f(x)}{t}$$

However, this is not possible, for a number of reasons, that are worth discussing in detail. So, here is the discussion, answering all kinds of questions that you might have:

(1) First of all, the above formula does not make any sense for a function $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$ with $N \neq M$, because we cannot divide oranges by apples. And it doesn't make sense either at $N = M \in \mathbb{N}$, because, well, here we have \mathbb{R}^N oranges, I agree with you, but there is no way of dividing these oranges, unless we are in the special cases $N = 1, 2$.

(2) More philosophically know, we have seen that having $f'(x)$ defined as a number is difficult, but the question is, do we really want to have $f'(x)$ defined as a number? And my claim here is that, this would be a pity. Think at the case where $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$ is linear. Such a map is just “perfect”, and so should equal its own derivative, $f = f'$.

(3) Summarizing, our Definition 7.4 is just perfection, and is waiting for some further study, and this is what we will do. And in case you're still secretly dreaming about having $f'(x)$ defined as some sort of number, wait for it. When $N = M$ at least, there is indeed a lucky number, namely $\det(f'(x))$, called Jacobian, but more on this later.

Getting back now to Definition 7.4 as formulated, and agreed upon, we have there a linear map $f'(x) : \mathbb{R}^N \rightarrow \mathbb{R}^M$, waiting to be further understood. So, time now to use our linear algebra knowledge. We know from there that such linear maps correspond to rectangular matrices $A \in M_{M \times N}(\mathbb{R})$, and we are led in this way to:

QUESTION 7.5. *Given a differentiable map $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$, in the abstract sense of Definition 10.6, what exactly is its derivative*

$$f'(x) : \mathbb{R}^N \rightarrow \mathbb{R}^M$$

regarded as a rectangular matrix, $f'(x) \in M_{M \times N}(\mathbb{R})$?

Again, I might hear scream you here, arguing that you come after a long battle, just agreeing that the derivative is a linear map, and not a number, and now what, we are trying to replace this linear map by a matrix, and so by a bunch of numbers. Good point, and I have no good answer to this. What we are doing here, Definition 7.4, then Question 7.5, and finally Theorem 7.6 to follow, are things that took mankind several centuries to develop, and that we are now presenting in a compressed form. So yes, all this is difficult mathematics, when you first see it, I perfectly agree with you.

In any case, hope that you're still with me, and here is the answer to Question 7.5:

THEOREM 7.6. *The derivative of a differentiable function $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$, making the approximation formula*

$$f(x+t) \simeq f(x) + f'(x)t$$

work, is the matrix of partial derivatives at x , namely

$$f'(x) = \left(\frac{df_i}{dx_j}(x) \right)_{ij} \in M_{M \times N}(\mathbb{R})$$

acting on the vectors $t \in \mathbb{R}^N$ by usual multiplication.

PROOF. As a first observation, the formula in the statement makes sense indeed, as an equality, or rather approximation, of vectors in \mathbb{R}^M , as follows:

$$f \begin{pmatrix} x_1 + t_1 \\ \vdots \\ x_N + t_N \end{pmatrix} \simeq f \begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix} + \begin{pmatrix} \frac{df_1}{dx_1}(x) & \cdots & \frac{df_1}{dx_N}(x) \\ \vdots & & \vdots \\ \frac{df_M}{dx_1}(x) & \cdots & \frac{df_M}{dx_N}(x) \end{pmatrix} \begin{pmatrix} t_1 \\ \vdots \\ t_N \end{pmatrix}$$

In order to prove now this formula, which does make sense, the idea is as follows:

(1) First of all, at $N = M = 1$ what we have is a usual 1-variable function $f : \mathbb{R} \rightarrow \mathbb{R}$, and the formula in the statement is something that we know well, namely:

$$f(x+t) \simeq f(x) + f'(x)t$$

(2) Let us discuss now the case $N = 2, M = 1$. Here what we have is a function $f : \mathbb{R}^2 \rightarrow \mathbb{R}$, and by using twice the basic approximation result from (1), we obtain:

$$\begin{aligned} f \begin{pmatrix} x_1 + t_1 \\ x_2 + t_2 \end{pmatrix} &\simeq f \begin{pmatrix} x_1 + t_1 \\ x_2 \end{pmatrix} + \frac{df}{dx_2}(x)t_2 \\ &\simeq f \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \frac{df}{dx_1}(x)t_1 + \frac{df}{dx_2}(x)t_2 \\ &= f \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} \frac{df}{dx_1}(x) & \frac{df}{dx_2}(x) \end{pmatrix} \begin{pmatrix} t_1 \\ t_2 \end{pmatrix} \end{aligned}$$

(3) More generally, we can deal in this way with the general case $M = 1$, with the formula here, obtained via a straightforward recurrence, being as follows:

$$\begin{aligned} f \begin{pmatrix} x_1 + t_1 \\ \vdots \\ x_N + t_N \end{pmatrix} &\simeq f \begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix} + \frac{df}{dx_1}(x)t_1 + \cdots + \frac{df}{dx_N}(x)t_N \\ &= f \begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix} + \begin{pmatrix} \frac{df}{dx_1}(x) & \cdots & \frac{df}{dx_N}(x) \end{pmatrix} \begin{pmatrix} t_1 \\ \vdots \\ t_N \end{pmatrix} \end{aligned}$$

(4) But this gives the result in the case where both $N, M \in \mathbb{N}$ are arbitrary too. Indeed, consider a function $f : \mathbb{R}^N \rightarrow \mathbb{R}^M$, and let us write it as follows:

$$f = \begin{pmatrix} f_1 \\ \vdots \\ f_M \end{pmatrix}$$

We can apply (3) to each of the components $f_i : \mathbb{R}^N \rightarrow \mathbb{R}$, and we get:

$$f_i \begin{pmatrix} x_1 + t_1 \\ \vdots \\ x_N + t_N \end{pmatrix} \simeq f_i \begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix} + \left(\frac{df_i}{dx_1}(x) \quad \dots \quad \frac{df_i}{dx_N}(x) \right) \begin{pmatrix} t_1 \\ \vdots \\ t_N \end{pmatrix}$$

But this collection of M formulae tells us precisely that the following happens, as an equality, or rather approximation, of vectors in \mathbb{R}^M :

$$f \begin{pmatrix} x_1 + t_1 \\ \vdots \\ x_N + t_N \end{pmatrix} \simeq f \begin{pmatrix} x_1 \\ \vdots \\ x_N \end{pmatrix} + \begin{pmatrix} \frac{df_1}{dx_1}(x) & \dots & \frac{df_1}{dx_N}(x) \\ \vdots & & \vdots \\ \frac{df_M}{dx_1}(x) & \dots & \frac{df_M}{dx_N}(x) \end{pmatrix} \begin{pmatrix} t_1 \\ \vdots \\ t_N \end{pmatrix}$$

Thus, we are led to the conclusion in the statement. \square

The above result, while being very nice, clear and useful, does not close the discussion. Indeed, conversely, we would like to know if the existence of the partial derivatives guarantees the fact that f is differentiable, with derivative $f'(x)$ appearing as the rectangular matrix formed by the partial derivatives at x . The result here is as follows:

THEOREM 7.7. *For a function $f : X \rightarrow \mathbb{R}^M$, with $X \subset \mathbb{R}^N$, the following conditions are equivalent, and in this case we say that f is continuously differentiable:*

- (1) f is differentiable, and the map $x \rightarrow f'(x)$ is continuous.
- (2) f has partial derivatives, which are continuous with respect to $x \in X$.

If these conditions are satisfied, $f'(x)$ is the matrix formed by the partial derivatives at x .

PROOF. We already know, from Theorem 7.6, that the last assertion holds. Regarding now the proof of the equivalence, this goes as follows:

(1) \implies (2) Assuming that f is differentiable, we know from Theorem 7.6 that $f'(x)$ is the matrix formed by the partial derivatives at x . Thus, we have, for any $x, y \in X$:

$$\frac{df_i}{dx_j}(x) - \frac{df_i}{dx_j}(y) = f'(x)_{ij} - f'(y)_{ij}$$

By applying now the absolute value, we obtain from this the following estimate:

$$\begin{aligned} \left| \frac{df_i}{dx_j}(x) - \frac{df_i}{dx_j}(y) \right| &= |f'(x)_{ij} - f'(y)_{ij}| \\ &= |(f'(x) - f'(y))_{ij}| \\ &\leq \|f'(x) - f'(y)\| \end{aligned}$$

But this gives the result, because if the map $x \rightarrow f'(x)$ is assumed to be continuous, then the partial derivatives follow to be continuous with respect to $x \in X$.

(2) \implies (1) This is something more technical. For simplicity, let us assume $M = 1$, the proof in general being similar. Given $x \in X$ and $\varepsilon > 0$, let us pick $r > 0$ such that the ball $B = B_x(r)$ belongs to X , and such that the following happens, over B :

$$\left| \frac{df}{dx_j}(x) - \frac{df}{dx_j}(y) \right| < \frac{\varepsilon}{N}$$

Our claim is that, with this choice made, we have the following estimate, for any $t \in \mathbb{R}^N$ satisfying $\|t\| < r$, with A being the vector of partial derivatives at x :

$$|f(x+t) - f(x) - At| \leq \varepsilon \|t\|$$

In order to prove this claim, the idea will be that of suitably applying the mean value theorem, over the N directions of \mathbb{R}^N . Indeed, consider the following vectors:

$$t^{(k)} = \begin{pmatrix} t_1 \\ \vdots \\ t_k \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

In terms of these vectors, we have the following formula:

$$f(x+t) - f(x) = \sum_{j=1}^N f(x+t^{(j)}) - f(x+t^{(j-1)})$$

Also, the mean value theorem gives a formula as follows, with $s_j \in [0, 1]$:

$$f(x+t^{(j)}) - f(x+t^{(j-1)}) = \frac{df}{dx_j}(x + s_j t^{(j)} + (1-s_j)t^{(j-1)}) \cdot t_j$$

But, according to our assumption on $r > 0$ from the beginning, the derivative on the right differs from $\frac{df}{dx_j}(x)$ by something which is smaller than ε/N :

$$\left| \frac{df}{dx_j}(x + s_j t^{(j)} + (1-s_j)t^{(j-1)}) - \frac{df}{dx_j}(x) \right| < \frac{\varepsilon}{N}$$

Now by putting everything together, we obtain the following estimate:

$$\begin{aligned}
|f(x+t) - f(x) - At| &= \left| \sum_{j=1}^N f(x+t^{(j)}) - f(x+t^{(j-1)}) - \frac{df}{dx_j}(x) \cdot t_j \right| \\
&\leq \sum_{j=1}^N \left| f(x+t^{(j)}) - f(x+t^{(j-1)}) - \frac{df}{dx_j}(x) \cdot t_j \right| \\
&= \sum_{j=1}^N \left| \frac{df}{dx_j}(x + s_j t^{(j)} + (1-s_j)t^{(j-1)}) \cdot t_j - \frac{df}{dx_j}(x) \cdot t_j \right| \\
&= \sum_{j=1}^N \left| \frac{df}{dx_j}(x + s_j t^{(j)} + (1-s_j)t^{(j-1)}) - \frac{df}{dx_j}(x) \right| \cdot |t_j| \\
&\leq \sum_{j=1}^N \frac{\varepsilon}{N} \cdot |t_j| \\
&\leq \varepsilon \|t\|
\end{aligned}$$

Thus we have proved our claim, and this gives the result. \square

This was for the basic theory of partial derivatives. In practice, there are far more things that can be said, both at the abstract and the concrete level, including of course many examples. We will be back to this, after developing some more general theory.

Before getting into this, however, let me formulate a definition that you will certainly appreciate, bringing a bit of humanity, and more specifically a good old real number, in this world of vectors, matrices and other beasts which is multivariable calculus:

DEFINITION 7.8. *Given a differentiable function $f : \mathbb{R}^N \rightarrow \mathbb{R}^N$, its Jacobian at $x \in \mathbb{R}^N$ is the number*

$$\det(f'(x)) \in \mathbb{R}$$

measuring the infinitesimal rate of the volume inflation by f , at the point x .

Here the first part is standard, because when $N = M$, as above, the derivative is a linear map $f'(x) : \mathbb{R}^N \rightarrow \mathbb{R}^N$, which is the same as a square matrix $f'(x) \in M_N(\mathbb{R})$, and so we can consider the determinant of this matrix, $\det(f'(x)) \in \mathbb{R}$. As for the second part, this comes from our knowledge of the determinant from linear algebra.

All this is very nice, and as a first observation, according to our formula of $f'(x)$ as being the matrix formed by the partial derivatives, we have:

$$\det(f'(x)) = \begin{vmatrix} \frac{df_1}{dx_1}(x) & \cdots & \frac{df_1}{dx_N}(x) \\ \vdots & & \vdots \\ \frac{df_N}{dx_1}(x) & \cdots & \frac{df_N}{dx_N}(x) \end{vmatrix}$$

Thus, the Jacobian can be explicitly computed. We will be back to this.

Generally speaking, Theorem 7.6 is what you need to know for upgrading from calculus to multivariable calculus. As a standard result here, we have:

THEOREM 7.9. *We have the chain derivative formula*

$$(f \circ g)'(x) = f'(g(x)) \cdot g'(x)$$

as an equality of matrices.

PROOF. This is something standard in one variable, and in several variables the proof is similar, by using the notion of derivative coming from Theorem 7.6. To be more precise, consider a composition of functions, as follows:

$$f : \mathbb{R}^N \rightarrow \mathbb{R}^M \quad , \quad g : \mathbb{R}^K \rightarrow \mathbb{R}^N \quad , \quad f \circ g : \mathbb{R}^K \rightarrow \mathbb{R}^M$$

According to Theorem 7.6, the derivatives of these functions are certain linear maps, corresponding to certain rectangular matrices, as follows:

$$f'(g(x)) \in M_{M \times N}(\mathbb{R}) \quad , \quad g'(x) \in M_{N \times K}(\mathbb{R}) \quad (f \circ g)'(x) \in M_{M \times K}(\mathbb{R})$$

Thus, our formula makes sense indeed. As for proof, this comes from:

$$\begin{aligned} (f \circ g)(x+t) &= f(g(x+t)) \\ &\simeq f(g(x) + g'(x)t) \\ &\simeq f(g(x)) + f'(g(x))g'(x)t \end{aligned}$$

Thus, we are led to the conclusion in the statement. \square

The above formula is quite interesting, and working its main particular cases, when some of parameters M, N, K equal 1, is a very instructive exercise.

Regarding now multiple integrals, as a main goal, we would like for instance to compute the factor $J = dx dy / dr dt$ making work the following formula:

$$\int_{\mathbb{R}^2} f(z) dz = \int_0^{2\pi} \int_0^\infty f(r \cos t, r \sin t) J dr dt$$

However, this is not obvious, and will require a lot of preliminaries. To start with, let us recall from one variable calculus that we have the following result:

PROPOSITION 7.10. *We have the change of variable formula*

$$\int_a^b f(x)dx = \int_c^d f(\varphi(t))\varphi'(t)dt$$

where $c = \varphi^{-1}(a)$ and $d = \varphi^{-1}(b)$.

PROOF. This follows with $f = F'$, from the following differentiation rule, that we know well, and whose proof is something elementary:

$$(F\varphi)'(t) = F'(\varphi(t))\varphi'(t)$$

Indeed, by integrating between c and d , we obtain the result. \square

In several variables now, we can only expect the above $\varphi'(t)$ factor to be replaced by something similar, a sort of “derivative of φ , arising as a real number”. However, we perfectly know from the above that the derivative of $\varphi : \mathbb{R}^N \rightarrow \mathbb{R}^N$ is a square matrix, $\varphi'(t) \in M_N(\mathbb{R})$, and death penalty for thinking otherwise.

So, what to do? The solution comes from linear algebra. Indeed, we know from there that associated to any matrix $A \in M_N(\mathbb{R})$ is the “volume inflation coefficient” of the associated linear map $\phi(x) = Ax$, which is a real number, denoted $\det A \in \mathbb{R}$, and called determinant of A . So, we have our real number, this should be just $\det(\varphi'(t))$, and with this in mind, we are led to the following statement:

THEOREM 7.11. *Given a transformation $\varphi = (\varphi_1, \dots, \varphi_N)$, we have*

$$\int_E f(x)dx = \int_{\varphi^{-1}(E)} f(\varphi(t))|J_\varphi(t)|dt$$

with the J_φ quantity, called *Jacobian*, being given by

$$J_\varphi(t) = \det \left[\left(\frac{d\varphi_i}{dx_j}(x) \right)_{ij} \right]$$

and with this generalizing the formula from Proposition 7.10.

PROOF. This is something quite tricky, the idea being as follows:

(1) Observe first that this generalizes indeed the change of variable formula in 1 dimension, from Proposition 7.10, the point here being that the absolute value on the derivative appears as to compensate for the lack of explicit bounds for the integral.

(2) In general, the proof is quite similar, the idea being that of assuming that the change of variables is linear, and by using the definition of the determinant as a volume. More specifically, this follows from the theory of the determinant. \square

All the above was of course quite tricky, and you may wonder if there is a simpler proof for this. Good question, and in answer, yes this is a difficult problem, which is actually open, and every now and then mathematicians still publish papers about this. In the hope that one day we will see a smart new paper on this from you too, reader.

7d. Into the heat

Hang on, we are not done yet with calculus. In order to get results about the heat equation, we will need a tough piece of mathematics, namely the formula of the Laplace operator in spherical coordinates. Ready for this? First, we have:

PROPOSITION 7.12. *We have polar coordinates in 2 dimensions,*

$$\begin{cases} x = r \cos t \\ y = r \sin t \end{cases}$$

the corresponding Jacobian being $J = r$.

PROOF. This is elementary, the Jacobian being:

$$\begin{aligned} J &= \begin{vmatrix} \frac{\partial r \cos t}{\partial r} & \frac{\partial r \cos t}{\partial t} \\ \frac{\partial r \sin t}{\partial r} & \frac{\partial r \sin t}{\partial t} \end{vmatrix} \\ &= \begin{vmatrix} \cos t & -r \sin t \\ \sin t & r \cos t \end{vmatrix} \\ &= r \cos^2 t + r \sin^2 t \\ &= r \end{aligned}$$

Thus, we have indeed the formula in the statement. □

In 3 dimensions the formula is similar, as follows:

PROPOSITION 7.13. *We have spherical coordinates in 3 dimensions,*

$$\begin{cases} x = r \cos s \\ y = r \sin s \cos t \\ z = r \sin s \sin t \end{cases}$$

the corresponding Jacobian being $J(r, s, t) = r^2 \sin s$.

PROOF. The fact that we have indeed spherical coordinates is clear. Regarding now the Jacobian, this is given by the following formula:

$$\begin{aligned}
& J(r, s, t) \\
&= \begin{vmatrix} \cos s & -r \sin s & 0 \\ \sin s \cos t & r \cos s \cos t & -r \sin s \sin t \\ \sin s \sin t & r \cos s \sin t & r \sin s \cos t \end{vmatrix} \\
&= r^2 \sin s \sin t \begin{vmatrix} \cos s & -r \sin s \\ \sin s \sin t & r \cos s \sin t \end{vmatrix} + r \sin s \cos t \begin{vmatrix} \cos s & -r \sin s \\ \sin s \cos t & r \cos s \cos t \end{vmatrix} \\
&= r \sin s \sin^2 t \begin{vmatrix} \cos s & -r \sin s \\ \sin s & r \cos s \end{vmatrix} + r \sin s \cos^2 t \begin{vmatrix} \cos s & -r \sin s \\ \sin s & r \cos s \end{vmatrix} \\
&= r \sin s (\sin^2 t + \cos^2 t) \begin{vmatrix} \cos s & -r \sin s \\ \sin s & r \cos s \end{vmatrix} \\
&= r \sin s \times 1 \times r \\
&= r^2 \sin s
\end{aligned}$$

Thus, we have indeed the formula in the statement. \square

Finally, in arbitrary N dimensions, the formula is as follows:

THEOREM 7.14. *We have spherical coordinates in N dimensions,*

$$\begin{cases} x_1 &= r \cos t_1 \\ x_2 &= r \sin t_1 \cos t_2 \\ &\vdots \\ x_{N-1} &= r \sin t_1 \sin t_2 \dots \sin t_{N-2} \cos t_{N-1} \\ x_N &= r \sin t_1 \sin t_2 \dots \sin t_{N-2} \sin t_{N-1} \end{cases}$$

the corresponding Jacobian being given by the following formula:

$$J(r, t) = r^{N-1} \sin^{N-2} t_1 \sin^{N-3} t_2 \dots \sin^2 t_{N-3} \sin t_{N-2}$$

PROOF. As before, the fact that we have spherical coordinates is clear. Regarding now the Jacobian, also as before, by developing over the last column, we have:

$$\begin{aligned}
J_N &= r \sin t_1 \dots \sin t_{N-2} \sin t_{N-1} \times \sin t_{N-1} J_{N-1} \\
&+ r \sin t_1 \dots \sin t_{N-2} \cos t_{N-1} \times \cos t_{N-1} J_{N-1} \\
&= r \sin t_1 \dots \sin t_{N-2} (\sin^2 t_{N-1} + \cos^2 t_{N-1}) J_{N-1} \\
&= r \sin t_1 \dots \sin t_{N-2} J_{N-1}
\end{aligned}$$

Thus, we obtain the formula in the statement, by recurrence. \square

Now let us go back to $N = 3$. We would like to reformulate our equations in spherical coordinates, and for this we need the formula of the Laplace operator Δ in spherical coordinates. Our undergraduate students in Cergy do this on a regular basis at exams, often with A grades, but since you might have a slightly less reliable calculus training than them, here is the result, accompanied by a more or less complete proof:

THEOREM 7.15. *The Laplace operator in spherical coordinates is:*

$$\Delta = \frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \cdot \frac{d}{dr} \right) + \frac{1}{r^2 \sin s} \cdot \frac{d}{ds} \left(\sin s \cdot \frac{d}{ds} \right) + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2}{dt^2}$$

PROOF. There are several proofs here, a short, elementary one being as follows:

(1) Let us first see how Δ behaves under a change of coordinates $\{x_i\} \rightarrow \{y_i\}$, in arbitrary N dimensions. Our starting point is the chain rule for derivatives:

$$\frac{d}{dx_i} = \sum_j \frac{d}{dy_j} \cdot \frac{dy_j}{dx_i}$$

By using this rule, then Leibnitz for products, then again this rule, we obtain:

$$\begin{aligned} \frac{d^2 f}{dx_i^2} &= \sum_j \frac{d}{dx_i} \left(\frac{df}{dy_j} \cdot \frac{dy_j}{dx_i} \right) \\ &= \sum_j \frac{d}{dx_i} \left(\frac{df}{dy_j} \right) \cdot \frac{dy_j}{dx_i} + \frac{df}{dy_j} \cdot \frac{d}{dx_i} \left(\frac{dy_j}{dx_i} \right) \\ &= \sum_j \left(\sum_k \frac{d}{dy_k} \cdot \frac{dy_k}{dx_i} \right) \left(\frac{df}{dy_j} \right) \cdot \frac{dy_j}{dx_i} + \frac{df}{dy_j} \cdot \frac{d^2 y_j}{dx_i^2} \\ &= \sum_{jk} \frac{d^2 f}{dy_k dy_j} \cdot \frac{dy_k}{dx_i} \cdot \frac{dy_j}{dx_i} + \sum_j \frac{df}{dy_j} \cdot \frac{d^2 y_j}{dx_i^2} \end{aligned}$$

(2) Now by summing over i , we obtain the following formula, with A being the derivative of $x \rightarrow y$, that is to say, the matrix of partial derivatives dy_i/dx_j :

$$\begin{aligned} \Delta f &= \sum_{ijk} \frac{d^2 f}{dy_k dy_j} \cdot \frac{dy_k}{dx_i} \cdot \frac{dy_j}{dx_i} + \sum_{ij} \frac{df}{dy_j} \cdot \frac{d^2 y_j}{dx_i^2} \\ &= \sum_{ijk} A_{ki} A_{ji} \frac{d^2 f}{dy_k dy_j} + \sum_{ij} \frac{d^2 y_j}{dx_i^2} \cdot \frac{df}{dy_j} \\ &= \sum_{jk} (AA^t)_{jk} \frac{d^2 f}{dy_k dy_j} + \sum_j \Delta(y_j) \frac{df}{dy_j} \end{aligned}$$

(3) So, this will be the formula that we will need. Observe that this formula can be further compacted as follows, with all the notations being self-explanatory:

$$\Delta f = \text{Tr}(AA^t H_y(f)) + \langle \Delta(y), \nabla_y(f) \rangle$$

(4) Getting now to spherical coordinates, $(x, y, z) \rightarrow (r, s, t)$, the derivative of the inverse, obtained by differentiating x, y, z with respect to r, s, t , is given by:

$$A^{-1} = \begin{pmatrix} \cos s & -r \sin s & 0 \\ \sin s \cos t & r \cos s \cos t & -r \sin s \sin t \\ \sin s \sin t & r \cos s \sin t & r \sin s \cos t \end{pmatrix}$$

The product $(A^{-1})^t A^{-1}$ of the transpose of this matrix with itself is then:

$$\begin{pmatrix} \cos s & \sin s \cos t & \sin s \sin t \\ -r \sin s & r \cos s \cos t & r \cos s \sin t \\ 0 & -r \sin s \sin t & r \sin s \cos t \end{pmatrix} \begin{pmatrix} \cos s & -r \sin s & 0 \\ \sin s \cos t & r \cos s \cos t & -r \sin s \sin t \\ \sin s \sin t & r \cos s \sin t & r \sin s \cos t \end{pmatrix}$$

But everything simplifies here, and we have the following remarkable formula, which by the way is something very useful, worth to be memorized:

$$(A^{-1})^t A^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2 \sin^2 s \end{pmatrix}$$

Now by inverting, we obtain the following formula, in relation with the above:

$$AA^t = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/r^2 & 0 \\ 0 & 0 & 1/(r^2 \sin^2 s) \end{pmatrix}$$

(5) Let us compute now the Laplacian of r, s, t . We first have the following formula, that we will use many times in what follows, and is worth to be memorized:

$$\begin{aligned} \frac{dr}{dx} &= \frac{d}{dx} \sqrt{x^2 + y^2 + z^2} \\ &= \frac{1}{2} \cdot \frac{2x}{\sqrt{x^2 + y^2 + z^2}} \\ &= \frac{x}{r} \end{aligned}$$

Of course the same computation works for y, z too, and we therefore have:

$$\frac{dr}{dx} = \frac{x}{r} \quad , \quad \frac{dr}{dy} = \frac{y}{r} \quad , \quad \frac{dr}{dz} = \frac{z}{r}$$

(6) By using the above formulae, twice, we can compute the Laplacian of r :

$$\begin{aligned}
 \Delta(r) &= \Delta\left(\sqrt{x^2 + y^2 + z^2}\right) \\
 &= \frac{d}{dx}\left(\frac{x}{r}\right) + \frac{d}{dy}\left(\frac{y}{r}\right) + \frac{d}{dz}\left(\frac{z}{r}\right) \\
 &= \frac{r^2 - x^2}{r^3} + \frac{r^2 - y^2}{r^3} + \frac{r^2 - z^2}{r^3} \\
 &= \frac{2}{r}
 \end{aligned}$$

(7) In what regards now s , the computation here goes as follows:

$$\begin{aligned}
 \Delta(s) &= \Delta\left(\arccos\left(\frac{x}{r}\right)\right) \\
 &= \frac{d}{dx}\left(-\frac{\sqrt{r^2 - x^2}}{r^2}\right) + \frac{d}{dy}\left(\frac{xy}{r^2\sqrt{r^2 - x^2}}\right) + \frac{d}{dz}\left(\frac{xz}{r^2\sqrt{r^2 - x^2}}\right) \\
 &= \frac{2x\sqrt{r^2 - x^2}}{r^4} + \frac{r^2(z^2 - 2y^2) + 2x^2y^2}{r^4\sqrt{r^2 - x^2}} + \frac{r^2(y^2 - 2z^2) + 2x^2z^2}{r^4\sqrt{r^2 - x^2}} \\
 &= \frac{2x\sqrt{r^2 - x^2}}{r^4} + \frac{x(2x^2 - r^2)}{r^4\sqrt{r^2 - x^2}} \\
 &= \frac{x}{r^2\sqrt{r^2 - x^2}} \\
 &= \frac{\cos s}{r^2 \sin s}
 \end{aligned}$$

(8) Finally, in what regards t , the computation here goes as follows:

$$\begin{aligned}
 \Delta(t) &= \Delta\left(\arctan\left(\frac{z}{y}\right)\right) \\
 &= \frac{d}{dx}(0) + \frac{d}{dy}\left(-\frac{z}{y^2 + z^2}\right) + \frac{d}{dz}\left(\frac{y}{y^2 + z^2}\right) \\
 &= 0 - \frac{2yz}{(y^2 + z^2)^2} + \frac{2yz}{(y^2 + z^2)^2} \\
 &= 0
 \end{aligned}$$

(9) We can now plug the data from (4) and (6,7,8) in the general formula that we found in (2) above, and we obtain in this way:

$$\begin{aligned} \Delta f &= \frac{d^2 f}{dr^2} + \frac{1}{r^2} \cdot \frac{d^2 f}{ds^2} + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2 f}{dt^2} + \frac{2}{r} \cdot \frac{df}{dr} + \frac{\cos s}{r^2 \sin s} \cdot \frac{df}{ds} \\ &= \frac{2}{r} \cdot \frac{df}{dr} + \frac{d^2 f}{dr^2} + \frac{\cos s}{r^2 \sin s} \cdot \frac{df}{ds} + \frac{1}{r^2} \cdot \frac{d^2 f}{ds^2} + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2 f}{dt^2} \\ &= \frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \cdot \frac{df}{dr} \right) + \frac{1}{r^2 \sin s} \cdot \frac{d}{ds} \left(\sin s \cdot \frac{df}{ds} \right) + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2 f}{dt^2} \end{aligned}$$

Thus, we are led to the formula in the statement. \square

With the above results in hand, we can now say a few interesting things about the heat equation, first in 1D and 2D, and then in the real-life case, 3D. All this is very nice and fundamental, and in fact modern PDE theory basically comes from this.

There is a lot of further mathematics that can be done, along these lines. In fact, if there is a cult equation in mathematics, hiding many interesting things about manifolds and their shapes, not necessarily related to physics, that is the heat equation.

7e. Exercises

Exercises.

CHAPTER 8

Van der Waals gases

8a. Van der Waals gases

We kept the best of thermodynamics for the end of the present half of this book. Honestly, are you satisfied with the theory of the ideal gases? That is certainly nice, no question about it, but in practice, on my side at least, what I can see around are all sorts of phenomena like vaporization, condensation, sublimation and so on, in short critical state physics, going well beyond what we know about the ideal gases, which are too “simple” for such things, and that I would like to understand.

Fortunately, there is an entry point to all this, namely the theory of the Van der Waals gases, which refine the ideal gases. Their definition is very simple, as follows:

THEOREM 8.1. *Beyond the ideal gas setting, stating that we should have*

$$PV = kT$$

the gases are subject to the Van der Waals equation

$$\left(P + \frac{\alpha}{V^2}\right)(V - \beta) = kT$$

depending on two parameters $\alpha, \beta > 0$.

PROOF. This is something quite tricky, with the correction parameters $\alpha, \beta > 0$ appearing from a detailed study of the gas, from a kinetic viewpoint. For an introduction to all this, we refer for instance to Huang [44], or Schroeder [73]. \square

In practice, the Van der Waals equation is quite close to what can be observed in the real life, for the various gases surrounding us. It is possible of course to specify the parameters $\alpha, \beta > 0$, via various lists and tables, and even make some speculations on the precise meaning of these two parameters, based on elementary chemistry.

8b. Curves, geometry

The above result is of key importance, and takes us into rethinking everything that we know about the ideal gases, which must be replaced with Van der Waals gases, at the advanced level. Among the main consequences of this replacement, the isobars, isochores, isothermals and adiabatics of the ideal gases, given by simple formulae, must

be replaced by isobars, isochores, isothermals and adiabatics for the Van der Waals gases, which are no longer something trivial, with some interesting math being now involved.

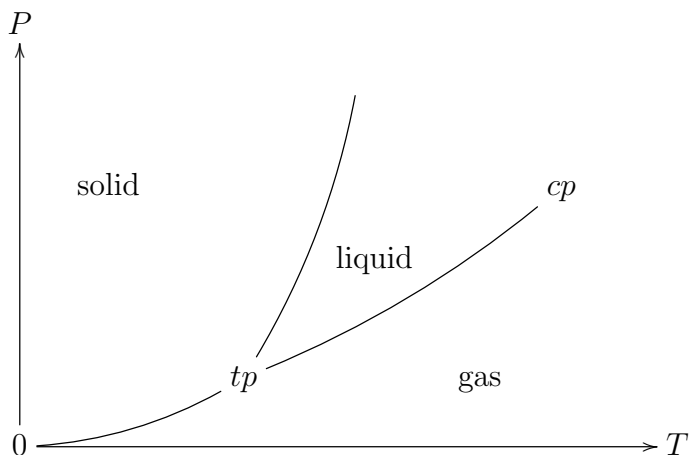
8c. Critical points

Among others, the Van der Waals gas study makes appear some interesting points on the isothermals, called triple and critical points of the gas.

8d. States of matter

The results that we obtained so far make the connection with the general theory of matter, which can be summarized as follows:

FACT 8.2. Ordinary matter appears in 3 forms, namely solid, liquid and gaseous, roughly appearing according to the following generic diagram



with tp , cp standing for the triple and critical points. Also, at low or high temperatures we have interesting phenonema like Bose-Einstein condensation, and plasma.

All this is extremely interesting, and as already mentioned above, part of it simply comes by looking at the Van der Waals gases, with elementary mathematical tools. We will be back to all this later, in Parts III-IV, when doing statistical mechanics.

8e. Exercises

Exercises.

Part III

Kinetic theory

House of mystic lights
Home is where my heart is
Calling Dr. Hyde
I was looking for my name

CHAPTER 9

Molecules

9a. Quantum mechanics

Welcome to statistical mechanics. In this second part of the present book we refine our thermodynamic knowledge about gases, and matter in general, by using an advanced modelling method, of mechanical type, called kinetic theory. Needless to say, this method will be correct, corresponding to what happens in the real life, when looking at your gas under a very good microscope. And in practice, this will lead to a lot of probability and statistics computations, with the whole approach being called “statistical mechanics”.

Generally speaking, the idea of kinetic theory is that gases are made of molecules, which move and collide, and it is this movement and collisions that produce things like pressure, or temperature. However, as you might have noticed when in the chemistry lab, and throwing that big plastic molecules at each other, when professor is not there, the collision mechanism can be quite complicated, depending on the molecules involved.

To be more precise, not only the size of the molecules is involved in the collision mechanism, but also their geometry. For instance two plastic H_2O molecules will bounce differently when colliding, depending of course on the angle of collision, but also on the precise orientation of our two H_2O molecules, at the moment of the collision.

In short, want it or not, we are led into the following deep question:

QUESTION 9.1. *What are molecules, and what is their geometry?*

You probably know the answer to this, at least vaguely, from chemistry classes in high school, or later. However, all this is beautiful science, so we will spend this whole chapter in explaining this. And then, in chapter 10, with all this knowledge in hand, we will get back to thermodynamics, with the aim of understanding it via molecules colliding.

To start with, and you surely know this, molecules are made of atoms, which atoms are very small, and are the business of quantum mechanics. So, the beginning of our story will be quantum mechanics. But, what is quantum mechanics? Here is the answer:

DEFINITION 9.2. *Quantum mechanics is the science of everything, starting from the nanoscale level ($1 \text{ nm} = 10^{-9} \text{ m}$), and all the way below.*

This certainly deserves some explanations. Really everything? Why quantum? Why mechanics? And also, what does 10^{-9} have to do with all this?

In what regards “everything”, yes the claim is that quantum mechanics has answers to everything happening at $d < 10^{-9}$, including mathematics, physics, chemistry, biology, engineering, and even things like philosophy, literature and sports. To be more precise, in what regards sports for instance, if one day we’ll learn that everything is made of tiny little particles, far smaller than those presently known, who spend their time playing soccer and making fun of us, believe me, it is physicists doing quantum mechanics that will discover them, and not the sports anchors from your local TV station.

In what regards “mechanics”, no surprise here, in view of what we’ve seen so far in this book. Everything in life is some sort of mechanics, with forces acting, experiments needed for writing equations, and then math needed for solving these equations. So, business as usual, with mechanics meaning more or less “physics”. In fact, if you hear people talking about “quantum physics”, that is exactly the same thing as quantum mechanics.

In what regards “quantum”, things here are trickier. To start with, we have:

TERMINOLOGY 9.3. *Quantum, plural quanta, comes from the Latin quantus, meaning “how much”. In the context of physics, a quantum is the minimum possible amount of any physical quantity. And with quantity coming by the way from quantus, too.*

And isn’t this confusing. Leaving now aside the Latin quantus, and the word quantity naturally derived from it, the key words in the above are “minimum possible amount”. So, that is the precise definition of quantum, in physics parlance.

As an example here, money is quantized, that is, made of quanta, a quantum of money being 1 cent, if you live in the US. Sugar in a sugar box is quantized too, a quantum being here a cube of sugar. And so on. Note in passing that quantum has not necessarily something to do with “small”, in the usual sense. For instance a herd of elephants is quantized too, a quantum here being 1 elephant. But things are relative, and assuming that you are interested in elephants only, 1 elephant is certainly something small.

Getting back now to physics, what is quantized, and what not? Common sense would suggest that all the basic physical quantities, such as distance, mass, energy and so on, vary continuously, and so are not quantized. And here comes the whole point, with quantum mechanics making the following bold statement:

CLAIM 9.4. *Quantum mechanics claims that all the basic physical quantities are in fact quantized, and that below the 10^{-9} m range, nothing cannot be really understood, if not taking into account the quantized nature of things.*

Summarizing, in regards with the questions raised after Definition 9.2, we have solved all of them, and by killing two rabbits with one shot, Claim 9.4 explaining both “quantum” and 10^{-9} . So, it simply remains to justify a bit this claim, and then get to work.

So, why should be things quantized in physics, and in life in general. Good question, going back to the cavern men, thinking about it. In the lack of anything spectacular, let us start with some philosophy. Our first piece of support for Claim 9.4 comes from:

FACT 9.5. Life is quantized, the quanta being the cells, and not even need for a microscope for that, the orange cells for instance being big enough. That’s how this world is made, quantized, or at least the fancy, living part of it. So if you look long enough at a rock, as to fall in love with that rock, that rock will become quantized too.

It is possible to further build along these lines, with this being the occupation of mankind and philosophers for long millennia in a row. In order to reach however to something more precise, as in Claim 9.4, some modern physics is needed.

Summarizing, with some modern physics knowledge, we have some serious evidence for Claim 9.4. Or at least for the quantization claim there, with the precise figure 10^{-9} still needing to be discussed. And so, to end this discussion, Definition 9.2 seems to be justified, we know what quantum mechanics should be, and where its name comes from, and all that is left now is to find this quantum mechanics, its laws and everything.

The first thought goes to experiments, but here we stumble upon:

FACT 9.6. You cannot really measure tiny little things, smaller than the resolution of your machinery. In addition, for the same reasons, measuring might perturb them.

This is of course something as old as engineering, and the solution is always to wait for long years, for technology to evolve. But in our case, we are really looking for tiny little things, well beyond the range of usual scientific machinery, so don’t really count on that machinery, and better try to develop some theory first.

But what to start with? Fortunately, there is an answer to this, as follows:

IDEA 9.7 (Let there be light). Burning matter, and observing the color of the flame, gives you information about the intimate, infinitesimal structure of that matter.

And isn’t this amazing. This says more or less that when burning some gas, or wood, or salt, or whatever other substance, you’re doing first-class quantum mechanics there, observing things so small that you never dreamed of coming upon.

So, this will be our starting point, in order to get into quantum mechanics, burning matter and recording the color of the light. We can in fact do even better, by avoiding the chemical reactions associated with burning, which will affect the matter that we are observing, and proceeding in a perhaps less glamorous way, as follows:

IDEA 9.8 (Let there be heat). *Heating matter, and observing the changing colors, gives you information about the intimate, infinitesimal structure of that matter.*

The above two ideas are of course as old as physics, or perhaps as fire and metallurgy, and the whole human civilization, in what concerns their everyday, macroscopic uses. Try cooking some food, or a blade, and you'll naturally get into them. In what concerns however their microscopic use, as suggested above, things are more recent, and the discipline of modern physics based on them is called spectroscopy.

9b. Atomic theory

Getting started now, we first need to talk about light. This is actually far less obvious than it seems, involving some advanced physics. We will need:

THEOREM 9.9 (Maxwell theory). *In regions of space where there is no charge or current present the Maxwell equations for electrodynamics read*

$$\langle \nabla, E \rangle = \langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \dot{E}/c^2$$

and both the electric field E and magnetic field B are subject to the wave equation

$$\ddot{\varphi} = c^2 \Delta \varphi$$

where $\Delta = \sum_i d^2/dx_i^2$ is the Laplace operator, and $c = 299,792,458$.

PROOF. This is something fundamental, appearing as a tricky mixture of physics facts and mathematical results, the idea being as follows:

(1) To start with, electrodynamics is the science of moving electrical charges. And this is something quite complicated, because unlike in classical mechanics, where the Newton law is good for both the static and the dynamic setting, the Coulomb law, which is actually very similar to the Newton law, does the job when the charges are static, but no longer describes well the situation when the charges are moving.

(2) The problem comes from the fact that moving charges produce magnetism, and with this being visible when putting together two electric wires, which will attract or repel, depending on orientation. Thus, in contrast with classical mechanics, where static or dynamic problems are described by a unique field, the gravitational one, in electrodynamics we have two fields, namely the electric field E , and the magnetic field B .

(3) Fortunately, there is a full set of equations relating the electric field E and the magnetic field B . These are the Maxwell equations, which look as follows:

$$\langle \nabla, E \rangle = \frac{\rho}{\varepsilon_0} \quad , \quad \langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \dot{E}$$

(4) To be more precise, regarding first the math, the dots denote derivatives with respect to time, and ∇ is the gradient operator, or space derivative, given by:

$$\nabla = \begin{pmatrix} \frac{d}{dx} \\ \frac{d}{dy} \\ \frac{d}{dz} \end{pmatrix}$$

(5) Regarding the physics, the first formula is the Gauss law, ρ being the charge, and ε_0 being a constant, and with this Gauss law more or less replacing the Coulomb law from electrostatics. The second formula is something basic, and anonymous. The third formula is the Faraday law. As for the fourth formula, this is the Ampère law, as modified by Maxwell, with J being the volume current density, and μ_0 being a constant.

(6) Without bothering too much about the precise meaning of all this, we can see right away that under the circumstances in the statement, namely in the regions of space where there is no charge or current present, the Maxwell equations take a simple and comprehensible form, readable even without much physics background, namely:

$$\begin{aligned} \langle \nabla, E \rangle &= \langle \nabla, B \rangle = 0 \\ \nabla \times E &= -\dot{B} \quad , \quad \nabla \times B = \mu_0 \varepsilon_0 \dot{E} \end{aligned}$$

(7) Thus, we have reached to the equations in the statement, modulo a discussion about the constant $\mu_0 \varepsilon_0$. And the point here is that, according to a remarkable discovery of Biot and Savart, the main electrodynamics constants μ_0, ε_0 are magically related to the observed speed of light in vacuum $c = 299,792,458$ by the following formula:

$$\mu_0 \varepsilon_0 = \frac{1}{c^2}$$

(8) Summarizing, we have our equations. Leaving aside the first two equations, by applying the curl operator to the last two equations, we obtain:

$$\begin{aligned} \nabla \times (\nabla \times E) &= -\nabla \times \dot{B} = -(\nabla \times B)' = -\ddot{E}/c^2 \\ \nabla \times (\nabla \times B) &= \nabla \times \dot{E}/c^2 = (\nabla \times E)' / c^2 = -\ddot{B}/c^2 \end{aligned}$$

But the double curl operator is subject to the following formula:

$$\nabla \times (\nabla \times \varphi) = \nabla \langle \nabla, \varphi \rangle - \Delta \varphi$$

Now by using the first two equations, we are led to the conclusion in the statement. \square

So, what is light? Light is the wave predicted by Theorem 9.9, travelling at speed c , and with an important extra property being that it depends on a real positive parameter, that can be called, upon taste, frequency, wavelength, or color.

In what regards the creation of light, the mechanism here is as follows:

FACT 9.10. *An accelerating or decelerating charge produces electromagnetic radiation, called light, whose frequency and wavelength can be explicitly computed.*

This phenomenon can be observed in a variety of situations, such as the usual light bulbs, where electrons get decelerated by the filament, acting as a resistor, or in usual fire, which is a chemical reaction, with the electrons moving around, as they do in any chemical reaction, or in more complicated machinery like nuclear plants, particle accelerators, and so on, leading there to all sorts of eerie glows, of various colors.

In view of the above, and especially of the light bulb example, a natural question appears, that you surely have on your mind, right now: what about a resistor which is not a light bulb filament, what happens to the light produced there?

This is a good question, and we already know a part of answer to it, from the Joule law that we met in chapter 4, saying that the resistor will start heating. The second part of it, that we will discuss in a moment, states that responsible for heat is, guess who, light again, but this time in non-visible wavelengths, typically IR.

Getting back now to Fact 9.10, in general, as stated above, this is something which can be deduced via some math, based on the Maxwell equations. However, all this math is not exactly trivial, and for details here, you can see for instance Griffiths [37].

Let us go back now to the wave equation $\ddot{\varphi} = v^2 \Delta \varphi$ from Theorem 9.9, and try to understand its simplest solutions. In 1D, the situation is as follows:

THEOREM 9.11. *The 1D wave equation, with speed v , namely*

$$\ddot{\varphi} = v^2 \frac{d^2 \varphi}{dx^2}$$

has as basic solutions the following functions,

$$\varphi(x) = A \cos(kx - wt + \delta)$$

with A being called amplitude, $kx - wt + \delta$ being called the phase, k being the wave number, w being the angular frequency, and δ being the phase constant. We have

$$\lambda = \frac{2\pi}{k} \quad , \quad T = \frac{2\pi}{kv} \quad , \quad \nu = \frac{1}{T} \quad , \quad w = 2\pi\nu$$

relating the wavelength λ , period T , frequency ν , and angular frequency w . Moreover, any solution of the wave equation appears as a linear combination of such basic solutions.

PROOF. There are several things going on here, the idea being as follows:

(1) Our first claim is that the function φ in the statement satisfies indeed the wave equation, with speed $v = w/k$. For this purpose, observe that we have:

$$\ddot{\varphi} = -w^2 \varphi \quad , \quad \frac{d^2 \varphi}{dx^2} = -k^2 \varphi$$

Thus, the wave equation is indeed satisfied, with speed $v = w/k$:

$$\ddot{\varphi} = \left(\frac{w}{k}\right)^2 \frac{d^2\varphi}{dx^2} = v^2 \frac{d^2\varphi}{dx^2}$$

(2) Regarding now the other things in the statement, all this is basically terminology, which is very natural, when thinking how $\varphi(x) = A \cos(kx - wt + \delta)$ propagates.

(3) Finally, the last assertion is something standard, coming from Fourier analysis, that we will not really need, in what follows. \square

As a first observation, the above result invites the use of complex numbers. Indeed, we can write the solutions that we found in a more convenient way, as follows:

$$\varphi(x) = \operatorname{Re} [A e^{i(kx - wt + \delta)}]$$

And we can in fact do even better, by absorbing the quantity $e^{i\delta}$ into the amplitude A , which becomes now a complex number, and writing our formula as:

$$\varphi = \operatorname{Re}(\tilde{\varphi}) \quad , \quad \tilde{\varphi} = \tilde{A} e^{i(kx - wt)}$$

Moving ahead now towards electromagnetism and 3D, let us formulate:

DEFINITION 9.12. *A monochromatic plane wave is a solution of the 3D wave equation which moves in only 1 direction, making it in practice a solution of the 1D wave equation, and which is of the special form found in Theorem 9.11, with no frequencies mixed.*

In other words, we are making here two assumptions on our wave. First is the 1-dimensionality assumption, which gets us into the framework of Theorem 9.11. And second is the assumption, in connection with the Fourier decomposition result from the end of Theorem 9.11, that our solution is of “pure” type, meaning a wave having a well-defined wavelength and frequency, instead of being a “packet” of such pure waves.

All this is still mathematics, and making now the connection with physics and electromagnetism, and more specifically with Theorem 9.9 and Fact 9.10, we have:

FACT 9.13. *Physically speaking, a monochromatic plane wave is the electromagnetic radiation appearing as in Theorem 9.9 and Fact 9.10, via equations of type*

$$\begin{aligned} E = \operatorname{Re}(\tilde{E}) & \quad : \quad \tilde{E} = \tilde{E}_0 e^{i(\langle k, x \rangle - wt)} \\ B = \operatorname{Re}(\tilde{B}) & \quad : \quad \tilde{B} = \tilde{B}_0 e^{i(\langle k, x \rangle - wt)} \end{aligned}$$

with the wave number being now a vector, $k \in \mathbb{R}^3$. Moreover, it is possible to add to this an extra parameter, accounting for the possible polarization of the wave.

To be more precise, what we are doing here is to import the conclusions of our mathematical discussion so far, from Theorem 9.11 and Definition 9.12, into the context of our original physics discussion, from Theorem 9.9 and Fact 9.10. And also to add an extra twist coming from physics, and more specifically from the notion of polarization.

In any case, we have now a decent intuition about what light is, and more on this later, and let us discuss now the examples. The idea is that we have various types of light, depending on frequency and wavelength. These are normally referred to as “electromagnetic waves”, but for keeping things simple and luminous, we will keep using the familiar term “light”. The classification, in a rough form, is as follows:

Frequency	Type	Wavelength
	—	
$10^{18} - 10^{20}$	γ rays	$10^{-12} - 10^{-10}$
$10^{16} - 10^{18}$	X – rays	$10^{-10} - 10^{-8}$
$10^{15} - 10^{16}$	UV	$10^{-8} - 10^{-7}$
	—	
$10^{14} - 10^{15}$	blue	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	yellow	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	red	$10^{-7} - 10^{-6}$
	—	
$10^{11} - 10^{14}$	IR	$10^{-6} - 10^{-3}$
$10^9 - 10^{11}$	microwave	$10^{-3} - 10^{-1}$
$1 - 10^9$	radio	$10^{-1} - 10^8$

Observe the tiny space occupied by the visible light, all colors there, and the many more missing, being squeezed under the $10^{14} - 10^{15}$ frequency banner. Here is a zoom on that part, with of course the remark that all this, colors, is something subjective:

Frequency THz = 10^{12} Hz	Color	Wavelength nm = 10^{-9} m
	—	
670 – 790	violet	380 – 450
620 – 670	blue	450 – 485
600 – 620	cyan	485 – 500
530 – 600	green	500 – 565
510 – 530	yellow	565 – 590
480 – 510	orange	590 – 625
400 – 480	red	625 – 750

Outside visible light we have, as you probably know it, UV on higher frequencies, and IR on lower frequencies. At the high frequency end we have X-rays, that you surely know about too, and γ rays, which are usually associated with various bad things, such as thunderstorms, solar flares, and small bugs with our nuclear energy technology.

As for the lower frequency end of the scale, first we have microwaves, but if you love physics and chemistry you should learn some cooking, that’s first-class chemistry, that you can practice every day. And then we have all sorts of radio wavelengths, including FM, followed by AM, and then by several more obscure low-frequency waves.

Importantly, both ends of the table are a bit loose. At the high frequency end there are some restrictions coming from quantum mechanics, and more on them later. As for the low frequency end, what's wave and what's not is a bit of a philosophical question, but which is actually not that philosophical, because waves having huge wavelengths can easily turn around mountains, full countries and so on, and so are of military interest. Secret research here, more of engineering type of course, is still ongoing.

Back now to our business, with all the above in hand, we can do some optics. Light usually comes in "bundles", with waves of several wavelengths coming at the same time, from the same source, and the first challenge is that of separating these wavelengths. In order to discuss this, let us start with the following fact:

FACT 9.14. *Inside a linear, homogeneous medium, where there is no free charge or current present, the Maxwell equations for electrodynamics read*

$$\langle \nabla, E \rangle = \langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \varepsilon\mu\dot{E}$$

with E, B being as before the electric and the magnetic field, and with $\varepsilon > \varepsilon_0$ and $\mu > \mu_0$ being the electric permittivity and magnetic permeability of the medium.

Observe that this is precisely the first part of Theorem 9.9, with the vacuum constants ε_0, μ_0 being replaced by their versions ε, μ , concerning the medium in question. In what regards now the second part of Theorem 9.9, which was a theorem, we have:

THEOREM 9.15. *Inside a linear, homogeneous medium, where there is no free charge or free current present, both E and B are subject to the wave equation*

$$\ddot{\varphi} = v^2 \Delta \varphi$$

with v being the speed of light inside the medium, given by

$$v = \frac{c}{n} \quad : \quad n = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}}$$

with the quantity on the right $n > 1$ being called *refraction index* of the medium.

PROOF. This is something that we know well in vacuum, and the proof in general is identical, with the resulting speed being:

$$v = \frac{1}{\sqrt{\varepsilon\mu}}$$

But this formula can be written in a more familiar form, as above. □

As a first observation here, while the above is something quite trivial, mathematically speaking, from the physical viewpoint we are here into complicated things. Materials can be transparent or opaque, with the distinction between them being something very subtle, and advanced, and Theorem 9.15 obviously deals with the transparent case.

Next in line, and for interest for us, we have:

FACT 9.16. *When travelling through a material, and hitting a new material, some of the light gets reflected, at the same angle, and some of it gets refracted, at a different angle, depending both on the old and the new material, and on the wavelength.*

Again, this is something deep, and very old as well, and there are many things that can be said here, ranging from various computations based on the Maxwell equations, to all sorts of considerations belonging to advanced materials theory.

As a basic formula here, we have the famous Snell law, which relates the incidence angle θ_1 to the refraction angle θ_2 , via the following simple formula:

$$\frac{\sin \theta_2}{\sin \theta_1} = \frac{n_1(\lambda)}{n_2(\lambda)}$$

Here $n_i(\lambda)$ are the refraction indices of the two materials, adjusted for the wavelength, and with this adjustment for wavelength being the whole point, which is something quite complicated. For an introduction to all this, we refer for instance to Griffiths [37].

As a simple consequence of the above, we have:

THEOREM 9.17. *Light can be decomposed, by using a prism.*

PROOF. This follows from Fact 9.16. Indeed, when hitting a piece of glass, provided that the hitting angle is not 90° , the light will decompose over the wavelengths present, with the corresponding refraction angles depending on these wavelengths. And we can capture these split components at the exit from the piece of glass, again deviated a bit, provided that the exit surface is not parallel to the entry surface. And the simplest device doing the job, that is, having two non-parallel faces, is a prism. \square

With this in hand, we can now talk about spectroscopy:

FACT 9.18. *We can study events via spectroscopy, by capturing the light the event has produced, decomposing it with a prism, carefully recording its “spectral signature”, consisting of the wavelengths present, and their density, and then doing some reverse engineering, consisting in reconstructing the event out of its spectral signature.*

This is the main principle of spectroscopy, and applications, of all kinds, abound. In practice, the mathematical tool needed for doing the “reverse engineering” mentioned above is the Fourier transform, which allows the decomposition of packets of waves, into monochromatic components. Finally, let us mention too that, needless to say, the event can be reconstructed only partially out of its spectral signature.

Getting now back to atoms, there is a long story here, involving many discoveries of many people, around 1890-1900, focusing on hydrogen H. We will present here things a

bit retrospectively, as to bet fit with science as we know it now, and with the present book. First on our list is the following discovery, by Lyman in 1906:

FACT 9.19 (Lyman). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R \left(1 - \frac{1}{n^2} \right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 2$, which are as follows,

n	Name	Wavelength	Color
—	—	—	—
2	α	121.567	UV
3	β	102.572	UV
4	γ	97.254	UV
\vdots	\vdots	\vdots	\vdots
∞	limit	91.175	UV

called *Lyman series of the hydrogen atom*.

Observe that all the Lyman series lies in UV. Due to this fact, namely the invisibility of UV to the human eye, this series, while theoretically being the most important, for certain reasons to be explained later, was discovered only second.

The first discovery, which was the big one, and the breakthrough, was by Balmer, the founding father of all this, back in 1885, in the visible range, as follows:

FACT 9.20 (Balmer). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 3$, which are as follows,

n	Name	Wavelength	Color
—	—	—	—
3	α	656.279	red
4	β	486.135	aqua
5	γ	434.047	blue
6	δ	410.173	violet
7	ε	397.007	UV
\vdots	\vdots	\vdots	\vdots
∞	limit	346.600	UV

called *Balmer series of the hydrogen atom*.

So, this was Balmer's original result, which started everything, and with his original wavelength formula being in fact something equivalent to the above formula, but a bit more complicated, as follows, with $B \simeq 3.645 \times 10^{-7}$ being the Balmer constant:

$$\lambda = \frac{Bn^2}{n^2 - 4}$$

As a third main result now, this time in IR, due to Paschen in 1908, we have:

FACT 9.21 (Paschen). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R \left(\frac{1}{9} - \frac{1}{n^2} \right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 4$, which are as follows,

n	Name	Wavelength	Color
	—	—	
4	α	1875	IR
5	β	1282	IR
6	γ	1094	IR
\vdots	\vdots	\vdots	\vdots
∞	limit	820.4	IR

called *Paschen series of the hydrogen atom*.

Observe the striking similarity between the above three results. In fact, we have here the following fundamental, grand result, due to Rydberg in 1888, based on the Balmer series, and with later contributions by Ritz in 1908, using the Lyman series as well:

CONCLUSION 9.22 (Rydberg, Ritz). *The spectral lines of the hydrogen atom are given by the Rydberg formula, depending on integer parameters $n_1 \leq n_2$,*

$$\frac{1}{\lambda_{n_1 n_2}} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

with R being the Rydberg constant for hydrogen, which is as follows:

$$R \simeq 1.096\,775\,83 \times 10^7$$

These spectral lines combine according to the Ritz-Rydberg principle, as follows:

$$\frac{1}{\lambda_{n_1 n_2}} + \frac{1}{\lambda_{n_2 n_3}} = \frac{1}{\lambda_{n_1 n_3}}$$

Similar formulae hold for other atoms, with suitable fine-tunings of R .

Here the first part, the Rydberg formula, generalizes the results of Lyman, Balmer, Paschen, which appear at $n_1 = 1, 2, 3$, at least retrospectively. The Rydberg formula predicts further spectral lines, appearing at $n_1 = 4, 5, 6, \dots$, and these were discovered

later, by Brackett in 1922, Pfund in 1924, Humphreys in 1953, and others afterwards, with all these extra lines being in far IR. The simplified complete table is as follows:

n_1	n_2	Series name	Wavelength $n_2 = \infty$	Color $n_2 = \infty$
		—	—	
1	2 – ∞	Lyman	91.13 nm	UV
2	3 – ∞	Balmer	364.51 nm	UV
3	4 – ∞	Paschen	820.14 nm	IR
		—	—	
4	5 – ∞	Brackett	1458.03 nm	far IR
5	6 – ∞	Pfund	2278.17 nm	far IR
6	7 – ∞	Humphreys	3280.56 nm	far IR
...

Regarding the last assertion, concerning other elements, this is something conjectured and partly verified by Ritz, and fully verified and clarified later, via many experiments, the fine-tuning of R being basically $R \rightarrow RZ^2$, where Z is the atomic number.

But from a theoretical physics viewpoint, the main result remains the middle assertion, called Ritz-Rydberg combination principle. This is something at the same time extremely simple, and completely puzzling, the informal conclusion being as follows:

THOUGHT 9.23. *The simplest observables of the hydrogen atom, combining via*

$$\frac{1}{\lambda_{n_1 n_2}} + \frac{1}{\lambda_{n_2 n_3}} = \frac{1}{\lambda_{n_1 n_3}}$$

look like quite weird quantities. Why wouldn't they just sum normally.

Getting now to quantum mechanics, and to our dreams about it, formulated before, well, good news, we have some serious data here. These spectral lines are basic and beautiful, obviously of quantized type, and in order to get started with our theory, we first need to solve the puzzle of the Ritz-Rydberg combination principle.

But, how to do this? Fortunately, matrix theory comes to the rescue, as follows:

THOUGHT 9.24. *The Ritz-Rydberg combination principle reminds the formula*

$$e_{n_1 n_2} e_{n_2 n_3} = e_{n_1 n_3}$$

for the usual matrix units, which are the elementary matrices given by

$$e_{ij} : e_j \rightarrow e_i$$

perhaps taken in infinite dimensions, as to allow infinite-ranging indices.

In short, we are in familiar territory here, and we can start dreaming of:

THOUGHT 9.25. *Observables in quantum mechanics should be some sort of infinite matrices, generalizing the Lyman, Balmer, Paschen lines of the hydrogen atom, and multiplying between them as the matrices do, as to produce further observables.*

And probably enough for now, this is the kind of discovery that should be celebrated with slaughtering 50 sheep and inviting your friends over, for a banquet, as the legend goes that Pythagoras did, after he discovered his $a^2 + b^2 = c^2$ theorem.

We will be back to all this in a moment, following Bohr, and then Heisenberg, and others, the idea being that Thought 9.25 is the main idea behind Heisenberg's first reasonable formulation of quantum mechanics, as a "matrix mechanics" theory. And for the story here, as a funny fact, Heisenberg did not know in fact about matrices, when starting his work, and rediscovered them by himself. More about this later.

9c. Periodic table

Time now to put everything together. As a main problem that we would like to solve, we have the understanding the intimate structure of matter, at the atomic level. There is of course a long story here, regarding the intimate structure of matter, going back centuries and even millennia ago, and our presentation here will be quite simplified. As a starting point, since we need a starting point, let us agree on:

CLAIM 9.26. *Ordinary matter is made of small particles called atoms, with each atom appearing as a mix of even smaller particles, namely protons +, neutrons 0 and electrons -, with the same number of protons + and electrons -.*

As a first observation, this is something which does not look obvious at all, with probably lots of work, by many people, being involved, as to lead to this claim. And so it is. The story goes back to the discovery of charges and electricity, which were attributed to a small particle, the electron -. Now since matter is by default neutral, this naturally leads to the consideration to the proton +, having the same charge as the electron.

But, as a natural question, why should be these electrons - and protons + that small? And also, what about the neutron 0? These are not easy questions, and the fact that it is so came from several clever experiments. Let us first recall from Fact 9.6 that careful experiments with tiny particles are practically impossible. However, all sorts of brutal experiments, such as bombarding matter with other pieces of matter, accelerated to the extremes, or submitting it to huge electric and magnetic fields, do work. And it is such kind of experiments, due to Thomson, Rutherford and others, "peeling off" protons +, neutrons 0 and electrons - from matter, and observing them, that led to the conclusion that these small beasts +, 0, - exist indeed, in agreement with Claim 9.26.

Of particular importance here was as well the radioactivity theory of Becquerel and Pierre and Marie Curie, involving this time such small beasts, or perhaps some related

radiation, peeling off by themselves, in heavy elements such as uranium ${}_{92}\text{U}$, polonium ${}_{84}\text{Po}$ and radium ${}_{88}\text{Ra}$. And there was also Einstein's work on the photoelectric effect, light interacting with matter, suggesting that even light itself might have associated to it some kind of particle, called photon. All this goes of course beyond Claim 9.26, with further particles involved, and more on this later, but as a general idea, all this deluge of small particle findings, all coming around 1900-1910, further solidified Claim 9.26.

So, taking now Claim 9.26 for granted, how are then the atoms organized, as mixtures of protons $+$, neutrons 0 and electrons $-$? The answer here lies again in the above-mentioned "brutal" experiments of Thomson, Rutherford and others, which not only proved Claim 9.26, but led to an improved version of it, as follows:

CLAIM 9.27. *The atoms are formed by a core of protons $+$ and neutrons 0 , surrounded by a cloud of electrons $-$, gravitating around the core.*

This is a considerable advance, because we are now into familiar territory, namely some kind of mechanics. Remember from the beginning of this book the planets orbiting around the Sun, on ellipses, as found by Kepler? Well, the same should happen with electrons orbiting around the core, but this time due to the Coulomb force. And with this in mind, all the pieces of our puzzle start fitting together, and lead to:

CLAIM 9.28 (Bohr and others). *The atoms are formed by a core of protons and neutrons, surrounded by a cloud of electrons, basically obeying to a modified version of electromagnetism. And with a fine mechanism involved, as follows:*

- (1) *The electrons are free to move only on certain specified elliptic orbits, labelled $1, 2, 3, \dots$, situated at certain specific heights.*
- (2) *The electrons can jump or fall between orbits $n_1 < n_2$, absorbing or emitting light and heat, that is, electromagnetic waves, as accelerating charges.*
- (3) *The energy of such a wave, coming from $n_1 \rightarrow n_2$ or $n_2 \rightarrow n_1$, is given, via the Planck viewpoint, by the Rydberg formula, applied with $n_1 < n_2$.*
- (4) *The simplest such jumps are those observed by Lyman, Balmer, Paschen. And multiple jumps explain the Ritz-Rydberg formula.*

And isn't this beautiful. Moreover, some further claims, also by Bohr and others, are that the theory can be further extended and fine-tuned as to explain many other phenomena, such as the above-mentioned findings of Einstein, and of Becquerel and Pierre and Marie Curie, and generally speaking, all the physics and chemistry known.

And the story is not over here. Following now Heisenberg, the next claim is that the underlying math in all the above can lead to a beautiful axiomatization of quantum mechanics, as a "matrix mechanics", along the lines of Thought 9.25.

In practice now, quantum mechanics can be developed along these lines, and this was something which was done by Heisenberg and Schrödinger, using various methods, and

then Dirac and others. Among their main discoveries, obtained by solving the hydrogen atom along the lines of Claim 9.28, is the fact that the electron orbits depend not only on the energy level $n \in \mathbb{N}$, as above, but in fact on a triple of parameters n, l, m , with the extra parameters l, m having something to do with the geometry of the orbit:

$$n \rightarrow (n, l, m)$$

On top of this, comes the spin of the electron, which is something that we ignored so far. And spin is in fact a key component to our problem, because we have:

FACT 9.29 (Pauli exclusion principle). *Two electrons cannot occupy the same quantum numbers n, l, m , with same spin $s = \pm 1/2$.*

But this Pauli exclusion principle gives in fact the key to the understanding of the arbitrary, $Z \geq 2$ atoms. There are of course many things that can be said about it. A sample quantum mechanics book will probably tell you first something about bosons and fermions, coming with exactly 0 evidence, then some more things about electrons, of type “they are the same, but not really, and everything is entangled, but is it really entangled”, and finally formulate the Pauli exclusion principle, as a theorem.

We will not get into this here, and take the Pauli exclusion principle as it is, a physics fact. However, talking philosophy, personally I always think at it as coming from the “human nature of electrons”. To be more precise, when I’m at my office typing the present book, I feel like occupying some precise quantum numbers, with precise spin. And if 30 colleagues, all typing physics books too, manage to come by surprise to my office, and squeeze there like sardines, I will surely find a way of getting rid of them, and disposing of their bodies. So now that a poor human like me can do this, why shouldn’t a mighty electron be able to do the same. This is the Pauli exclusion principle.

We have now all the ingredients for discussing the known atoms, or chemical elements, $Z = 1, \dots, 118$. These can be arranged in a table, called periodic table, as follows:

	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	$\frac{\text{H}}{1}$																		$\frac{\text{He}}{2}$
2	$\frac{\text{Li}}{3}$	$\frac{\text{Be}}{4}$												$\frac{\text{B}}{5}$	$\frac{\text{C}}{6}$	$\frac{\text{N}}{7}$	$\frac{\text{O}}{8}$	$\frac{\text{F}}{9}$	$\frac{\text{Ne}}{10}$
3	$\frac{\text{Na}}{11}$	$\frac{\text{Mg}}{12}$												$\frac{\text{Al}}{13}$	$\frac{\text{Si}}{14}$	$\frac{\text{P}}{15}$	$\frac{\text{S}}{16}$	$\frac{\text{Cl}}{17}$	$\frac{\text{Ar}}{18}$
4	$\frac{\text{K}}{19}$	$\frac{\text{Ca}}{20}$		$\frac{\text{Sc}}{21}$	$\frac{\text{Ti}}{22}$	$\frac{\text{V}}{23}$	$\frac{\text{Cr}}{24}$	$\frac{\text{Mn}}{25}$	$\frac{\text{Fe}}{26}$	$\frac{\text{Co}}{27}$	$\frac{\text{Ni}}{28}$	$\frac{\text{Cu}}{29}$	$\frac{\text{Zn}}{30}$	$\frac{\text{Ga}}{31}$	$\frac{\text{Ge}}{32}$	$\frac{\text{As}}{33}$	$\frac{\text{Se}}{34}$	$\frac{\text{Br}}{35}$	$\frac{\text{Kr}}{36}$
5	$\frac{\text{Rb}}{37}$	$\frac{\text{Sr}}{38}$		$\frac{\text{Y}}{39}$	$\frac{\text{Zr}}{40}$	$\frac{\text{Nb}}{41}$	$\frac{\text{Mo}}{42}$	$\frac{\text{Tc}}{43}$	$\frac{\text{Ru}}{44}$	$\frac{\text{Rh}}{45}$	$\frac{\text{Pd}}{46}$	$\frac{\text{Ag}}{47}$	$\frac{\text{Cd}}{48}$	$\frac{\text{In}}{49}$	$\frac{\text{Sn}}{50}$	$\frac{\text{Sb}}{51}$	$\frac{\text{Te}}{52}$	$\frac{\text{I}}{53}$	$\frac{\text{Xe}}{54}$
6	$\frac{\text{Cs}}{55}$	$\frac{\text{Ba}}{56}$	l	$\frac{\text{Lu}}{71}$	$\frac{\text{Hf}}{72}$	$\frac{\text{Ta}}{73}$	$\frac{\text{W}}{74}$	$\frac{\text{Re}}{75}$	$\frac{\text{Os}}{76}$	$\frac{\text{Ir}}{77}$	$\frac{\text{Pt}}{78}$	$\frac{\text{Au}}{79}$	$\frac{\text{Hg}}{80}$	$\frac{\text{Tl}}{81}$	$\frac{\text{Pb}}{82}$	$\frac{\text{Bi}}{83}$	$\frac{\text{Po}}{84}$	$\frac{\text{At}}{85}$	$\frac{\text{Rn}}{86}$
7	$\frac{\text{Fr}}{87}$	$\frac{\text{Ra}}{88}$	a	$\frac{\text{Lr}}{103}$	$\frac{\text{Rf}}{104}$	$\frac{\text{Db}}{105}$	$\frac{\text{Sg}}{106}$	$\frac{\text{Bh}}{107}$	$\frac{\text{Hs}}{108}$	$\frac{\text{Mt}}{109}$	$\frac{\text{Ds}}{110}$	$\frac{\text{Rg}}{111}$	$\frac{\text{Cn}}{112}$	$\frac{\text{Nh}}{113}$	$\frac{\text{Fl}}{114}$	$\frac{\text{Mc}}{115}$	$\frac{\text{Lv}}{116}$	$\frac{\text{Ts}}{117}$	$\frac{\text{Og}}{118}$
			l :	$\frac{\text{La}}{57}$	$\frac{\text{Ce}}{58}$	$\frac{\text{Pr}}{59}$	$\frac{\text{Nd}}{60}$	$\frac{\text{Pm}}{61}$	$\frac{\text{Sm}}{62}$	$\frac{\text{Eu}}{63}$	$\frac{\text{Gd}}{64}$	$\frac{\text{Tb}}{65}$	$\frac{\text{Dy}}{66}$	$\frac{\text{Ho}}{67}$	$\frac{\text{Er}}{68}$	$\frac{\text{Tm}}{69}$	$\frac{\text{Yb}}{70}$		
			a :	$\frac{\text{Ac}}{89}$	$\frac{\text{Th}}{90}$	$\frac{\text{Pa}}{91}$	$\frac{\text{U}}{92}$	$\frac{\text{Np}}{93}$	$\frac{\text{Pu}}{94}$	$\frac{\text{Am}}{95}$	$\frac{\text{Cm}}{96}$	$\frac{\text{Bk}}{97}$	$\frac{\text{Cf}}{98}$	$\frac{\text{Es}}{99}$	$\frac{\text{Fm}}{100}$	$\frac{\text{Md}}{101}$	$\frac{\text{No}}{102}$		

Here the horizontal parameter $1, \dots, 18$ is called the group, and the vertical parameter $1, \dots, 7$ is called the period. The two rows on the bottom consist of lanthanum $_{57}\text{La}$ and its followers, called lanthanides, and of actinium $_{89}\text{Ac}$ and its followers, called actinides. These are to be inserted in the main table, where indicated, lanthanides between barium $_{56}\text{Ba}$ and lutetium $_{71}\text{Lu}$, and actinides between radium $_{88}\text{Ra}$ and lawrencium $_{103}\text{Lr}$.

9d. Basic chemistry

Let us not forget about quantum mechanics, and what we wanted to do, namely discuss electron structure. As a first observation, we have:

FACT 9.30. *Any $Z = 1, \dots, 118$ corresponds to a unique element, having Z protons in the core, and Z electrons around it. This element might come with isotopes, depending on the number of neutrons in the core, can be in ground state or excited states, can get ionized, and so on, but all these versions are “family”, and the element is unique.*

In fact, we can now understand the electron structure of the various elements, and also how the periodic table is exactly made, the conclusions here being as follows:

FACT 9.31. *For the element having atomic number Z , the electrons will occupy successively the various positions with quantum numbers $n, l, m \in \mathbb{N}$ and spin $s = \pm 1/2$, such as the total binding energy to be minimal. In practice, the period $1, \dots, 7$ corresponds to the highest n occupied, and the group $1, \dots, 18$ comes from l, m, s .*

This is of course something very basic, and there is a detailed analysis to be done afterwards, for $Z = 1, \dots, 118$. For the elements up to krypton ${}_{36}\text{Kr}$, the list of electron configurations can be found for instance in Feynman [30] or Griffiths [38].

With this in hand, we can now start doing some chemistry. There is an enormous quantity of things that can be said here, the simplest of which being:

THEOREM 9.32. *The group 18 elements, helium ${}_{2}\text{He}$, neon ${}_{10}\text{Ne}$, argon ${}_{18}\text{Ar}$, krypton ${}_{36}\text{Kr}$, xenon ${}_{54}\text{Xe}$ and radon ${}_{86}\text{Rn}$, called noble gases, are allergic to chemistry.*

PROOF. This follows from the above discussion, because the group 18 elements are precisely those with all possible electron positions fully occupied, up to a certain $n \in \mathbb{N}$, which makes them very unfriendly to any chemistry proposition from the outside. By the way, oganesson ${}_{118}\text{Og}$ is normally part of this group too, but since this element has only been created and observed for a tiny fraction of a second, who really knows, and by the standard scientific etiquette, in the lack of experiments, no comment about it. \square

So long for the chemical elements, and the periodic table. Unfortunately business is business, and we will have to stop here, and go back to thermodynamics.

Observe however that, in relation with what we originally wanted to do, explained in the beginning of this chapter, job done. We have now proof that quantum mechanics is in relation with everything happening at 10^{-9} and below, as claimed before.

9e. Exercises

Exercises.

CHAPTER 10

Collisions, Boltzmann

10a. Collisions

We have seen in Parts I-II that some basic thermodynamics theory can be developed for the gases, by using the mathematics of their equation of state $f(P, V, T) = 0$, regarded as defining a surface in the 3D space of all possible parameters $P, V, T \in \mathbb{R}$. As a main finding, we have seen that the obvious conditions $P > 0$, $V > 0$ can be complemented with $T > 0$, and with this finding being something universal, beyond the gas level.

Here we get back to the usual 3D, with the x, y, z coordinates referring, as before in mechanics, to the usual \mathbb{R}^3 space that we live in. All our substances, be them gases, or liquids or solids, will be bodies $B \subset \mathbb{R}^3$. We will be interested in how heat flows between, and inside such bodies $B \subset \mathbb{R}^3$, as function of the time $t \in \mathbb{R}$.

Obviously, what we want to do here is to unify thermodynamics with mechanics. Or perhaps, more modestly, we want to upgrade our basic knowledge of thermodynamics, dealing so far only with gases, and with such gases being abstract (P, V, T) creatures, into something more advanced, of mechanical type, and covering liquids and solids too.

The discipline dealing with this is statistical mechanics. Mechanics because what we want to do is some sort of mechanics. And statistical because what we know so far about gases, and thermodynamics in general, suggests that at the level of subtle things, such as the second law of thermodynamics, everything is of deep statistical nature.

To start with, let us go back to gases, and improve our previous knowledge about them. You surely know that ordinary matter is made of molecules, and that in the case of gases, these molecules are free to move. Let us axiomatize this situation as follows:

DEFINITION 10.1. *A gas is made of molecules which are free to move, in a certain volume $B \subset \mathbb{R}^3$, with each molecule moving with its own speed. These molecules have perceptible size, and are subject to elastic collisions, when they meet.*

Obviously, this is something quite general. A first simplification is by assuming that the volume $B \subset \mathbb{R}^3$ is something standard, such as a sphere, or a cube, with this allowing

us to forget about B , and talk instead about the volume of the gas, $V = \text{vol}(B) > 0$. With this assumption made, the problem is that of finding the equation of state:

$$f(P, V, T) = 0$$

Another problem appears at the level of speeds. Molecules are of course, by definition, free to move in any direction, but if the speed is assumed to have the same magnitude $\|v\| > 0$ for all molecules, this will bring of course some simplifications.

Finally, the big problem appears in connection with collisions. We know from classical mechanics that elastic collisions in 3D, even between bodies of the same mass, and in fact even between bodies of same mass arriving with the same speed, are uniquely determined up to a scattering angle θ . Thus, in order to clarify our collision formalism, we need to know more about the chemical structure of the gas, telling us about θ .

Before anything, we should mention that the internal collisions are a phenomenon of considerable magnitude, which can only substantially modify our physics, due to:

FACT 10.2. At standard temperature and pressure (STP), meaning freezing water temperature, and pressure a tad lower than the average pressure at sea level,

$$T = 0^\circ \text{ C} = 273.15$$

$$P = 1 \text{ bar} = 10^5$$

a gas molecule undergoes about 10^{10} collisions per second, on average.

Here we refer as usual to standard units, namely meters, kilograms, seconds, coulombs not needed here, and kelvins. Let us also mention that the average pressure at sea level is $1 \text{ atm} = 1.013 \times 10^5$, with the previous STP standard, until the 80s, being 0° C and 1 atm . Not to be confused with normal temperature and pressure (NTP), which means 20° C and 1 atm . Or with many other standards, the situation here being a bit similar to that of the boxing world, with WBA, WBC, IBF, WBO all involved.

Speaking numbers and STP, let us record as well some data for gases, in order to have a clue on what we are talking about. Here it is, for 1 m³ of hydrogen H₂, at STP:

Quantity	Data	Comments
	—	
pressure P	1 bar = 10 ⁵	STP
volume V	1	by assumption
temperature T	0° C = 273.15	STP
	—	
number of molecules N	2.689 × 10 ²⁵	idealized
molecular density ρ	2.689 × 10 ²⁵	cf. $V = 1$
molecule mass m	3.347 × 10 ⁻²⁷	2.016 amu
	—	
total mass M	9 × 10 ⁻²	$M = Nm$
total energy K	1.5 × 10 ⁵	$K = 3PV/2$
	—	
molecular energy K_0	5.578 × 10 ⁻²¹	$K_0 = K/N$
molecular speed v	1.825 × 10 ³	cf. $K_0 = mv^2/2$
molecular momentum p	6.108 × 10 ⁻²⁴	$p = mv$
	—	
pressure reading t_f	1.896 × 10 ⁻³	$t_f = 2\sqrt{3}V^{1/3}/v$

Observe, as simple conclusions, to be kept in mind, that 1 m³ of hydrogen H₂ at STP weights 90 grams, that the molecular speed is about 1-2 km/s, and with this being also the speed of expansion of STP hydrogen in vacuum, and finally that the time needed for measuring pressure of hydrogen H₂ at STP is about 2 milliseconds.

Getting started now, as mentioned before, we must incorporate the about 10¹⁰ collisions per second from Fact 10.2 into our physics. Let us start with:

THEOREM 10.3. *For a general 1D gas the previous formula, namely*

$$PV = 2K$$

still holds in the collision setting, and the physics of the 1D gases stops here.

PROOF. This is something a bit philosophical, as follows:

(1) We know from chapter 2 that at $d = 1$ we have $PV = 2K$, under the assumptions there, and the problem now is to understand what happens when the molecules are assumed to have perceptible size, with elastic collisions between them.

(2) But, for an elastic 1D collision between particles having the same mass m , we know from classical mechanics, as a consequence of the conservation of energy and momentum, that the only thing that happens is that the speeds of our particles gets switched:

$$v'_1 = v_2 \quad , \quad v'_2 = v_1$$

(3) Thus, during such a 1D collision, formally the particles get switched, and so to say, nothing happens. Thus, we can simply ignore these collisions, and so we are back to the formalism in chapter 2, namely point masses, and we are done.

(4) Finally, in what regards the last assertion, it is pretty much clear, in view of the above, that we cannot speak of the temperature of a 1D gas, or of other more complicated such things, and so the physics of such gases stops here, as claimed. \square

Moving ahead with 2D, 3D, let us first review the collision formulae, in the case where the colliding masses are equal. We have here the following result:

THEOREM 10.4. *In the context of an elastic 2D collision between particles having the same mass m , the output speeds are given by the fomulae*

$$v'_1 = v_1 + u \quad , \quad v'_2 = v_2 - u$$

or alternatively, by the following equivalent formulae

$$v'_1 = v_2 - w \quad , \quad v'_2 = v_1 + w$$

where u, w with $u + w = v_2 - v_1$ form with $v_2 - v_1$ a right triangle, $u \perp w$.

PROOF. This follows from the general collision formulae, as follows:

(1) We recall that the general output speeds are $v'_1 = v_1 + q/m_1$ and $v'_2 = v_2 - q/m_2$, with the parameter $q \in \mathbb{R}^2$ being subject to the following equation:

$$2 \langle v_2 - v_1, q \rangle = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \|q\|^2$$

(2) In the case of equal masses, $m_1 = m_2 = m$, if we set $u = q/m$ then we have the first formulae in the statement, $v'_1 = v_1 + u$ and $v'_2 = v_2 - u$, with $u \in \mathbb{R}^2$ satisfying:

$$\langle v_2 - v_1, u \rangle = \|u\|^2$$

(3) Now by setting $w = v_2 - v_1 - u$, the first formulae in the statement transform into the second ones, namely $v'_1 = v_2 - w$ and $v'_2 = v_1 + w$, and we have:

$$\langle u, w \rangle = \langle u, v_2 - v_1 - u \rangle = 0$$

(4) Thus, we are led to the conclusion in the statement, and with the remark that everything depends, equivalently, on the angle $\theta \in \mathbb{R}$ between $(u, v_2 - v_1)$, which fully determines the right triangle $(u, w, v_2 - v_1)$ in the statement.

(5) To be more precise, when this angle is $\theta = 0$ we have $w = 0$ and so, as in the 1D case, the collision simply amounts in an exchange of particles. However, for $\theta \neq 0$ this exchange is perturbed, by the vector w , having magnitude $\|w\| = \|v_2 - v_1\| \sin \theta$. \square

In the general 3D case, the situation becomes even more complicated, because the output speeds v'_1, v'_2 consist of $3 + 3 = 6$ unknowns, and conservation of energy and momentum give us only $1 + 3 = 4$ equations. Thus, we have here 2 free parameters, unless of course we want to declare that the collision stays in the 2D plane (v_1, v_2) , in which case the problem is fully solved by Theorem 10.4, with just 1 parameter.

However, in practice, this latter assumption is not very realistic, due to the usually complex 3D shape of the gas molecules. As an example here, you can go to your chemistry lab, pick two big plastic H_2O molecules, and make them collide on a table. And, even if you always throw them with the same speeds v_1, v_2 , what happens at the moment of the impact can vary, depending on which side of the first H_2O will hit which side of the second H_2O . To be more precise, you can observe in this way the above-mentioned angle θ , and if you throw hard enough, one of the two H_2O might even take off upon impact, making it clear that there is as well a 2nd parameter involved there.

Getting now back to gases, we would like to find their equation of state, relating the pressure P , volume V and temperature T into a single formula, as follows:

$$f(P, V, T) = 0$$

Normally we have a bit of math and physics already, for dealing with such questions. The starting point would be the pressure formula that we already have, namely:

$$PV = \frac{2K}{3}$$

Now imagining that we have a good model for the piston, along the lines of the previous section, and with that model being smart enough as to read the temperature too, via heat diffusion at the piston, and perhaps some friction too, and imagining too that we are good enough at math for incorporating into the physics the 10^{10} collisions per second from Fact 10.2, via the math in Theorem 10.4, and finally imagining that chemists can help us a bit in understanding the basic differences between various gases, in relation with their internal collision mechanisms, well, good news, we can compute the equation of state.

In practice, however, this looks more like insanity. And so modesty, and instead of formulating a theorem, with proof and everything, we'll have to begin with a fact:

FACT 10.5. *The ideal gas is subject to the equation of state*

$$PV = kT \quad : \quad k = Nb$$

where N is the number of molecules present, and where

$$b = 1.380\,649 \times 10^{-23}$$

is an exact constant, called Boltzmann constant.

As a first comment, this fact is something old as ever, going back to the 18th century greats, such as Boyle and Charles, and then with further important contributions in the 19th century, by Gay-Lussac and Clausius, and then Maxwell and Boltzmann.

As a second comment, from a modern perspective, this fact lies somewhere between fact and theorem. We know that we have $PV = 2K/3$, and somehow the argument would be that the total kinetic energy K of the gas corresponds to temperature T , via:

$$\frac{2K}{3} = kT$$

Equivalently, by dividing everything by the number of molecules N , the individual molecular kinetic energy K_0 should correspond to temperature T , via:

$$\frac{2K_0}{3} = bT$$

But is this obvious? We know from thermodynamics that temperature T measures heat Q , which is a form of energy, and with this in mind, having $K_0 \sim T$ perfectly makes sense. But finding the precise proportionality factor amounts in doing the math for that 10^{10} collisions per second added to the theory, and with this leading us into countless challenges, as explained before Fact 10.5. And in addition to this, above everything, even if you manage to do the math, you still need afterwards experimental physicists to confirm the fact that your model is indeed the correct one, physically speaking. But such a confirmation can only come via a statement similar to Fact 10.5, so here we are, back to the starting point, after an interesting theoretical physics loop.

But perhaps enough talking for now, let us do a verification. We have here:

VERIFICATION 10.6. *For hydrogen H_2 at STP we have*

$$PV = 0.986 \times kT$$

based on the 1 m^3 data from the beginning of this chapter.

PROOF. We have indeed the following computation, based on that data:

$$\frac{PV}{NbT} = \frac{10^5 \times 1}{2.689 \times 10^{25} \times 1.381 \times 10^{-23} \times 273.15} = 0.986$$

Thus, we are led to the conclusion in the statement. \square

Still commenting on Fact 10.5, a common misconception states that the formula there comes from the physics of the internal collisions, needed to keep the gas in place “at perfect equilibrium”, with this meaning without container. But this does not make much sense, because, while collisions are certainly responsible for turning back certain molecules willing to escape, they can do nothing against half of the molecules at the boundary, those with speeds oriented towards freedom. And once these molecules are gone, you will never

see them again, and then also the boundary will shrink, and more molecules will escape, and so on. In fact, it is always good to remember here that we have:

FACT 10.7. *The average density of the intergalactic space is 1 particle / m³.*

Here by particle we mean atom or molecule, depending on the precise story of that particle. Observe that we are here in the region where the Maxwell demon can strike, and also that there might be some gravitation involved too. So we will leave now this trip to the outer space, with as usual, as conclusion, a bit more wisdom and modesty.

10b. Maxwell-Boltzmann

Back now to work, and to our problems in thermodynamics, at a more advanced level, dealing now with the internal mechanism of the $PV = kT$ formula, we have:

FACT 10.8 (Maxwell). *The molecular speeds $v \in \mathbb{R}^3$ of a gas in thermal equilibrium are subject to the Maxwell-Boltzmann distribution formula*

$$P(v) = \left(\frac{m}{2\pi bT}\right)^{3/2} \exp\left(-\frac{m\|v\|^2}{2bT}\right)$$

with m being the mass of the molecules, and b being the Boltzmann constant.

PROOF. As before with other things, this is something in between fact and theorem. Maxwell came upon it as a fact, or perhaps as a sort of pseudo-theorem, and a bit later Boltzmann came with a proof. In what follows we will discuss the original argument of Maxwell, then go towards Boltzmann's proof. Here is Maxwell's argument:

(1) We are looking for the precise probability distribution P of the molecular speeds $v = (v_1, v_2, v_3)$ which makes the mechanics of gases work. Intuition tells us that P has no correlations between the x, y, z directions of space, and so we must have:

$$P(v) = f(v_1)g(v_2)h(v_3)$$

Moreover, by rotational symmetry the functions f, g, h must coincide, and so:

$$P(v) = f(v_1)f(v_2)f(v_3)$$

(2) Further thinking, again invoking rotational symmetry, leads to the conclusion that $P(v)$ must depend only on the magnitude $\|v\|$ of the velocity $v \in \mathbb{R}^3$, and not on the direction. Thus, we must have as well a formula of the following type:

$$P(v) = \varphi(\|v\|^2)$$

(3) Now by comparing the requirements in (1) and (2), we are led via some math to the conclusion that φ must be an exponential, which amounts in saying that:

$$P(v) = \lambda \exp(-C\|v\|^2)$$

(4) Obviously we must have $C > 0$, for things to be bounded, and then by integrating we can obtain λ as function of C , and our formula becomes:

$$P(v) = \left(\frac{C}{\pi}\right)^{3/2} \exp(-C\|v\|^2)$$

(5) It remains to find the value of $C > 0$. But for this purpose, observe that, now that we have our distribution, be that still depending on $C > 0$, we can compute everything that we want to, just by integrating. In particular, we find that on average:

$$v_1^2 = v_2^2 = v_3^2 = \frac{1}{2C}$$

Thus the average magnitude of the molecular speed is given by:

$$\|v\| = \frac{3}{2C}$$

It follows that the average kinetic energy of the molecules is:

$$K_0 = \frac{m\|v\|^2}{2} = \frac{3m}{4C}$$

(6) On the other hand, recall from our discussions above that one of the many equivalent formulations of $PV = kT$, using $PV = 2K/3$, was as follows:

$$\frac{2K_0}{3} = bT$$

(7) Thus we obtain $m/(2C) = bT$, and so $C = m/(2bT)$, as desired. □

Observe that the above proof has in fact little physical content, with the whole thing being basically obtained by using $PV = 2K/3$, which is a mathematical theorem, then $PV = kT$, which is a crucial physics fact, and finally by invoking several times a number of clever symmetry arguments, and doing some calculus.

We will be back to this in a moment, with a more rigorous argument, following Boltzmann, fully establishing the above formula. Which, needless to say, is correct.

10c. Kinetic theory

In order to further discuss all this, following Boltzmann, and then Gibbs and others, the idea will be that of connecting all the above to the key notion of entropy.

So, let us go back to basic thermodynamics, as in Parts I-II, and more specifically to chapter 6, dealing with entropy. We recall from there that we have:

THEOREM 10.9. *Given a gas, with states denoted $S = (P, V, T) \in \mathbb{R}^3$, subject to the equation of state $f(S) = 0$, define the entropy of a state by the formula*

$$\mathfrak{E}(S) = \int_{S_0}^S \frac{dQ}{T}$$

where S_0 is a chosen state, and the integral is over a reversible transformation from S_0 to S . Then \mathfrak{E} is well-defined up to an additive scalar, and we have the inequality

$$\mathfrak{E}(S_1) \leq \mathfrak{E}(S_2)$$

for any transformation $S_1 \rightarrow S_2$, with equality when this transformation is reversible. That is, entropy increases, and there is nothing much that you can do about it.

PROOF. This is something that we know well from Part II, with the proof using the standard methods there, namely calculus, and Carnot machines. \square

Following now Boltzmann, we have the following key result:

THEOREM 10.10 (Boltzmann). *The kinetic theory of gases, taking into account the collisions between molecules, leads to the formula for entropy*

$$\mathfrak{E}(S) = -b \int P(S) \log P(S) dS$$

with P being the probability on the state space, around our given state S .

PROOF. This is something quite complicated, and for a proof here, we refer to any solid statistical mechanics book. Note in the above the obvious similarity with the Shannon entropy formula from information theory, if you ever came across that. Finally, observe that \mathfrak{E} as computed above is given by an exact formula, not depending on an additive constant, the point here being that, in the context of Theorem 10.9, we can formally choose the state S_0 there to be the one, which is unique, at temperature $T = 0$. \square

Moving ahead now, as a second key result, also due to Boltzmann, we have:

THEOREM 10.11 (Boltzmann). *Given a gas with initial molecular speed distribution P , the collisions between molecules, leading to equilibrium, will work such as the quantity*

$$H = \int P(v) \log P(v) dv$$

decreases over time. The final distribution reached, over time, which is the one at equilibrium, is precisely the one which minimizes H , given by the formula

$$P(v) = \left(\frac{m}{2\pi bT} \right)^{3/2} \exp \left(-\frac{m||v||^2}{2bT} \right)$$

which is the Maxwell-Boltzmann distribution, that we knew before from Maxwell.

PROOF. Again, this is something at the same time a bit complicated, but of utter beauty, and for the proof, we again refer to any solid statistical mechanics book. \square

Observe the obvious similarity between Theorem 10.10 and Theorem 10.11, and also the important theoretical consequences of the above, in view of the comments that we previously made in connection with the Maxwell-Boltzmann distribution.

10d. Gibbs theorem

In order to further clarify all the above, we will explain now a key result of Gibbs, called H theorem. This is something quite abstract and general, as follows:

THEOREM 10.12. *For a large system, with states denoted S , the quantity*

$$H = \int P(S) \log P(S) dS$$

can only decrease over time, as to reach a minimum, where we have

$$P(S) \sim \exp \left(\sum_i \lambda_i E_i \right)$$

where E_i are the conserved quantities, and $\lambda_i \in \mathbb{R}$ are scalars.

PROOF. This is something quite tricky, the idea being as follows:

(1) In order to prove this result, let us define quantities $A(S, T)$, depending on two states S, T , close to each other, such that the rate at which the system transitions $S \rightarrow T$ equals $A(S, T)dT$. With this convention, we have the following formula:

$$\frac{dP(S)dS}{dt} = \int \left[P(T)A(T, S)dS - P(S)A(S, T)dS \right] dT$$

By cancelling the differentials dS , this gives the following formula:

$$\frac{dP(S)}{dt} = \int \left[P(T)A(T, S) - P(S)A(S, T) \right] dT$$

(2) On the other hand, consider the quantity in the statement, namely:

$$H = \int P(S) \log P(S) dS$$

By using the formula found in (1), we obtain the following formula:

$$\frac{dH}{dt} = \int \int \left[P(T)A(T, S) - P(S)A(S, T) \right] (\log P(S) + 1) dS dT$$

Now by interchanging S, T in the second integral, this gives:

$$\frac{dH}{dt} = \int \int P(T)A(T, S) \log \frac{P(S)}{P(T)} dS dT$$

(3) We use now the following standard inequality, whose proof is elementary:

$$x, y \geq 0 \implies y \log \frac{x}{y} \leq x - y$$

By applying this to the last formula found in (2), that formula gives:

$$\frac{dH}{dt} \leq \int \int (P(S) - P(T))A(T, S)dSdT$$

Now by interchanging again S, T , this inequality can be written as follows:

$$\frac{dH}{dt} \leq \int \int P(T)(A(S, T) - A(T, S))dSdT$$

(4) Normally this latter estimate allows us to conclude that H decreases, as claimed in the statement, because since the laws of physics must be invariant under time reversal, we should have $A(S, T) = A(T, S)$, and so our inequality simply reads:

$$\frac{dH}{dt} \leq 0$$

However, our argument has a flaw, in the context of advanced quantum mechanics, but as good news, the same advanced quantum mechanics tells us that we have:

$$\int (A(S, T) - A(T, S))dS = 0$$

Thus, either way, we obtain $dH/dt \leq 0$, and so that H decreases, as claimed.

(5) In order to prove now the second assertion, regarding what happens when H is minimal, observe that for an infinitesimal change $\Delta P(S)$, we have:

$$\Delta H = \int \Delta P(S)(\log P(S) + 1)dS$$

Now assuming that H is minimal, we must have $\Delta H = 0$ for any allowed infinitesimal change $\Delta P(S)$, with this meaning that the change $\Delta P(S)$ must preserve the conserved quantities of the system, as for instance the energy $E(S)$, and also be such that:

$$\int P(S)dS = 1$$

But this can only happen when $P(S)$ is of the following form, where E_i are the conserved quantities of the system, and $\lambda_i \in \mathbb{R}$ are certain scalars:

$$P(S) \sim \exp \left(\sum_i \lambda_i E_i \right)$$

Thus, we are led to the conclusion in the statement. □

In practice now, assuming that the energy E is the only conserved quantity, Theorem 10.12 leads to the following distribution, called “canonical ensemble”:

$$P(S) = \exp \left[C - \frac{E(S)}{\theta} \right]$$

To be more precise, here θ is a certain constant, and C is another constant, uniquely determined by $\int P(S)dS = 1$. But, in practice, we have $\theta = kT$, which gives:

$$P(S) = \exp \left[C - \frac{E(S)}{kT} \right]$$

More generally now, in case our system has other conserved quantities N_i , Theorem 10.12 leads to the following distribution, called “grand canonical ensemble”:

$$P(S) = \exp \left[C - \frac{E(S) - \sum_i \lambda_i N_i(S)}{kT} \right]$$

We will be back to canonical ensembles in chapter 11. For the moment, let us record the following result, coming as a complement to Theorem 10.12:

THEOREM 10.13. *We have the formula*

$$\mathfrak{E}(S) = -kH$$

with \mathfrak{E} being the thermodynamical entropy.

PROOF. In the context of our equations above, adding some heat ΔQ to the system gives the following formula, for the corresponding change in the quantity H :

$$\begin{aligned} \Delta H &= \int \Delta P(S)(\log P(S) + 1)dS \\ &= -\frac{1}{kT} \int \Delta P(S)E(S)dS \\ &= -\frac{\Delta Q}{kT} \end{aligned}$$

Now since the thermodynamical entropy satisfies by definition $d\mathfrak{E} = dQ/kT$, we conclude from the above equation that we have $\mathfrak{E}(S) = -kH$, as claimed. \square

10e. Exercises

Exercises.

CHAPTER 11

Statistical mechanics

11a. Partition function

Partition function.

11b. Grand ensembles

Grand ensembles.

11c. Ideal gases, revised

Ideal gases, revised.

11d. Further results

So long for basic statistical mechanics. For more on all this, we refer to any specialized book on statistical mechanics, or even physics at large, such as Huang [44], Kadanoff [52], Pathria and Beale [69], Schroeder [73] or Weinberg [90]. In what concerns us, we will keep building on all this, in connection with some carefully chosen topics.

11e. Exercises

Exercises.

CHAPTER 12

States of matter

12a. Gases, again

We briefly discuss in this chapter all sorts of things, that must be discussed, for the most in relation with matter, subject to heating or cooling. Our scope will be quite broad, because we would like to talk about all sorts of matter, solid, liquid or gaseous, with a look into the extremes $T \rightarrow 0$ and $T \gg 0$ too, where other forms of matter appear, and finally with our matter being as 3D as possible, with this meaning occupying a precise body $B \subset \mathbb{R}^3$, instead of just a volume $V = \text{vol}(B) \in \mathbb{R}$, as it was the case so far.

Let us first record, regarding the gases, at a more advanced level:

THEOREM 12.1. *Beyond the ideal gas setting, stating that we should have*

$$PV = kT$$

the gases are subject to the Van der Waals equation

$$\left(P + \frac{\alpha}{V^2}\right)(V - \beta) = kT$$

depending on two parameters $\alpha, \beta > 0$.

PROOF. This is something quite tricky, with the correction parameters $\alpha, \beta > 0$ appearing from a detailed study of the gas, from a kinetic viewpoint. For an introduction to all this, we refer for instance to Huang [44], or Schroeder [73]. \square

The above result is of key importance, and takes us into rethinking everything that what we know about the ideal gases, which must be replaced with Van der Waals gases, at the advanced level. Among the main consequences of this replacement, the isobars, isochores, isothermals and adiabatics of the ideal gases, given by simple formulae, must be replaced by isobars, isochores, isothermals and adiabatics for the Van der Waals gases, which are no longer something trivial, with some interesting math being now involved.

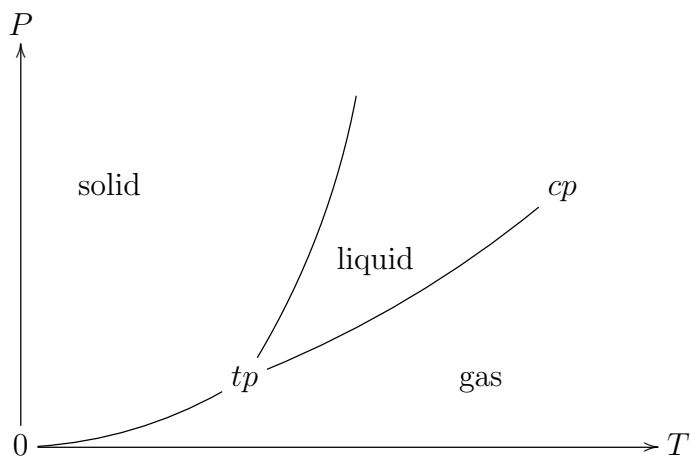
12b. Critical points

Among others, the Van der Waals gas study makes appear some interesting points on the isothermals, called triple and critical points of the gas.

12c. States of matter

Our study of the gases so far, using various techniques from thermodynamics and statistical mechanics, which makes appear various critical points, makes the connection with the general theory of matter, which can be summarized as follows:

FACT 12.2. *Ordinary matter appears in 3 forms, namely solid, liquid and gaseous, roughly appearing according to the following generic diagram*



with tp, cp standing for the triple and critical points. Also, at low or high temperatures we have interesting phenomena like Bose-Einstein condensation, and plasma.

Needless to say, the quantity of things that can be said about all this is enormous.

12d. Extreme physics

Passed the gases, that we are quite familiar with, the problem is with the liquids and solids, plus of course with all sorts of exotic matter that can appear at the extremes.

12e. Exercises

Exercises.

Part IV

Statistical mechanics

*Cause you are young
You will always be so strong
Hold on tight to your dreams, hold on
You are right, don't give up*

CHAPTER 13

Max Planck

13a. Radiation, light

Welcome to advanced statistical mechanics. In this chapter we go directly for one of the most interesting questions here, namely computing the blackbody radiation, following Planck and others, and with this being a key ingredient for quantum mechanics.

To start with, let us recall from chapter 9 that light is an electromagnetic wave, the formation mechanism of such waves being as follows:

FACT 13.1. *In regions of space where there is no charge or current present the Maxwell equations for electrodynamics read*

$$\langle \nabla, E \rangle = \langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \dot{E}/c^2$$

and both the electric field E and magnetic field B are subject to the wave equation

$$\ddot{\varphi} = c^2 \Delta \varphi$$

where $\Delta = \sum_i d^2/dx_i^2$ is the Laplace operator, and $c = 299,792,458$. An accelerating or decelerating charge produces such electromagnetic radiation, called light.

To be more precise here, the starting point are the usual Maxwell equations, relating the electric field E and the magnetic field B , namely:

$$\langle \nabla, E \rangle = \frac{\rho}{\varepsilon_0} \quad , \quad \langle \nabla, B \rangle = 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \dot{E}$$

The point now is that, under the assumption in the statement, that there is no charge or current present, these equations reduce to the equations above, by using the Biot-Savart formula $\mu_0 \varepsilon_0 = 1/c^2$. Then the wave equation follows from some simple mathematics, based on these equations, and finally the last assertion, which is something less trivial, can be deduced as well from the Maxwell equations, by doing some mathematics.

We will also need, as a second piece of preliminaries, the following fact:

FACT 13.2. *The 1D wave equation, with speed v , namely*

$$\ddot{\varphi} = v^2 \frac{d^2\varphi}{dx^2}$$

has as basic solutions the following functions,

$$\varphi(x) = A \cos(kx - wt + \delta)$$

with A being called amplitude, $kx - wt + \delta$ being called the phase, k being the wave number, w being the angular frequency, and δ being the phase constant. We have

$$\lambda = \frac{2\pi}{k} \quad , \quad T = \frac{2\pi}{kv} \quad , \quad \nu = \frac{1}{T} \quad , \quad w = 2\pi\nu$$

relating the wavelength λ , period T , frequency ν , and angular frequency w . Moreover, any solution of the wave equation appears as a linear combination of such basic solutions.

Here, as before with Fact 13.1, what we have is basically some mathematics. To be more precise, our first claim is that the function φ in the statement satisfies indeed the wave equation, with speed $v = w/k$. For this purpose, observe that we have:

$$\ddot{\varphi} = -w^2\varphi \quad , \quad \frac{d^2\varphi}{dx^2} = -k^2\varphi$$

Thus, the wave equation is indeed satisfied, with speed $v = w/k$:

$$\ddot{\varphi} = \left(\frac{w}{k}\right)^2 \frac{d^2\varphi}{dx^2} = v^2 \frac{d^2\varphi}{dx^2}$$

Regarding now the other things in the statement, all this is basically terminology, which is very natural, when thinking how $\varphi(x) = A \cos(kx - wt + \delta)$ propagates. Finally, the last assertion is something standard, coming from Fourier analysis.

As a first observation, the above result invites the use of complex numbers. Indeed, we can write the solutions that we found in a more convenient way, as follows:

$$\varphi(x) = \operatorname{Re} [A e^{i(kx - wt + \delta)}]$$

And we can in fact do even better, by absorbing the quantity $e^{i\delta}$ into the amplitude A , which becomes now a complex number, and writing our formula as:

$$\varphi = \operatorname{Re}(\tilde{\varphi}) \quad , \quad \tilde{\varphi} = \tilde{A} e^{i(kx - wt)}$$

Now by using this, we can formulate the following key definition:

DEFINITION 13.3. *A monochromatic plane wave is a solution of the 3D wave equation which moves in only 1 direction, making it in practice a solution of the 1D wave equation, and which is of the special form found in Fact 13.2, with no frequencies mixed.*

Finally, the classification of such waves, in a quite rough form, is as follows:

Frequency	Type	Wavelength
	—	
$10^{18} - 10^{20}$	γ rays	$10^{-12} - 10^{-10}$
$10^{16} - 10^{18}$	X-rays	$10^{-10} - 10^{-8}$
$10^{15} - 10^{16}$	UV	$10^{-8} - 10^{-7}$
	—	
$10^{14} - 10^{15}$	blue	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	yellow	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	red	$10^{-7} - 10^{-6}$
	—	
$10^{11} - 10^{14}$	IR	$10^{-6} - 10^{-3}$
$10^9 - 10^{11}$	microwave	$10^{-3} - 10^{-1}$
$1 - 10^9$	radio	$10^{-1} - 10^8$

For more on all this, including mathematical proofs of the above facts, then some basic optics, and then applications to basic quantum mechanics, we refer to chapter 9.

13b. Rayleigh-Jeans

Our discussion so far implicitly used the fact that heat is light too, and so time now, before getting into quantum mechanics, to get back to the theory of heat, as developed before, and see what our new viewpoint on it can bring. The main problem here is to compute the radiation of black bodies, and we will discuss this now.

Consider a black body, that is to say, a body at thermal equilibrium, assumed to be at temperature T . This body radiates heat, and we are interested in computing the energy density of the radiation $\mathcal{E}(\nu, T)$, around a given frequency ν of this radiation.

Quite surprisingly, the intuitive and honest modelling of the problem, and the subsequent math, done honestly too, lead to a spectacularly wrong result, as follows:

THEOREM 13.4. *We have the Rayleigh-Jeans formula for the energy density*

$$\mathcal{E}(\nu, T) = \frac{8\pi bT}{c^3} \nu^2$$

where b is the Boltzmann constant, leading globally to the divergent integral

$$\mathcal{E} = \frac{8\pi bTV}{c^3} \int_0^\infty \nu^2 d\nu$$

over a volume V , with this divergence phenomenon being called *UV catastrophe*.

PROOF. This is arguably the most famous wrong result in the history of physics, so we will spend some time in trying to understand its proof. And with the comment that this will be no waste of time, because the fix, found later by Max Planck, uses exactly the same ideas and computations, but with an unexpected twist at the end.

(1) Our starting point are the equations for the electromagnetic radiation, that we will now regard as heat, as formulated before, namely:

$$\begin{aligned} E &= \operatorname{Re}(\tilde{E}) & : & \quad \tilde{E} = e_n e^{i(\langle k_n, x \rangle - w_n t)} \\ B &= \operatorname{Re}(\tilde{B}) & : & \quad \tilde{B} = b_n e^{i(\langle k_n, x \rangle - w_n t)} \end{aligned}$$

Here n is a certain parameter, that will appear later on, and that we can for the moment ignore. Now inserting this data into the Maxwell equations gives the following formulae, connecting the parameters, that we will use several times in what follows:

$$\begin{aligned} k_n \times b_n + \frac{w_n}{c} e_n &= 0 \\ k_n \times e_n - \frac{w_n}{c} b_n &= 0 \\ \langle k_n, e_n \rangle &= \langle k_n, b_n \rangle = 0 \end{aligned}$$

(2) Let us compute the electromagnetic energy in a finite volume $V = L^3$. We will use here the well-known fact, coming from classical electrodynamics, that the energy density in radiation is $(\|E\|^2 + \|B\|^2)/8\pi$. Thus, the energy we are looking for is given by:

$$\mathcal{E} = \frac{1}{8\pi} \int_V (\|E\|^2 + \|B\|^2)$$

(3) In order to compute this integral, let us better model our question. Due to obvious periodicity reasons, the wave number k and the angular frequency w must be of the following form, with $n \in \mathbb{Z}^3$ being a vector with integer components:

$$k_n = \frac{2\pi}{L} \cdot n \quad , \quad w_n = c \|k_n\|$$

Thus, the electric and magnetic fields in our enclosure $V = L^3$ appear as linear combinations as follows, for certain vectors $e_n, b_n \perp n$, related by the formulae in (1):

$$\begin{aligned} E &= \operatorname{Re}(\tilde{E}) & : & \quad \tilde{E} = \sum_n e_n e^{i(\langle k_n, x \rangle - w_n t)} \\ B &= \operatorname{Re}(\tilde{B}) & : & \quad \tilde{B} = \sum_n b_n e^{i(\langle k_n, x \rangle - w_n t)} \end{aligned}$$

(4) According to the above formula of E , we have:

$$\begin{aligned}
\|E\|^2 &= \|Re(\tilde{E})\|^2 \\
&= \frac{1}{4} \left\| \sum_n e_n e^{i(\langle k_n, x \rangle - w_n t)} + \bar{e}_n e^{-i(\langle k_n, x \rangle - w_n t)} \right\|^2 \\
&= \frac{1}{4} \sum_{nm} \langle e_n, e_m \rangle e^{i(\langle k_n - k_m, x \rangle - (w_n - w_m)t)} \\
&\quad + \frac{1}{4} \sum_{nm} \langle e_n, \bar{e}_m \rangle e^{i(\langle k_n + k_m, x \rangle - (w_n + w_m)t)} \\
&\quad + \frac{1}{4} \sum_{nm} \langle \bar{e}_n, e_m \rangle e^{i(-\langle k_n + k_m, x \rangle + (w_n + w_m)t)} \\
&\quad + \frac{1}{4} \sum_{nm} \langle \bar{e}_n, \bar{e}_m \rangle e^{i(-\langle k_n - k_m, x \rangle + (w_n - w_m)t)}
\end{aligned}$$

(5) Now by integrating, we obtain the following formula:

$$\begin{aligned}
\frac{1}{V} \int_V \|E\|^2 &= \frac{1}{4} \sum_n \langle e_n, e_n \rangle + \frac{1}{4} \sum_n \langle e_n, \bar{e}_{-n} \rangle e^{-2iw_n t} \\
&\quad + \frac{1}{4} \sum_n \langle \bar{e}_n, e_{-n} \rangle e^{2iw_n t} + \frac{1}{4} \sum_n \langle \bar{e}_n, \bar{e}_n \rangle
\end{aligned}$$

(6) Similarly, according to the above formula of B , we have:

$$\begin{aligned}
\frac{1}{V} \int_V \|B\|^2 &= \frac{1}{4} \sum_n \langle b_n, b_n \rangle + \frac{1}{4} \sum_n \langle b_n, \bar{b}_{-n} \rangle e^{-2iw_n t} \\
&\quad + \frac{1}{4} \sum_n \langle \bar{b}_n, b_{-n} \rangle e^{2iw_n t} + \frac{1}{4} \sum_n \langle \bar{b}_n, \bar{b}_n \rangle
\end{aligned}$$

(7) Before summing the integrals that we found, let us use the formulae connecting the parameters k_n, e_n, b_n found in (1) above, namely:

$$k_n \times b_n + \frac{w_n}{c} e_n = 0$$

$$k_n \times e_n - \frac{w_n}{c} b_n = 0$$

$$\langle k_n, e_n \rangle = \langle k_n, b_n \rangle = 0$$

By using these formulae, we first obtain the following identity:

$$\begin{aligned} \langle b_n, b_n \rangle &= \frac{c^2}{w_n^2} \langle k_n \times e_n, k_n \times e_n \rangle \\ &= \frac{c^2 \|k_n\|^2}{w_n^2} \langle e_n, e_n \rangle \\ &= \langle e_n, e_n \rangle \end{aligned}$$

Similarly, we have we well the following identity:

$$\begin{aligned} \langle b_n, \bar{b}_{-n} \rangle &= \frac{c^2}{w_n^2} \langle k_n \times e_n, k_{-n} \times \bar{e}_n \rangle \\ &= -\frac{c^2 \|k_n\|^2}{w_n^2} \langle e_n, \bar{e}_{-n} \rangle \\ &= -\langle e_n, \bar{e}_{-n} \rangle \end{aligned}$$

Also similarly, we have as well the following identity:

$$\begin{aligned} \langle \bar{b}_n, b_{-n} \rangle &= \frac{c^2}{w_n^2} \langle k_n \times \bar{e}_n, k_{-n} \times e_n \rangle \\ &= -\frac{c^2 \|k_n\|^2}{w_n^2} \langle \bar{e}_n, e_{-n} \rangle \\ &= -\langle \bar{e}_n, e_{-n} \rangle \end{aligned}$$

Finally, we have as well the following identity:

$$\begin{aligned} \langle \bar{b}_n, \bar{b}_n \rangle &= \frac{c^2}{w_n^2} \langle k_n \times \bar{e}_n, k_n \times \bar{e}_n \rangle \\ &= \frac{c^2 \|k_n\|^2}{w_n^2} \langle \bar{e}_n, \bar{e}_n \rangle \\ &= \langle \bar{e}_n, \bar{e}_n \rangle \end{aligned}$$

(8) We conclude that when summing the integrals computed in (5) and (6), all the terms involving phases will cancel, and we obtain the following formula:

$$\frac{1}{V} \int_V \|E\|^2 + \|B\|^2 = \frac{1}{2} \sum_n \langle e_n, e_n \rangle + \frac{1}{2} \sum_n \langle \bar{e}_n, \bar{e}_n \rangle$$

Now by multiplying everything by $V/8\pi$, as explained in (2), we obtain:

$$\mathcal{E} = \frac{V}{16\pi} \sum_n (\langle e_n, e_n \rangle + \langle \bar{e}_n, \bar{e}_n \rangle)$$

(9) The point now is that, by computing this sum, we are led to the Rayleigh-Jeans formula in the statement for the corresponding radiation energy density, namely:

$$\mathcal{E}(\nu, T) = \frac{8\pi bT}{c^3} \nu^2$$

(10) And this is certainly wrong, because the total energy which is radiated by our black body, all over the frequency spectrum, follows to be:

$$\mathcal{E} = \frac{8\pi bTV}{c^3} \int_0^\infty \nu^2 d\nu = \infty$$

More precisely, the Rayleigh-Jeans formula works quite well all across the frequency spectrum, in particular fitting well with the known data, except for the UV range, where things diverge. And with this phenomenon being called “UV catastrophe”. \square

13c. Max Planck

Well, looks like we are in deep trouble here. Fortunately, the solution to the UV catastrophe, and to the black body problem in general, was found a few years later by Max Planck, his bold new modelling method, and result, being as follows:

THEOREM 13.5. *The correct formula for the black body radiation, obtained by assuming that energy is quantized, is the Planck formula*

$$\mathcal{E}(\nu, T) d\nu = \frac{8\pi h_0}{c^3} \cdot \frac{\nu^3 d\nu}{e^{h_0\nu/bT} - 1}$$

with h_0 being a new constant, called Planck constant. This formula fits with all known data, fits as well with Rayleigh-Jeans outside the UV range, and globally leads to

$$\mathcal{E} = \int_0^\infty \mathcal{E}(\nu, T) d\nu = aT^4$$

with the radiation energy constant on the right being given by:

$$a = \frac{16\pi^8 b^4}{15h_0^3 c^3}$$

PROOF. This is something quite technical, obtained by further building on the formula found in (8) above, but counting this time in a new way, by assuming that the energy is quantized. For details here, and for more, we refer for instance to Weinberg [91]. \square

So, this is the famous Planck formula, whose consequences go far beyond its scope. Indeed, regardless on what the original problem was about, namely black bodies, and who cares after all about them, we have now proof for the fact that the energy is quantized. And this, simply because any attempt of solving the problem without assuming that energy is quantized leads to a catastrophe, as explained before.

Finally, a word about the new constant appearing in the above, namely the Planck constant. Due to some technical reasons, we will use here a non-standard notation for this constant, with the figures and our conventions being as follows:

FACT 13.6. *The Planck constant is given by the exact formula*

$$h_0 = 6.626\ 070\ 15 \times 10^{-34}$$

as per latest SI regulations. We will also use the reduced Planck constant, given by

$$h = \frac{h_0}{2\pi}$$

which is numerically given by

$$h \simeq 1.054\ 571\ 817 \times 10^{-34}$$

with everything being as usual in standard units.

To be more precise here, the point is that in quantum mechanics the constant which appears all the time is the reduced Planck constant, usually denoted $\hbar = h/2\pi$, with the original Planck constant being denoted h . However, the point is that, at least in what concerns us, we will heavily use for our quantum mechanics computations both this reduced Planck constant \hbar and the unnormalized trace of matrices tr . And the problem is that, in quick handwriting, tr , \hbar often get confused, and when you compute you can't stop cursing, and you end up adopting the convention $h = h_0/2\pi$, as above.

13d. Some cosmology

Finally, let us mention that a very interesting continuation of Planck's work concerns the black body radiation of the early universe, with the microwave part of it, via a Doppler shift, still permeating the space that we live in. And with this phenomenon, called "cosmic microwave background", being at the origin of all modern cosmology.

13e. Exercises

Exercises.

CHAPTER 14

Bosons, fermions

14a. States, observables

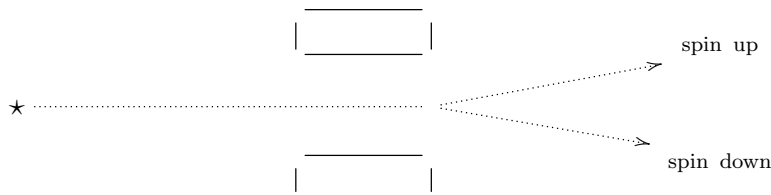
As a continuation of the quantum mechanics developed so far, first in chapter 9 as an introduction to molecules, and then in the previous chapter in relation with blackbody radiation, let us talk now about particle spin. We have already met spin in chapter 9, via the Pauli principle, which is needed for advanced atomic theory, but we still have:

QUESTION 14.1. *What is the electron spin? That is, what experiments prove that the electron spins? And then, importantly, what is the mathematics of the spin?*

Talking mathematics first, the spin, if that beast exists indeed, is certainly not visible on the wave function ψ , because this wave function deals with position only. Thus, at least we know one thing, once the spin observed, we will most likely have to incorporate it into our theory by using the matrix mechanics formalism of Heisenberg.

Talking physics now, the main experiment leading to spin is as follows:

FACT 14.2 (Stern-Gerlach experiment). *When passing a beam of electrons through an inhomogeneous magnetic field, these electrons get deflected 50 – 50 up or down,*



with the only possible explanation being that the electrons have a spin, which is 50 – 50 up or down. The same happens with a beam of neutral atoms, and a magnetic field strong enough, to be put at blame being the statistics of the spins of the constituents.

So, this was the experiment, and what we call here “up” and “down” is of course the binary choice of the spin orientation, a bit as for usual, round objects in \mathbb{R}^3 . That is, our Earth turns to the right, and in physics we would say that it has “spin up”. Was the Earth turning to the left, we would say in physics that it has “spin down”.

Of course, our presentation above is over-simplified. The original experiment was with neutral particles, namely silver atoms, and this in order to avoid the Lorentz force, which

will curve the trajectory of any charged particle, to a much greater extent than the spin up/down deviation to be observed. Later experiments, with charged particles, used some extra apparatus, namely a suitable electric field, positioned after the electromagnet in the above diagram, designed to cancel the effects of the Lorentz force.

As an important observation, the Stern-Gerlach experiment does not observe the absolute, 3D spin up/down feature of the particles, but just a 1D component of it. However, it is possible to cascade experiments, by sending each of the output beams into separate Stern-Gerlach devices, and with these devices having various 3D orientations, and deduce some further conclusions from this. We refer here to Feynman [30].

But, what is spin? Many things can be said here, but fortunately, there is a simple way of viewing things, inspired from classical mechanics, or even from the movement of our good old Earth, which rotates and spins at the same time, which is as follows:

PHILOSOPHY 14.3. *In analogy with classical mechanics, spin should be something of same nature as angular momentum, coming on top of it.*

In practice now, following Uhlenbeck, Goudsmit, Pauli, we will first talk angular momentum, then we will axiomatize spin as being the quantity which naturally “complements” the angular momentum. Then we will talk about 2×2 matrices, and more.

But before this, we must first build on the quantum mechanics briefly explained in chapter 9, following Heisenberg, Schrödinger and others. Let us start with:

CLAIM 14.4 (Schrödinger). *In the context of the hydrogen atom, the amplitude function of the electron $\psi = \psi_t(x)$ is subject to the Schrödinger equation*

$$ih\dot{\psi} = -\frac{h^2}{2m}\Delta\psi + V\psi$$

m being the mass, h the modified Planck constant, and V the Coulomb potential of the proton. The same holds for movements of the electron under an arbitrary potential V .

Observe the similarity with the wave equation $\ddot{\varphi} = v^2\Delta\varphi$, and with the heat equation $\dot{\varphi} = \alpha\Delta\varphi$ too. There might be of course some speculations to be made here, but passed that, this is certainly not your easy to decipher equation. So, where does this equation come from? Is there a way of deducing it from simpler principles? And so on.

Generally speaking, however, any axiomatic explanation for the Schrödinger equation can only introduce some possible mistakes in our theory. And so we are led by precaution to the following preliminary answer, to such questions, that you might have:

COMMENT 14.5. *The Schrödinger equation comes from Schrödinger.*

And please do not take this as a joke. We are mainly interested in solving the hydrogen atom, and the Schrödinger equation can only solve it, via some calculus. So why not enjoying this, solving the hydrogen atom by using this equation, and see later what further things, beyond Schrödinger, can be said about quantum mechanics.

This being said, before getting into computations, let us discuss however, a bit in advance, some possible ways of getting into the Schrödinger equation. We first have:

COMMENT 14.6. *The Schrödinger equation appears naturally from an abstract claim of de Broglie, regarding the precise wave properties of the electron.*

To be more precise here, the above-mentioned abstract claim of de Broglie leads to the following equations for the wave function of a free electron:

$$\psi_t = e^{-iEt/\hbar}\psi_0 \quad , \quad E\psi_0 = -\frac{\hbar^2}{2m}\Delta\psi_0$$

Now in the context of movement under a time-independent potential V , as is the potential coming from the proton, these equations can be naturally modified into:

$$\psi_t = e^{-iEt/\hbar}\psi_0 \quad , \quad E\psi_0 = -\frac{\hbar^2}{2m}\Delta\psi_0 + V\psi_0$$

But this is exactly the simplified form of the general Schrödinger equation from Claim 14.4, in the case of a time-independent potential, as we will soon see.

We have as well a second method for getting into the Schrödinger equation, a bit more powerful, but based on more powerful assumptions too, as follows:

COMMENT 14.7. *The Schrödinger equation appears naturally by invoking a bit of matrix mechanics of Heisenberg type, and the Hamiltonian.*

To be more precise here, according to the viewpoint of Heisenberg, the total energy, or Hamiltonian, $H = T + V$ is represented by the following “operator”:

$$\widehat{H} = -\frac{\hbar^2\Delta}{2m} + V$$

And in terms of this operator, the Schrödinger equation simply appears as:

$$i\hbar\dot{\psi} = \widehat{H}\psi$$

This is actually the explanation offered by Schrödinger himself in his paper, and we will comment on this a bit later, when having a better knowledge of the subject. We refer also to Feynman [30], Griffiths [38], Weinberg [91] for more on all this.

Now, let us go back to the Schrödinger equation from Claim 14.4, and try to solve it. Let us start with some computations. As a first question, we would like to see how the probability density $\varphi = |\psi|^2$ evolves in time, and we have here:

PROPOSITION 14.8. *In the context of the general Schrödinger equation,*

$$ih\dot{\psi} = -\frac{\hbar^2}{2m}\Delta\psi + V\psi$$

we have the following formula,

$$\dot{\varphi} = \frac{ih}{2m} (\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi)$$

for the time derivative of the probability density function $\varphi = |\psi|^2$.

PROOF. According to the Leibnitz product rule, we have the following formula:

$$\dot{\varphi} = \frac{d}{dt}|\psi|^2 = \frac{d}{dt}(\psi\bar{\psi}) = \dot{\psi}\bar{\psi} + \psi\dot{\bar{\psi}}$$

On the other hand, the Schrödinger equation and its conjugate read:

$$\begin{aligned}\dot{\psi} &= \frac{ih}{2m} \left(\Delta\psi - \frac{2m}{\hbar^2}V\psi \right) \\ \dot{\bar{\psi}} &= -\frac{ih}{2m} \left(\Delta\bar{\psi} - \frac{2m}{\hbar^2}V\bar{\psi} \right)\end{aligned}$$

By plugging this data, we obtain the following formula:

$$\dot{\varphi} = \frac{ih}{2m} \left[\left(\Delta\psi - \frac{2m}{\hbar^2}V\psi \right) \bar{\psi} - \left(\Delta\bar{\psi} - \frac{2m}{\hbar^2}V\bar{\psi} \right) \psi \right]$$

But this gives, after simplifying, the formula in the statement. □

As an important application of Proposition 14.8, we have:

THEOREM 14.9. *The general Schrödinger equation, namely*

$$ih\dot{\psi} = -\frac{\hbar^2}{2m}\Delta\psi + V\psi$$

conserves probability amplitudes, in the sense that we have

$$\int_{\mathbb{R}^3} |\psi_0|^2 = 1 \implies \int_{\mathbb{R}^3} |\psi_t|^2 = 1$$

in agreement with the basic probabilistic requirement, $P = 1$ overall.

PROOF. According to the formula in Proposition 14.8, we have:

$$\begin{aligned}\frac{d}{dt} \int_{\mathbb{R}^3} |\psi|^2 dx &= \int_{\mathbb{R}^3} \frac{d}{dt} |\psi|^2 dx \\ &= \int_{\mathbb{R}^3} \dot{\varphi} dx \\ &= \frac{ih}{2m} \int_{\mathbb{R}^3} (\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi) dx\end{aligned}$$

Now by remembering the definition of the Laplace operator, we have:

$$\begin{aligned}
 \frac{d}{dt} \int_{\mathbb{R}^3} |\psi|^2 dx &= \frac{i\hbar}{2m} \int_{\mathbb{R}^3} \sum_i \left(\frac{d^2\psi}{dx_i^2} \cdot \bar{\psi} - \frac{d^2\bar{\psi}}{dx_i^2} \cdot \psi \right) dx \\
 &= \frac{i\hbar}{2m} \sum_i \int_{\mathbb{R}^3} \frac{d}{dx_i} \left(\frac{d\psi}{dx_i} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx_i} \cdot \psi \right) dx \\
 &= \frac{i\hbar}{2m} \sum_i \int_{\mathbb{R}^2} \left[\frac{d\psi}{dx} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx} \cdot \psi \right]_{-\infty}^{\infty} \frac{dx}{dx_i} \\
 &= \frac{i\hbar}{2m} \sum_i \int_{\mathbb{R}^2} 0 \frac{dx}{dx_i} \\
 &= 0
 \end{aligned}$$

Here we have used at the end the assumption, which is physically speaking, something reasonable, that the wave function and its derivatives vanish at ∞ . Now with this in hand, since the quantity under consideration is constant, we obtain the result. \square

Let us do now some computations, in order to get some insight into the quantum mechanics of the particle, as dictated by the Schrödinger equation. We first have:

THEOREM 14.10. *The average position and momentum of the particle are*

$$\begin{aligned}
 \langle x \rangle &= \int_{\mathbb{R}^3} x |\psi|^2 dx \\
 \langle p \rangle &= -i\hbar \int_{\mathbb{R}^3} \nabla\psi \cdot \bar{\psi} dx
 \end{aligned}$$

with the convention that the average speed is the derivative of the average position.

PROOF. This follows again by doing some math, as follows:

(1) The formula for the average position $\langle x \rangle$ is clear from definitions. Regarding now the average speed $\langle v \rangle$, we have here the following computation:

$$\begin{aligned}
 \langle v \rangle &= \frac{d \langle x \rangle}{dt} \\
 &= \int_{\mathbb{R}^3} x \cdot \frac{d}{dt} |\psi|^2 dx \\
 &= \int_{\mathbb{R}^3} x \dot{\varphi} dx \\
 &= \frac{i\hbar}{2m} \int_{\mathbb{R}^3} x (\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi) dx
 \end{aligned}$$

(2) But each of the components can be computed as follows, by taking into account the vanishing formula found in the proof of Theorem 14.9:

$$\begin{aligned}
\langle v \rangle_i &= \frac{ih}{2m} \int_{\mathbb{R}^3} x_i (\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi) dx \\
&= \frac{ih}{2m} \int_{\mathbb{R}^3} x_i \sum_j \left(\frac{d^2\psi}{dx_j^2} \cdot \bar{\psi} - \frac{d^2\bar{\psi}}{dx_j^2} \cdot \psi \right) dx \\
&= \frac{ih}{2m} \sum_j \int_{\mathbb{R}^3} x_i \left(\frac{d^2\psi}{dx_j^2} \cdot \bar{\psi} - \frac{d^2\bar{\psi}}{dx_j^2} \cdot \psi \right) dx \\
&= \frac{ih}{2m} \int_{\mathbb{R}^3} x_i \left(\frac{d^2\psi}{dx_i^2} \cdot \bar{\psi} - \frac{d^2\bar{\psi}}{dx_i^2} \cdot \psi \right) dx
\end{aligned}$$

(3) We can now finish the computation by doing two partial integrations, as follows:

$$\begin{aligned}
\langle v \rangle_i &= \frac{ih}{2m} \int_{\mathbb{R}^3} x_i \cdot \frac{d}{dx_i} \left(\frac{d\psi}{dx_i} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx_i} \cdot \psi \right) dx \\
&= -\frac{ih}{2m} \int_{\mathbb{R}^3} \left(\frac{d\psi}{dx_i} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx_i} \cdot \psi \right) dx \\
&= -\frac{ih}{m} \int_{\mathbb{R}^3} \frac{d\psi}{dx_i} \cdot \bar{\psi} dx
\end{aligned}$$

(4) We conclude that the average speed is given by the following formula:

$$\langle v \rangle = -\frac{ih}{m} \int_{\mathbb{R}^3} \nabla\psi \cdot \bar{\psi} dx$$

By multiplying by the mass, we obtain the formula for $\langle p \rangle$ in the statement. \square

As an interesting speculation now, based on the above two formulae, and inspired from Heisenberg's idea of matrix mechanics, we have:

SPECULATION 14.11. *The average position and momentum formulae, written as*

$$\begin{aligned}
\langle x \rangle &= \int_{\mathbb{R}^3} \bar{\psi} \cdot x \cdot \psi dx \\
\langle p \rangle &= \int_{\mathbb{R}^3} \bar{\psi} \cdot (-ih\nabla) \cdot \psi dx
\end{aligned}$$

suggest that x represents position, and $-ih\nabla$ represents momentum.

Here we don't quite know what the quantities x and $-ih\nabla$ really are, mathematically speaking, so let us call them "operators", and we'll see later for axioms. Now with this convention, the above tells us that for computing the average value of x, p , we must "sandwich" the corresponding operator between $\bar{\psi}, \psi$, and then integrate.

Which is something quite remarkable, and we are now very tempted to formulate something extremely general, and of course still a bit vague, as follows:

SPECULATION 14.12. *The average value of an observable O should appear as*

$$\langle O \rangle = \int_{\mathbb{R}^3} \bar{\psi} \cdot \hat{O} \cdot \psi \, dx$$

“sandwich between $\bar{\psi}, \psi$ and integrate”, where \hat{O} is the operator associated to O .

As an illustration, let us see if this sandwiching method works for the kinetic energy of the particle. The kinetic energy is given by the following formula:

$$T = \frac{m||v||^2}{2} = \frac{\langle p, p \rangle}{2m}$$

Thus, the operator associated to the energy should be given by:

$$\hat{T} = \frac{\langle -ih\nabla, -ih\nabla \rangle}{2m} = -\frac{h^2\Delta}{2m}$$

We obtain in this way something which looks quite reasonable, as follows:

$$\langle T \rangle = -\frac{h^2}{2m} \int_{\mathbb{R}^3} \Delta\psi \cdot \bar{\psi} \, dx$$

More generally now, we can incorporate into this the potential energy too, and we are led in this way to the following interesting, conceptual conclusion:

CONCLUSION 14.13. *According to the above speculations, the operator associated to the total energy, or Hamiltonian, $H = T + V$ is given by*

$$\hat{H} = -\frac{h^2\Delta}{2m} + V$$

and so the Schrödinger equation itself appears as

$$ih\dot{\psi} = \hat{H}\psi$$

in terms of this operator, as claimed in Comment 14.7.

To be more precise, according to the above, \hat{H} appears indeed via the formula in the statement. But now, let us look back at the Schrödinger equation, namely:

$$ih\dot{\psi} = -\frac{h^2}{2m}\Delta\psi + V\psi$$

We recognize on the right the operator \hat{H} acting on ψ , and we are led to the conclusion in the statement. But probably enough for now on this topic, and more later.

14b. Momentum, spin

With the above general theory in hand, getting back now to our particle spin questions, as previously agreed, we will first talk about angular momentum, and we will get to spin later. We will need the following basic result, for doing computations:

PROPOSITION 14.14. *The components of the position operator $x = (x_1, x_2, x_3)$ and momentum operator $p = -ih\nabla$ satisfy the following relations,*

$$\begin{aligned} [x_i, x_j] &= [p_i, p_j] = 0 \\ [x_i, p_j] &= ih\delta_{ij} \end{aligned}$$

where $[a, b] = ab - ba$, called canonical commutation relations.

PROOF. All the above formulae are elementary, as follows:

(1) The components of the position operator $x = (x_1, x_2, x_3)$ obviously commute with each other, $x_i x_j = x_j x_i$, which makes their commutators vanish, $[x_i, x_j] = 0$.

(2) Regarding the momentum operator $p = -ih\nabla$, its components are as follows:

$$p_1 = -ih \cdot \frac{d}{dx_1} \quad , \quad p_2 = -ih \cdot \frac{d}{dx_2} \quad , \quad p_3 = -ih \cdot \frac{d}{dx_3}$$

Since partial derivatives commute with each other, we obtain $[p_i, p_j] = 0$.

(3) It remains to prove the last formula, and we have here:

$$\begin{aligned} [x_i, p_j]f &= (x_i p_j - p_j x_i)f \\ &= -ih \left(x_i \cdot \frac{df}{dx_j} - \frac{d}{dx_j}(x_i f) \right) \\ &= -ih \left(x_i \cdot \frac{df}{dx_j} - \frac{dx_i}{dx_j} \cdot f - x_i \cdot \frac{df}{dx_j} \right) \\ &= ih \cdot \frac{dx_i}{dx_j} \cdot f \\ &= ih\delta_{ij} \cdot f \end{aligned}$$

Thus, we are led to the conclusion in the statement. \square

The above might look a bit complicated, and the simplest way to remember it is that “everything commutes”, that is, $ab = ba$, except for the coordinates and momenta coordinates taken in the same direction, which are subject to the following rule:

$$x_i p_i = p_i x_i + ih$$

Getting now to angular momentum, it is convenient to change notation, with (x, y, z) instead of (x_1, x_2, x_3) , due to the vector product involved, which will break the symmetry between coordinates. We have the following result, to start with:

THEOREM 14.15. *The components of the angular momentum operator*

$$L = x \times (-i\hbar\nabla)$$

satisfy the following equations,

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

called commutation relations for the angular momentum.

PROOF. With the more familiar notation $p = -i\hbar\nabla$ for momentum, or rather for the associated operator, the components of the angular momentum operator are:

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

Let us prove the first commutation relation. We have:

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \end{aligned}$$

By heavily using the commutation relations from Proposition 14.14, we have:

$$[yp_z, zp_x] = yp_z zp_x - zp_x yp_z = y(zp_z - i\hbar)p_x - zp_x p_z = -i\hbar yp_x$$

$$[yp_z, xp_z] = yp_z xp_z - xp_z yp_z = 0$$

$$[zp_y, zp_x] = zp_y zp_x - zp_x zp_y = 0$$

$$[zp_y, xp_z] = zp_y xp_z - xp_z zp_y = zxp_y p_z - x(zp_z - i\hbar)p_y = i\hbar xp_y$$

We conclude that the commutator that we were computing is given by the following formula, which is precisely the one in the statement:

$$\begin{aligned} [L_x, L_y] &= -i\hbar yp_x + i\hbar xp_y \\ &= i\hbar(xp_y - yp_x) \\ &= i\hbar L_z \end{aligned}$$

The proof of the other two commutation relations is similar, or can be simply obtained by invoking the cyclic invariance $x \rightarrow y \rightarrow z \rightarrow x$ of our problem, which cyclic invariance is not broken by the vector product \times used, and so can indeed be invoked. \square

As an interesting consequence of Theorem 14.15, we have:

PROPOSITION 14.16. *The following operator, called square of angular momentum*

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

commutes with all 3 operators L_x, L_y, L_z .

PROOF. We have the following computation, to start with:

$$\begin{aligned} [L^2, L_x] &= (L_x^2 + L_y^2 + L_z^2)L_x - L_x(L_x^2 + L_y^2 + L_z^2) \\ &= L_y^2 L_x + L_z^2 L_x - L_x L_y^2 - L_x L_z^2 \\ &= [L_y^2, L_x] + [L_z^2, L_x] \end{aligned}$$

The first commutator can be computed with a trick, as follows:

$$\begin{aligned} [L_y^2, L_x] &= L_y L_y L_x - L_x L_y L_y \\ &= L_y L_y L_x - L_y L_x L_y + L_y L_x L_y - L_x L_y L_y \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y \\ &= L_y (-i\hbar L_z) + (-i\hbar L_z) L_y \\ &= -i\hbar (L_y L_z + L_z L_y) \end{aligned}$$

The second commutator can be computed with the same trick, as follows:

$$\begin{aligned} [L_z^2, L_x] &= L_z L_z L_x - L_x L_z L_z \\ &= L_z L_z L_x - L_z L_x L_z + L_z L_x L_z - L_x L_z L_z \\ &= L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= i\hbar (L_z L_y + L_y L_z) \end{aligned}$$

Now by summing we obtain the following commutation relation, as desired:

$$[L^2, L_x] = 0$$

The proof of the other two commutation relations is similar, or we can simply invoke here the cyclic symmetry argument from the end of the proof of Theorem 14.15. \square

Let us discuss now the diagonalization of the momentum operators L_x, L_y, L_z . Since these operators do not commute, we cannot hope for a joint diagonalization for them. Thus, we must choose one of them, and for reasons that will become clear later, when writing things in spherical coordinates, we will choose L_x .

In view of Proposition 14.16, this operator L_x does commute with L^2 , and so we can hope for a joint diagonalization of L^2, L_x . And, so is what happens:

THEOREM 14.17. *The operators L^2, L_x diagonalize as*

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m$$

$$L_x f_l^m = \hbar m f_l^m$$

where $l \in \mathbb{N}/2$ and $m = -l, -l+1, \dots, l-1, l$.

PROOF. This is something quite long, the idea being as follows:

(1) For reasons that will become clear later on, let us introduce two operators as follows, called raising and lowering operators:

$$L_+ = L_y + iL_z$$

$$L_- = L_y - iL_z$$

We will often deal with these operators at the same time, using the following notation:

$$L_{\pm} = L_y \pm iL_z$$

(2) We have the following computation:

$$\begin{aligned} [L_x, L_{\pm}] &= [L_x, L_y] \pm i[L_x, L_z] \\ &= ihL_z \pm i(-ihL_y) \\ &= h(iL_z \pm L_y) \\ &= \pm h(\pm iL_z + L_y) \\ &= \pm hL_{\pm} \end{aligned}$$

(3) Our claim now is that $L^2 f = \lambda f$, $L_x f = \mu f$ imply:

$$L^2(L_{\pm}f) = \lambda(L_{\pm}f)$$

$$L_x(L_{\pm}f) = (\mu \pm h)(L_{\pm}f)$$

Indeed, the first formula follows from:

$$\begin{aligned} L^2(L_{\pm}f) &= L_{\pm}(L^2 f) \\ &= L_{\pm}(\lambda f) \\ &= \lambda(L_{\pm}f) \end{aligned}$$

As for the second formula, this follows from:

$$\begin{aligned} L_x(L_{\pm}f) &= L_x L_{\pm}f \\ &= (L_x L_{\pm} - L_{\pm} L_x)f + L_{\pm} L_x f \\ &= \pm h L_{\pm}f + L_{\pm}(\mu f) \\ &= (\mu \pm h)(L_{\pm}f) \end{aligned}$$

(4) Now in view of the formulae found in (3), the raising and lowering operators act on the joint eigenfunctions of L^2 , L_x , by leaving the L^2 eigenvalue unchanged, and by raising and lowering the eigenvalue of L_x . But both this raising process and lowering process for

the eigenvalue of L_x cannot go on forever, because of the following estimate:

$$\begin{aligned}
 \lambda &= \langle L^2 \rangle \\
 &= \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle \\
 &= \mu^2 + \langle L_y^2 \rangle + \langle L_z^2 \rangle \\
 &\geq \mu^2
 \end{aligned}$$

(5) In order to see exactly how the raising and lowering processes terminate, we will need some more computations. We have:

$$\begin{aligned}
 L_{\pm}L_{\mp} &= (L_y \pm iL_z)(L_y \mp iL_z) \\
 &= L_y^2 + L_z^2 \mp i(L_yL_z - L_zL_y) \\
 &= L_y^2 + L_z^2 \mp i(i\hbar L_x) \\
 &= L_y^2 + L_z^2 \pm \hbar L_x \\
 &= L^2 - L_x^2 \pm \hbar L_x
 \end{aligned}$$

Thus, we have the following formula:

$$L^2 = L_{\pm}L_{\mp} + L_x^2 \mp \hbar L_x$$

Now assuming $L_x f = \hbar l f$, at termination of the raising process, we have:

$$\begin{aligned}
 L^2(f) &= (L_-L_+ + L_x^2 + \hbar L_x)f \\
 &= (0 + \hbar^2 l^2 + \hbar^2 l)f \\
 &= \hbar^2 l(l+1)f
 \end{aligned}$$

Similarly, assuming $L_x f = \hbar l' f$, at termination of the lowering process, we have:

$$\begin{aligned}
 L^2(f) &= (L_+ - L_- + L_x^2 - \hbar L_x)f \\
 &= (0 + \hbar^2 l'^2 - \hbar^2 l')f \\
 &= \hbar^2 l'(l' - 1)f
 \end{aligned}$$

We conclude from this that we have the following equality:

$$l(l+1) = l'(l' - 1)$$

But since the formula $l' = l+1$ is impossible, due to raising vs lowering, we must have $l' = -l$, and this finishes the proof.

(6) Finally, for being complete, the full and conceptual understanding of all the above imperatively requires a certain cat climbing a certain ladder, and for full details here, and for other things missing from the above proof, we refer to Griffiths [38]. \square

Moving ahead now, let us write everything in spherical coordinates, and find the eigenfunctions. We have here the following remarkable result:

THEOREM 14.18. *In spherical coordinates r, s, t we have*

$$L_x = -\frac{i\hbar}{dt}$$

$$L_y = i\hbar \left(\frac{\sin t}{ds} + \frac{\cos s \cos t}{\sin s} \cdot \frac{1}{dt} \right)$$

$$L_z = -i\hbar \left(\frac{\cos t}{ds} - \frac{\cos s \sin t}{\sin s} \cdot \frac{1}{dt} \right)$$

and the spherical harmonics are joint eigenfunctions of L^2, L_x .

PROOF. We recall that, according to our usual, N -dimensional looking conventions, the spherical coordinates are as follows, with $r \in [0, \infty)$ being the radius, $s \in [0, \pi]$ being the polar angle, and $t \in [0, 2\pi]$ being the azimuthal angle:

$$\begin{cases} x = r \cos s \\ y = r \sin s \cos t \\ z = r \sin s \sin t \end{cases}$$

(1) We know that we have $L = -i\hbar \mathbf{x} \times \nabla$, so let us first compute ∇ in spherical coordinates. We have here, according to the chain rule for derivatives:

$$\begin{aligned} \nabla &= \begin{pmatrix} dr/dx & ds/dx & dt/dx \\ dr/dy & ds/dy & dt/dy \\ dr/dz & ds/dz & dt/dz \end{pmatrix} \begin{pmatrix} d/dr \\ d/ds \\ d/dt \end{pmatrix} \\ &= \begin{pmatrix} dx/dr & dy/dr & dz/dr \\ dx/ds & dy/ds & dz/ds \\ dx/dt & dy/dt & dz/dt \end{pmatrix}^{-1} \begin{pmatrix} d/dr \\ d/ds \\ d/dt \end{pmatrix} \end{aligned}$$

(2) On the other hand, it is routine to check that we have:

$$\begin{pmatrix} dx/dr & dx/ds & dx/dt \\ dy/dr & dy/ds & dy/dt \\ dz/dr & dz/ds & dz/dt \end{pmatrix} = \begin{pmatrix} \cos s & -r \sin s & 0 \\ \sin s \cos t & r \cos s \cos t & -r \sin s \sin t \\ \sin s \sin t & r \cos s \sin t & r \sin s \cos t \end{pmatrix}$$

It is also routine to see that this latter matrix, say A , satisfies:

$$A^t A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2 \sin^2 s \end{pmatrix}$$

Now if we call D the diagonal matrix on the right, we conclude that the matrix, say B , appearing in the above formula of ∇ is given by:

$$\begin{aligned} B &= (A^t)^{-1} \\ &= AD^{-1} \\ &= \begin{pmatrix} \cos s & -r \sin s & 0 \\ \sin s \cos t & r \cos s \cos t & -r \sin s \sin t \\ \sin s \sin t & r \cos s \sin t & r \sin s \cos t \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/r^2 & 0 \\ 0 & 0 & 1/(r^2 \sin^2 s) \end{pmatrix} \\ &= \begin{pmatrix} \cos s & -\sin s/r & 0 \\ \sin s \cos t & \cos s \cos t/r & -\sin t/(r \sin s) \\ \sin s \sin t & \cos s \sin t/r & \cos t/(r \sin s) \end{pmatrix} \end{aligned}$$

(3) Thus, the angular momentum operator that we are looking for, $L = -ihx \times \nabla$, written more conveniently as $L = -ihx/r \times r\nabla$, is given by:

$$L = -ih \begin{pmatrix} \cos s \\ \sin s \cos t \\ \sin s \sin t \end{pmatrix} \times \begin{pmatrix} r \cos s & -\sin s & 0 \\ r \sin s \cos t & \cos s \cos t & -\sin t/\sin s \\ r \sin s \sin t & \cos s \sin t & \cos t/\sin s \end{pmatrix} \begin{pmatrix} d/dr \\ d/ds \\ d/dt \end{pmatrix}$$

And computing now the vector product gives the formula for L in the statement.

(4) Now with our explicit formula for L in hand, we next find that the raising and lowering operators are given by:

$$L_{\pm} = \pm he^{\pm it} \left(\frac{d}{ds} \pm i \frac{\cos s}{\sin s} \cdot \frac{1}{dt} \right)$$

Next, we find that these two operators satisfy the following formula:

$$L_+ L_- = -h^2 \left(\frac{d^2}{ds^2} + \frac{\cos s}{\sin s} \cdot \frac{d}{ds} + \frac{\cos^2 s}{\sin^2 s} \cdot \frac{d^2}{dt^2} + i \frac{d}{dt} \right)$$

And finally, by using this latter formula, we find that L^2 is given by:

$$L^2 = -h^2 \left(\frac{1}{\sin s} \cdot \frac{d}{ds} \left(\sin s \cdot \frac{d}{ds} \right) + \frac{1}{\sin^2 s} \cdot \frac{d^2}{dt^2} \right)$$

(5) With all these formulae in hand, we can now finish. The eigenfunction equation for the above operator L^2 , with eigenvalue $h^2 l(l+1)$, is as follows:

$$-h^2 \left(\frac{1}{\sin s} \cdot \frac{d}{ds} \left(\sin s \cdot \frac{d}{ds} \right) + \frac{1}{\sin^2 s} \cdot \frac{d^2}{dt^2} \right) f = h^2 l(l+1) f$$

But this is precisely the angular equation for the hydrogen atom. As for the eigenfunction equation for the operator L_x , with eigenvalue hm , this is as follows:

$$-\frac{ih}{dt} f = hm f$$

But this latter equation is equivalent to the azimuthal equation, also for the hydrogen atom. Thus, we are dealing here with equations that we already know, and the solutions are the spherical harmonics for the hydrogen atom, as claimed. \square

In order to talk now about spin, we will regard, a bit as in the classical mechanics case, the spin and the angular momentum as being similar quantities. Thus, in analogy with the basic equations for angular momentum, we should have:

DEFINITION 14.19. *The components of the spin operator are subject to*

$$[S_x, S_y] = ihS_z$$

$$[S_y, S_z] = ihS_x$$

$$[S_z, S_x] = ihS_y$$

called commutation relations for the spin operator.

The point now is that, with the above relations in hand, which are identical to the commutation relations for the angular momentum, all the general results from the previous section, based on that commutation relations, extend to our present setting, simply by changing L into S everywhere. And in particular, we are led in this way to:

THEOREM 14.20. *We have the following diagonalization formulae*

$$S^2 f_s^m = h^2 s(s+1) f_s^m$$

$$S_x f_s^m = hm f_s^m$$

$$S_{\pm} f_s^m = h\sqrt{s(s+1) - m(m \pm 1)} f_s^{m \pm 1}$$

involving the operators $S^2 = S_x^2 + S_y^2 + S_z^2$, S_x and $S_{\pm} = S_y \pm iS_z$.

PROOF. Here the first two formulae are something that we already know, from the previous section, with L, j being replaced by S, s . As for the last formula, this is something that we did not need, in the L, j context, but that we will need now. We want to compute the constants $C_{s,\pm}^m$ making work the raising and lowering formula, namely:

$$S_{\pm} f_s^m = C_{s,\pm}^m f_s^{m \pm 1}$$

But this can be done by using $S^2 = S_{\pm} S_{\mp} + S_x^2 \mp hS_x$ and $S_{\pm}^* = S_{\mp}$, and we get:

$$C_{s,+}^m = h\sqrt{s(s+1) - m(m+1)}$$

$$C_{s,-}^m = h\sqrt{s(s+1) - m(m-1)}$$

Thus, we are led to the last formula in the statement, and we are done. \square

In practice now, let us look for the simplest mathematical realization of spin. We know from the Stern-Gerlach experiment that the spin is something binary, that can be either up, or down. Thus, we are led, for fixed particles, to a quantum mechanics over $H = \mathbb{C}^2$, with spin up and down being represented by the following two vectors:

$$e_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad e_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

It remains now to see how the equations in Theorem 14.20 reformulate, in this $H = \mathbb{C}^2$ setting. But here, not many choices, and we are led to:

DEFINITION 14.21. *In the quantum mechanics of the spin, over $H = \mathbb{C}^2$, with*

$$e_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad e_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

being spin up and down, the spin is subject to the following equations, for $f = e_1, e_2$,

$$S^2 f = h^2 s(s+1) f$$

$$S_x f = h m_f f$$

$$S_{\pm} f = h \sqrt{s(s+1) - m_f(m_f \pm 1)} \check{f}$$

with parameters $s = 1/2$, $m_{e_1} = 1/2$, $m_{e_2} = -1/2$, and with $\{e_1, e_2\} = \{f, \check{f}\}$.

Here all the choices, and notably $s = 1/2$, are very natural in view of Theorem 14.20, because these are the choices providing a “minimal” realization of the equations in Theorem 14.20, in the smallest possible number of dimensions, namely $N = 2$. However, all this comes with a shade of mystery, or at least is not rock-solid enough as to be called theorem, and it is probably safer to use the term “definition”, as we did above.

The point now is that the above questions can be solved, the result being:

THEOREM 14.22. *In the above $H = \mathbb{C}^2$ context, of the mechanics of a single, fixed electron, the components of the normalized spin $\sigma = 2S/h$ are as follows,*

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \quad \sigma_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_z = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

called Pauli matrices. In the general, dynamic context, where we already have a Hilbert space H for the wave function, spin can be introduced by using the space

$$H' = H \otimes \mathbb{C}^2$$

and using the above Pauli matrices for it, acting on the \mathbb{C}^2 part.

PROOF. The equations in Definition 14.21, written in full detail, are as follows:

$$\begin{aligned} S^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \frac{3h^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad S^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3h^2}{4} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ S_x \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \frac{h}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad S_x \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{h}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ S_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad , \quad S_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = h \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ S_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= h \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad , \quad S_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \end{aligned}$$

Thus, we have the following formulae, for the various matrices involved:

$$\begin{aligned} S^2 &= \frac{3h^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad , \quad S_x = \frac{h}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ S_+ &= h \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad S_- = h \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned}$$

In relation with what we want to prove, we have obtained the formula of S_x . Regarding now the formulae of S_y, S_z , these follow by solving the following system:

$$S_+ = S_y + iS_z \quad , \quad S_- = S_y - iS_z$$

To be more precise, the computation for S_y goes as follows:

$$S_y = \frac{S_+ + S_-}{2} = \frac{h}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

As for the computation for S_z , this goes as follows:

$$S_z = \frac{S_+ - S_-}{2i} = \frac{h}{2i} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \frac{h}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Thus, we are led to the conclusions in the statement. \square

As a first consequence of the above, coming from the formula $s = 1/2$ in Definition 14.21, we can say, a bit formally, that electrons have spin $1/2$. We will heavily use this fact in what follows, for all sorts of purposes. And we will talk about spin $\neq 1/2$ too, in a moment, with a general particle discussion, involving bosons and fermions.

14c. Bosons and fermions

Bosons and fermions.

14d. Fermi gases

Fermi gases.

14e. Exercises

Exercises.

CHAPTER 15

Liquids and solids

15a. Liquids, water

Liquids, water.

15b. Solids, crystals

Solids, crystals.

15c. Ising model

The Ising model.

15d. Magnetic fluids

Magnetic fluids.

15e. Exercises

Exercises.

CHAPTER 16

Exotic matter

16a. Plasma

Plasma.

16b. Bose-Einstein

Bose-Einstein.

16c. Neutron soups

Neutron soups.

16d. Black holes

Black holes.

16e. Exercises

Exercises.

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