PHYS20352 Thermal and statistical physics

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Chapter 1 Introduction

"A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown."

(Albert Einstein)

"The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results." (J. Willard Gibbs)

1.1 What this course is about

In this course we will broadly start to answer the question how to connect the behaviour of the macroscopic world with the rules that govern the behaviour of the microscopic world.

Microscopic systems:

consist of one or a small number of particles, say individuals electrons, atoms, molecules, photons, a hydrogen atom with one electron moving about one proton, a water molecule (H_2O) , etc.

Macroscopic systems:

consist of very large number of particles (typically ~ 10^{23} , Avogadro's number 6×10^{23} / mole), e.g., a piece of metal, a cup of water, a box of gas, etc.

We observe in experiments that macroscopic objects obey definitive laws: Water boils at 100 degrees Celsius at standard atmospheric pressure; the pressure exerted by a dilute gas on a containing wall is always given by the ideal gas law, etc.

General question: How to infer the laws that govern the behaviour of macroscopic systems from those of the micro-world?

Laws that govern the microscopic world are Newton's laws (classical), or Schrödinger's equation (quantum), etc. In principle, these laws are applicable to macroscopic systems (consisting of many microscopic constituents), but it is often impractical to solve individual equation for all particles contained in a macroscopic system (and taking into account their interactions).

Laplace's demon:

At the beginning of the 19th century the belief was that this is mostly a matter of solving the required equations. We quote Pierre-Simon Laplace (1814):

"We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eyes."

In the original French it reads

"Nous devons donc envisager l'état présent de l'univers comme l'effet de son état antérieur, et comme la cause de celui qui va suivre. Une intelligence qui pour un instant donné connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui la composent, si d'ailleurs elle était assez vaste pour soumettre ces données à l'analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'univers et ceux du plus léger atome; rien ne serait incertain pour elle, et l'avenir comme le passé serait présent à ses yeux."

(Pierre-Simon Laplace, Essai philosophique sur les probabilités, 1814)

Clearly, this is not practical. Even with modern-day computers we cannot solve Newton's equations for all particles in the universe. Also, we do not know their positions and momenta (initial conditions). Some additional problems with quantum mechanics too (uncertainty).

Furthermore, there are new relevant quantities and new laws which govern the relations between these new quantities in the macroscopic world. For example, if we film the collision of two balls in snooker, we cannot tell which way time is running. This is a demonstration of the time invariance of the laws in microscopic world, such as Newton's laws and the Schrödinger equation. Consider another example. If we set a volume of gas molecules expand into a larger volume by removing a partition, by experience we know that after equilibrium the gas will not go back to the restricted region. This implies that there is a direction in time.

There are two approaches to understanding macroscopic physics:

1. Thermodynamics:

Formulated without using knowledge of the microscopic nature of matter. Based on a small number of principles, the *laws of thermodynamics*. These are deduced from experiments. \rightarrow The first part of this course (approx. lectures 1 - 12) covers aspects of thermodynamics

2. Statistical mechanics:

Starts from the knowledge of the microscopic nature of matter (atomic and molecular interactions etc) and aims to <u>deduce</u> the thermodynamic behaviour at the macro-level. Verifies thermodynamics but also provides a systematic formalism and method of calculating quantities at the macro-level.

 \rightarrow The second part of this course (approx. lectures 12 - 24) covers aspects of statistical physics.

1.2 Why is this course interesting?

A lot of this course is about thing such as steam engines, their efficiency, etc. At first sight this may sound a little boring, and traditionally students have difficulty realising the importance of thermodynamics and statistical physics.

The place of thermodynamics in physics:

What you have to realise is that classical thermodynamics, along with classical mechanics, electrodynamics and quantum mechanics forms one of the key pillars of physics. You cannot call yourself a trained physicist without knowing about these theories and areas. The development of thermodynamics was key for the industrial revolution in the early 19th century, and it continues to be relevant for an incredibly broad range of applications. These include all areas of engineering and chemistry, climate, as well as the thermodynamics of living systems.

History of thermodynamics:

Reading about the history of thermodynamics you will get a feeling of the struggle the early figures of thermodynamics went through in order to understand concepts such as heat, its conversion to mechanical energy and what we now call the first law. These things seem trivial to us now, but they were only properly understood about 150 years ago. Up until that point people though heat was some kind of fluid, the 'caloric', and they had no appreciation of the underlying microscopic processes. It is fascinating to see how a systematic understanding of these issues, now compactly formulated in the first, second and third law of thermodynamics, have enabled and continue to enable both industrial and technological advances, as well as a deeper grasp of the world around us, including the living world.

Stochastic thermodynamics:

The theories of classical thermodynamics and statistical physics apply to systems composed of *many modern* particles. Concepts such as heat, work or entropy really only make sense in this context. More recently the new field of 'stochastic thermodynamics' has emerged. Here, researchers apply the above concepts to systems composed of single particles or a few particles. Examples include the work done, entropy produced etc when single molecules are being stretched with optical tweezers (e.g. a single DNA molecule). Concepts from classical mechanics can be modified and adapted to describe such processes. This is very much in development, the corresponding experiments have only become possible in the last decade or so. We will (unfortunately) not have time to cover these aspects in this course. If you want to read about it, google 'stochastic thermodynamics' or 'Jarzynski inequality'.

Non-equilibrium statistical physics:

This course covers aspects of <u>equilibrium</u> thermodynamics and statistical physics. This means

that we assume that all quantities of all systems we look at are time-independent, and that all changes of e.g. external conditions we apply, are applied to slowly (quasi-statistically) that the system is always in equilibrium. Most of the real world operates far from equilibrium though, the best example being biology as a whole. Systems are driven by external energy, conditions change rapidly, currents flow and there is heat exchange and motion for example in cellular motors, the heart beat, etc. The theory of equilibrium statistical physics is now essentially complete (the final rosetta stone was the so-called renormalisation group, invented in the 1960s and 1970s). Most ongoing research is on off-equilibrium statistical physics, very interesting applications are found in biological systems and the 'physics of life'.

Complex systems:

In the last 20-30 years ideas from non-equilibrium statistical physics have been applied to questions outside physics, in particular applications in economics, the social sciences and in biology. One here studies so-called agent-based or individual-based systems, consisting of a larger number if interacting agents. These can be traders in the context of a stock market, cars if you model road traffic, or genes and proteins in biology. Such systems are often intrinsically off-equilbrium, and the tools from statistical physics can be used to derive a description of the phenomena shown by these systems at the macro-level (e.g. a traffic jam, stock market crash), starting from the interactions at the micro-level. Again, we do not have time to talk about these topics in this course, but they are discussed in the third-year course on nonlinear physics and in the fourth-year module on advanced statistical physics.

1.3 A few practical things

I am this person here:

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There will be a 90-minute exam at the end of the course, and one problem sheet per week for this course. It is important that you do the weekly homework problems (before seeing the model answers), tutorial work and tutorial attendance contribute towards your mark. Please use the tutorials to ask any questions you may have, discuss these with your tutors in the first instance. If you cannot resolve a question, please approach me! There is also the physics help desk service.

I EXPLICITLY WELCOME QUESTIONS IMMEDIATELY BEFORE OR AFTER LECTURES. I am usually in the room a few minutes before and I hang around afterwards. So please approach me and ask any questions you may have. With 280 students in the course I may not be able to always answer them all, but I will try my best!

Important:

I give this course for the first time in 2014. You have to help me to make this a good course and a good experience for everyone. If you have any (constructive) feedback then please let me know, either directly or through your student representatives. Keep in mind though that this is a large class, and naturally different students will have different personal tastes and preferences. So I will not be able to make everybody happy all the time. If you have criticism and feedback then try to be considerate, and do not only think about your personal requirements, but keep in mind the needs of the group as a whole.

EVEN MORE IMPORTANT:

It is important that you go through all calculations, proofs etc in these notes step by step with a pencil and a piece of paper. Make absolutely sure that you understand all equalities, inequalities, logical conclusions etc. You should do this for all (!) calculations in these notes. Unfortunately I know of no other way of acquiring a good and thorough understanding of the material.

The most important thing is that we all **enjoy** ourselves while we explore this area of physics.

Recommended textbooks:

Mandl, F., Statistical Physics, 2nd edition (Wiley)

Bowley, R. & Sanchez, M., Introductory Statistical Mechanics, 2nd edition (Oxford)

Zemansky, M.W. & Dittman, R.H., Heat and Thermodynamics, 7th edition (McGraw-Hill)

Other sources:

Dr Judith McGovern has compiled extensive html-based material. It can be found here:

http://theory.physics.manchester.ac.uk/%7Ejudith/stat_therm/stat_therm.html

This material is very systematic and detailed. I highly recommend it. Some of my lecture notes rely on Dr McGovern's material, you will recognise some of the figures, and some of the text.

Acknowledgements:

In preparing this course I have used the notes and materials of lecturers who gave it before me. In sequence these are Prof. Alan McKane, Dr Judith McGovern, Prof. Ray Bishop and Dr Yang Xian. If you find these lecture notes useful, then credits should really go to these earlier lecturers. A lot of the text in these notes is taken directly from their materials. I have edited and re-organised the material to give it my personal 'spin', and I will continue to edit the notes. If you find typos or mistakes then they are likely to be mine. Please point them out to me, so that I can correct them.

1.4 A few basic concepts

1.4.1 Isolated system

A system completely isolated in a container with walls which prevent any thermal interaction with the exterior (adiabatic walls), and which are also rigid (so that the volume of the system is fixed) so that no work may be done on this system. No particles in or out.

1.4.2 Equilibrium state

A state of a macroscopic system which is independent of time. An isolated system will eventually settle into an equilibrium state, defined by thermodynamic variables such as temperature T, volume V and pressure p. For systems out of equilibrium these variables can vary with time and position (e.g. $T = T(\underline{\mathbf{r}}, t), V = V(\underline{\mathbf{r}}, t), P = P(\underline{\mathbf{r}}, t)$ etc). This is the subject of *non-equilibrium thermodynamics*, we will not cover this in this course (but you will discuss it in the 4th year Advanced Statistical Physics course). In this course we will look at processes that start and end in equilibrium states, although the system may go through non-equilibrium states during the process.

1.4.3 Thermodynamic variables

Measureable macroscopic quantities associated with a thermodynamic system, e.g. P, V, T, \ldots . These can be *extensive* or *intensive*. A thermodynamic state is specified by a set of all values of the thermodynamic variables necessary for a complete description of the system.

1.4.4 Equation of state

For some systems not all thermodynamic variables are independent. E.g. ideal gas, they are related by PV = RT (one mole of substance). For van der Waals gases, $P = \frac{RT}{V-b} - \frac{a}{V^2}$. Such a relationship between the thermodynamic variables is called 'equation of state'. For the ideal gas we can write P = P(V,T), T = T(V,P) and V = V(T,P), i.e. any of the thermodynamic variables P, T, V can be expressed as a function of the two others.

1.4.5 Quasi-static process

A quasi-static process is one which is carried out so slowly that every state through which the system passes is an equilibrium state. An example is that of a contained with adiabatic walls, containing a fluid. A piston could be pushed into the fluid infinitesimally slowly with the pressure exerted equal to pressure of the fluid. The fluid remains in equilibrium throughout, this is a quasi-static process. If the piston is driven in more rapidly, with a pressure exceeding that of the fluid, the fluid will be driven out of equilibrium.

1.4.6 Indicator diagram

A diagram, e.g. P - V-plot, on which all the equilibrium states during a quasi-static process are indicated.

1.4.7 Reversible process

An idealised process which is (i) quasi-static and (ii) frictionless, i.e. there must not be any hysteresis. E.g. fluid in container and piston: if there must be no friction between the cylinder walls and the piston, otherwise pushing the piston creates heat, which cannot be turned back into work to reverse the process

 \longrightarrow frictional processes are irreversible



Figure 1.1: Reversible processes (such as L_1 and L_2) and an irreversible process between initial (indicated by i) and final (f) states.

Because reversible process are (infinitely) slow, the system is always essentially in equilibrium. Thus, all its state variables are well defined and uniform (they do not depend on position), and the state of the system at all times can be represented on a diagram of the independent variables (e.g., a P - V diagram). A finite reversible process passes through an infinite set of such states, and so can be drawn as a solid line as shown by paths L_1 or L_2 in Fig. 1.1. By contrast, *irreversible* process pass through non-equilibrium states and cannot be so represented. They are often indicated schematically as a straight dashed line joining the initial and final states $i \to f$. (Note: in such irreversible cases, the work done during the process is NOT equal to the area under the line, as is the case for reversible processes.)

[Refs.: (1) Mandl Chap. 1.3, (2) Bowley and Sanchez Chap. 1.6, (3) Zemansky Chap. 8]

Chapter 2

The first law of thermodynamics

"The first law of thermodynamics is that you do not talk about thermodynamics." (seen on the internet)

"If the water flow down by a gradual natural channel, its potential energy is gradually converted into heat by fluid friction, according to an admirable discovery made by Mr Joule of Manchester above twelve years ago, which has led to the greatest reform that physical science has experienced since the days of Newton. From that discovery, it may be concluded with certainty that heat is not matter, but some kind of motion among the particles of matter; a conclusion established, it is true, by Sir Humphrey Davy and Count Rumford at the end of last century, but ignored by even the highest scientific men during a period of more than forty years."

(William Thomson, a.k.a. Lord Kelvin (1854))

2.1 A bit of history

See Ingo Müller, A History of Thermodynamics, Springer Berlin Heidelberg (2007) for further details. Most of what I say in this section is directly taken from this book. Images are from Wikipedia.

Antoine Laurent Lavoisier (1743-1794)

father of modern chemistry

insisted on accurate measurement, people say he did for chemistry what Galilei had done for physics

thought that heat was a fluid, he called it the 'caloric'

executed 1794 (guillotine) for 'having plundered the people' and having supplied the enemies of France with money; asked for stay of execution to continue experiments, but judge refused: "The Republic needs neither scientists nor chemists; the course of justice cannot be delayed.")



Benjamin Thompson (1753-1814), Graf von Rumford

inventor (modern kitchen with sink, overhead cupboards)

gifted organiser (distribution of soup in Munich, factory for military uniforms staffed by beggars from streets of Munich)

bored cannon barrels, could liberate more 'caloric' than needed to melt whole barrel, concluded that caloric theory was nonsense

married Lavoisier's widow and later said: 'Lavoisier was lucky to have been guillotined.'



Robert Julius Mayer (1814-1878)

The first to state the law of the conservation of energy.

still confused about terminology (potential energy was 'falling force', kinetic energy was 'life force')

attempted to compute mechanical equivalent of heat

Arrested and suspended from university for a year for 'attending a ball indecently dressed'

work not taken very seriously at the time, Mayer tried to commit suicide when he realised this

James Prescott Joule (1818-1889)

son of a rich brewer in Salford

published series of measurements of mechanical equivalent of heat

initial papers rejected by several journals, had to present results as public lecture in Manchester, and get them published in local newspaper, Joule's brother had worked as a music critic for the editor

Hermann Ludwig Ferdinand von Helmholtz (1821-1894)

'what has been called heat is firstly the life energy [he means kinetic energy] of thermal motion and secondly the elastic forces between the atoms'

energy still conserved at level of atoms

Helmholtz' work very clear by comparison

did not quote Mayer and was accused of plagiarism







2.2 The first law of thermodynamics

2.2.1 The first law

The first law of thermodynamics states

$$\Delta E = Q + W \tag{2.1}$$

in any change of a thermodynamic system. Here

- Q is the amount of heat added to the system
- W is the work done <u>on</u> the system
- ΔE is the change in the internal energy of the system

Note: Sometimes this is written as $\Delta E = Q - W$, where W is the work done by the system.

The first law is just a statement of the principle of conservation of energy, recognising the fact that heat is a form of energy.

Experimentally one finds that ΔE only depends on the initial and final states, and not on the whole process by which one goes from the initial to the final state. I.e. there exists a function, E, which is a function of the thermodynamic variables, E is characteristic of the system in equilibrium $\longrightarrow E$ is a function of state.

The quantities Q and W on the other hand are <u>not</u> changes in functions of state. They depend on the whole process, not just the endpoints. They are two different forms of energy transfer (into the system or out of the system).

Example: Consider two different ways of taking a fixed mass of an ideal gas from an initial state (V_0, T_0) to a final state $(2V_0, T_0)$: (a) Free expansion in a container with adiabatic walls as shown in the top of Fig. 2.2.1. Clearly Q = 0 and W = 0. We have $\Delta E = 0$. For an ideal gas, E = E(T) (more discussion of this later), hence $T = T_0 = \text{const}$; (b) Expansion against an external force, with T held fixed at T_0 by contact with a heat bath as shown in the bottom two diagrams of Fig. 2.2.1. In this case, work is done by the gas. As $\Delta E = 0$, we have Q = -W > 0, $W = -\int F dx < 0$.

Conclusion of this example: Q and W are not state functions.

Isolated systems:

Thermally isolated system are contained within adiabatic (perfectly insulated) walls. We then have

$$Q = 0, \quad \Delta E = W. \tag{2.2}$$

For mechanically isolated system: W = 0. Hence $\Delta E = Q$, all heat turns to internal energy.

First law for infinitesimal changes:

For infinitesimal changes the first law is

$$dE = dQ + dW, \tag{2.3}$$

where dE is the infinitesimal change of E. The quantities dQ and dW are not infinitesimal changes of any functions Q and W, there are no such functions of state. We indicate this by the 'slash'. The quantities dQ and dW are the infinitesimal amount of heat transferred and work done, respectively, during the process.



Figure 2.1: (a) Free expansion (top two diagrams). (b) Expansion against an external force (bottom two diagrams).

2.2.2 The first law for cycles

In thermodynamics we often deal with cycles, changes in a system which take it through various equilibrium (or non-equilibrium) states, but ending in exactly the same state as the start. Clearly – by definition – all state variables (such as E) are unchanged in a cycle, i.e.

$$\oint_C dE = 0 \tag{2.4}$$

around any closed cycle C in the indicator diagram, or

$$\oint_C dQ + \oint_C dW = 0; \tag{2.5}$$

We do in general <u>not</u> have $\oint_C dQ \neq 0$ and $\oint_C dW \neq 0$; such integrals may depend on the closed path C.

Example: for a heat engine (see next chapter below), Q_1 is absorbed in the outward path of cycle, Q_2 is emitted in return path of cycle: $\oint ddQ = Q_1 - Q_2 = Q$; work done by engine, $w = -W = Q_1 - Q_2$, so that W + Q = 0.

[Refs. (1) Mandl Chap. 1.3; (2) Zemansky Chap. 3.5]

2.3 The form of dW

We now consider the work done by infinitesimal change in various thermodynamic systems.

2.3.1 Fluid systems (or gases)

As shown in Fig. 2.2 a the piston move a distance dx to compress the gas or fluid. The volume of the fluid changes by dV = Adx, where A is the cross-sectional area of the cylinder. Force



Figure 2.2: Work done by changing the volume of hydrostatic system.

needed to push the piston is $F = P_0 A$, where P_0 is the pressure exerted. It follows

$$dW = -Fdx$$

= -P₀Adx
= -P₀dV. (2.6)

We have here adopted the convention dx < 0 if dW > 0. If the process is frictionless (i.e. reversible) the pressure exerted, P_0 , must equal the pressure of the fluid, P. In this case

$$dW = -PdV \tag{2.7}$$

If the process is irreversible, then dW > -PdV. Why is this so? The process can be irreversible (i) because it is not a quasi-static process and/or (ii) there can be friction.

- (i) If the process is not quasi-static then $P_0 > P$, and so $dW = -P_0 dV > -P dV$.
- (ii) If there is friction present, then the pressure exerted, P_0 , must be greater than the pressure of the fluid in order to overcome the friction.

[Keep in mind that we looked at a compression, so dV < 0.]

2.3.2 Work done in changing the length of a wire

Suppose a wire is held in tension by a force Γ so that the length of the wire is increased from l to l + dl. The work done on the wire (by the external agency exerting the force) is Γdl , if the process is reversible:

$$dW = \Gamma dl. \tag{2.8}$$

Note: the sign on RHS now is positive, since dW > 0 if dl > 0. More generally, $dW \ge \Gamma dl$, with equality for reversible processes.

2.3.3 Work done in changing the area of a surface film

The surface tension, σ , of the liquid is defined as the work required to isothermally increase the area of a surface by an amount of unity.

If the surface tension of the film is σ (energy/unit area) and the area is increased from A to A + dA, work done on the surface is

$$dW = \sigma dA. \tag{2.9}$$

Note: a similar comment as given in the previous examples applies.

2.3.4 Work done on magnetic materials by changing the field

Process: An initially unmagentised sample of material is magnetised by applying a magnetic field to it (see Fig. 2.3). This can be done in several different ways:

- Place the sample inside a solenoid in which a current is gradually switched on.
- Or: Move the sample into the field of a solenoid in which a constant current is maintained.

Either way one finds [see Mandl, 2nd Edition, Chapter 1.4 for details):

$$dW = \mu_0 \underline{h} \cdot d\underline{m}, \tag{2.10}$$

where

- \underline{m} is the magnetic moment of the sample ($\underline{m} = \underline{M}V$, where \underline{M} is the magnetisation, V the volume)
- \underline{h} is the applied magnetic field intensity, generated by the solenoid
- μ_0 is what it always is, the permeability of free space.

[Recall that the magnetic field is $\underline{B} = \mu_0(\underline{h} + \underline{M})$.] In different textbooks you will find different expressions for dW, for example

•
$$dW = \mu_0 \underline{h} \cdot d\underline{m}$$
 (as above)

•
$$dW = -\mu_0 \underline{m} \cdot d\underline{h}.$$

Different textbooks take different viewpoints. The difference between these two expressions is down the basic problem to agree what is considered part of the system and what is part of the surroundings. There is a mutual (or shared) energy between the solenoid and the sample, given by

$$E_{\text{mutual}} = \mu_0 \underline{h} \cdot \underline{m}, \qquad (2.11)$$

and one has the choice of including this as part of the energy of the system, or to leave it out. The difference between the two expressions above is in fact given by $dE_{\text{mutual}} = d(\mu_0 \underline{h} \cdot \underline{m})$ (use the product rule). More details can be found in Mandl, Chapter 1.4. In this course we will use

$$dW = -\mu_0 \underline{m} \cdot d\underline{h}. \tag{2.12}$$

This corresponds to conventions in which the mutual energy is $\underline{\text{not}}$ included as part of the energy of the system.

Notation:

This result is frequently written as

$$dW = -\mu_0 m dh \tag{2.13}$$

(<u>m</u> and <u>h</u> parallel to each other), or using $B = \mu_0 h$, where B is the <u>external</u> magnetic field not including the magnetisation

$$dW = -mdB, (2.14)$$

or, using m = MV,

$$dW = -VMdB. \tag{2.15}$$



Figure 2.3: A magnetizable material in a solenoid.



Figure 2.4: Geometrical interpretation of work done in an indicator diagram.

2.3.5 Work done and the indicator diagram

For a magnetic material the thermodynamic basic variables are (B, m, T); and (P, V, T) for a gas, (Γ, l, T) for a stretched wire and (σ, A, T) for a surface film. If we represent reversible process by lines on a P - V plot for a fluid (or a $\Gamma - l$ plot for a stretched wire etc.) then the magnitude of the work is equal to the area under the line. An example is shown in Fig. 2.4 The work done is compressing from V_2 to V_1 is

$$W = -\int_{V_2}^{V_1} P dV,$$
 (2.16)

and it depends on path.

E.g., path A: W_A = area under curve A; path B: W_B = area under curve B. The difference $W_A - W_B = -\oint_C P dV = \oint_C dW \neq 0$ where C is the cycle as shown in Fig. 2.4. For further examples see example sheets 2-4.

Reality check:

Let's make sure this makes sense for an ideal gas. Say we reversibly compress from V_2 to V_1 at constant temperature ('isothermally'), where V_2 obviously has to be greater than V_1 . See

Fig. 2.4. For the ideal gas we have PV = nRT, i.e. $P = \frac{nRT}{V}$. So we find

$$W = -\int_{V_2}^{V_1} P dV$$

= $-nRT \int_{V_2}^{V_1} \frac{dV}{V}$
= $\left[-nRT \ln V \right]_{V_2}^{V_1}$
= $nRT \ln \frac{V_2}{V_1}$. (2.17)

This is greater than zero as it should be.

[Refs. (1) Mandl Chap. 1.3-1.4, (2) Bowley and Sanchez Chap. 1.6, (3) Zemansky Chap. 3]

2.4 Specific heats

If a quantity dQ of heat is introduced reversibly into a system, by a process which keeps a quantity y constant, and this raises the temperature by dT, the specific heat capacity of the system for this process is defined by

$$C_y = \frac{dQ}{dT} \text{ (y fixed).}$$
(2.18)

Examples: C_V, C_P, C_M, \ldots

2.4.1 Example 1: y = V

In this case V = const, so dV = 0, i.e. dQ = dE + PdV = dE. On the other hand E = E(V, T) so

$$dE = \left(\frac{\partial E}{\partial T}\right)_{V} dT + \left(\frac{\partial E}{\partial V}\right)_{T} dV$$
$$= \left(\frac{\partial E}{\partial T}\right)_{V} dT.$$
(2.19)

Therefore

$$dQ = \left(\frac{\partial E}{\partial T}\right)_V dT \text{ (at constant V).}$$
 (2.20)

It follows

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{2.21}$$

Given that E is a function of state, so is C_V .

2.4.2 Example 2: y = P

We have dQ = dE + PdV. At the same time

$$dE = \left(\frac{\partial E}{\partial P}\right)_T dP + \left(\frac{\partial E}{\partial T}\right)_P dT$$
$$= \left(\frac{\partial E}{\partial T}\right)_P dT, \qquad (2.22)$$

where have used dP = 0. Similarly

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$
$$= \left(\frac{\partial V}{\partial T}\right)_P dT. \tag{2.23}$$

Substituting into dQ = dE + PdV, we have

$$dQ = \left\{ \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \right\} dT, \qquad (2.24)$$

and so

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$
(2.25)

2.4.3 Special case: ideal gas

For the ideal gas, E is a function of T only, it does not depend on V or P. So one has

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V.$$
(2.26)

From this and Eq. (2.21) one finds

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P.$$
(2.27)

But for one mole of an ideal gas, PV = RT, so $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$. From this we get

$$C_P - C_V = R \tag{2.28}$$

for the one mole of an ideal gas.

2.5 Real and Ideal gases: A Review

2.5.1 Ideal gas law

Ideal gases are experimentally found to obey the following two laws:

(i) Boyles's law

$$PV = \text{const.}$$
 at fixed temperature. (2.29)

(ii) Charles's law (Gay-Lussac's law): At constant pressure, the volume of a gas varies linearly with temperature

$$V = V_0 \frac{T}{T_0} \quad \text{at fixed} \quad P = P_0, \tag{2.30}$$

where T_0 is constant (experiments show T_0 nearly same for all gases).

This is assuming that the gas does not liquefy. If both laws are obeyed exactly

$$PV = P_0 V_0 \frac{T}{T_0} \tag{2.31}$$

(2.32)

where T is temperature on an absolute scale. As P and T are intensive, and V is extensive we must have

$$\frac{PV}{T} \propto N.$$

For an ideal gas one has

$$PV = Nk_BT = nRT \tag{2.33}$$

where k_B is the Boltzmann constant, $R = k_B N_A$ is universal gas constant, N_A is Avogadro's number, $n = N/N_A$ is number of moles.

So far we have stated these laws as empirical laws, found based on experimental observations. They can be derived from first principles using the kinetic theory of gases. This theory is based on the assumption that the gas is made of point-like particles, which bounce off each other and off the walls of the container, and with no other interaction between the particles. See the first-year module 'Properties of Matter', or e.g. Blundell and Blundell, 'Concepts in Thermal Physics', Oxford University Press, Chapter 6, the book by Zemansky and Dittman (chapter 5.9) or Young and Freedman, 12th Edition, Chapter 18.3.

For real gases, the above equation of state only applies in the limit of low pressures.

2.5.2 Heat capacity and further properties of ideal gases

Later in Statistical Physics, we can understand ideal gas microscopically as a gas with pointlike, non-interacting molecules. All gases tend to that of an ideal gas at low enough pressure. The noble gas (e.g., helium, argon) are very close to ideal at STP; even our air at STP is quite well approximated as ideal.

For real gas in general, the internal energy is a function of T, P and V. These three quantities are related by an equation of state, for example the ideal gas law for an ideal gas, or the

van-der-Waals equation in other cases. Either way, either of the variables, T, P and V, can be expressed as a function of the other two. This means that the internal energy can be expressed as a function of two of the variables, e.g. E = E(T, P), E = E(T, V) or E = E(P, V).

For an ideal gas, this simplifies to E = E(T), i.e. the internal energy is a function of T only. This is again a result obtained from the kinetic theory of ideal gases¹, see above for references. More precisely one finds

$$E = \frac{\nu_f}{2} N k_B T = \frac{\nu_f}{2} n R T \tag{2.34}$$

where ν_f is the active degrees of freedom. The above equation states that each molecule has an average internal energy of $\frac{1}{2}k_BT$ per active degree of freedom. For mono-atomic gases one has $\nu_f = 3$, for di-atomic gases $\nu_f = 5$ (3 translational and 2 rotational; assuming that vibrational modes do not contribute).

The fact that E = E(T) for a fixed quantity of an ideal gas implies

$$\left(\frac{\partial E}{\partial P}\right)_T = 0, \quad \left(\frac{\partial E}{\partial V}\right)_T = 0.$$

This means

$$C_V = \left(\frac{dQ}{dT}\right)_V = \frac{dE}{dT}$$
, and so $dE = C_V dT$. (2.35)

In general, the heat capacity, C_V , can be a function of temperature. If this is not the case, i.e. $C_V = const$ (independent of T), then $E = C_V T$, if we assume that E = 0 and T = 0. Using the above results, this means $C_V = \frac{\nu_f}{2}nR$.

We can also prove

$$C_P - C_V = nR; (2.36)$$

for the ideal gas, see example sheet 1. For reversible adiabatic processes on an ideal gas one has \sim

$$PV^{\gamma} = \text{const.}, \quad \gamma = \frac{C_P}{C_V},$$
(2.37)

see example sheet 2. For a mono-atomic ideal gas, $\gamma = 5/3$, for a di-atomic ideal gas $\gamma = 7/5$.

2.5.3 Real gases

Now we consider real gases. Many attempts exist to modify the ideal gas equation of state for real gases. Two common approaches are:

(i) **The hard-sphere gas:** We continue to neglect the interaction except at short range where we treat the molecules as hard spheres:

$$V(r) = \begin{cases} \infty, & \text{for } r \le r_0; \\ 0, & \text{for } r > r_0. \end{cases}$$
(2.38)

¹From the kinetic theory approach one obtains $PV = \frac{1}{3}Nm \langle v^2 \rangle$ for a mono-atomic gas, where *m* is the mass of a single gas particle, and $\langle v^2 \rangle$ the average squared-velocity. The RHS is proportional to the total kinetic energy of the gas $(\frac{1}{2}m \langle v^2 \rangle$ per particle). Now one needs experimental input, namely the ideal gas equation, PV = nRT, which is an empirical finding. Using this, one finds that $E \propto T$, where *E* is the total internal energy of the gas, i.e. the total kinetic energy of all gas particles. The exact expression is $E = \frac{3}{2}nRT$, it would be a good exercise to convince yourself of this!



Figure 2.5: The van der Waals gas: schematic diagram of the interaction potential between two molecules

Most of the ideal gas results continue to hold, but we have to make the replacement $V \rightarrow V - nb$, where b is the 'excluded volume', proportional to the volume occupied by one mole of gas (i.e., $b \propto N_A r_0^3$). The equation of state for a hard sphere gas becomes

$$P(V - nb) = nRT, \quad \text{or } P(V - N\beta) = Nk_BT, \quad \beta = \frac{b}{N_A}.$$
 (2.39)

(ii) The van der Waals gas: Apart from the hard-sphere interaction at short distance, we now allow the weak intermolecular attraction at larger distances, as shown in Fig. 2.5. The extra attraction for $r > r_0$ clearly reduces the pressure for a given V and T, since a molecule striking the vessel wall experiences an additional inward pull on this account. Call this intrinsic pressure π . So if the observed pressure is P and that expected if there were no attraction is $p, p - P = \pi$, the hard-sphere equation of state

$$P = \frac{nRT}{V - nb} \to P + \pi = \frac{nRT}{V - nb}.$$

Van der Waals argued that π is the result of mutual attraction between bulk of gas, i.e., the tendency of molecules forming pairs, and hence should be proportional to $N(N - 1)/2 \propto N^2$, or to N^2/V^2 as it is intensive. Hence $\pi = an^2/V^2$.

The equation of state for van der Waals gas is

$$(P + a \frac{n^2}{V^2})(V - nb) = nRT$$

 $(P + \frac{\alpha N^2}{V^2})(V - N\beta) = Nk_BT,$ (2.40)

or

where
$$\beta = b/N_A$$
 and $\alpha = a/N_A^2$.

2.6 The zeroth law of thermodynamics and temperature*

2.6.1 The zeroth law

After the first law we now turn to the zeroth law. The terminology is due to the historical order in which things were developed. What is now known as the zeroth law was recognised

only after the first, second and third laws of thermodynamics had been named. The most basic concept in thermodynamics (or statistical mechanics) is *temperature*, and the zero-th law is required for a meaningful definition of temperature. In this sense the zero-th law is a prerequisite to the first, second and third law, hence calling in the 'zero-th' law is appropriate. What is temperature? We have an intuitive feel for it, but it is somewhat elusive. It is relatively easy to understand what it means for a mass to be twice as large as another, or a force which is twice as strong as another. But what does it mean to say that something is twice as hot as something else? All attempts to quantify this rest on

The zeroth law of thermodynamics:

If a body C is in thermal equilibrium with A and with B, then A and B are also in thermal equilibrium with each other.

Why is this useful? We follow Young and Freedman, Chapter 17. Assume that C is a thermometer, and that it is in thermal equilibrium with A and B. The thermometer then measures the temperature of both A and B. But the reading would not change if A were removed, or if B were removed. Hence A and B have the same temperature. We can conclude that two systems are in thermal equilibrium with each other if and only if they have the same temperature. This is what makes a thermometer useful. Technically speaking, a thermometer measures its own temperature, but when in thermal equilibrium with another body, then its own temperature is that of the other system.

This is intuitively obvious, but it now permits the definition of something measurable, called *temperature*, whereby bodies in thermal equilibrium are at the same temperature.

2.6.2 Thermometers and temperature scales

To measure temperature we can use any property of matter that changes when heat is absorbed or emitted (e.g., resistance of a platinum wire, the volume (and hence length) of a volume of liquid mercury in a glass tube, the pressure of a given quantity of gas in a fixed volume, etc.). Such devices can be used to verify the zeroth law experimentally. They are called thermoscopes, for example the pressure of a given volume of an ideal gas is proportional to temperature. But since no scale has been defined, they are not yet thermometers.

A thermometer is a calibrated thermoscope. Any thermoscope can be used to define a numerical temperature scale over some range by using two fixed points (e.g., the ice freezing point and boiling point of water). However, thermoscopes based on the volume of gases finally led to the notion of an *absolute scale* based on a single fixed point. This is the *ideal gas temperature scale*, measured in Kelvin (K) which is defined to be 273.16 K at the triple point of water (the single fixed point of the scale), agreed universally in 1954. Note: The freezing point of water is some 0.01K lower (273.15 K) in temperature than the triple point (273.16 K).

Homework:

A nice exposition of the details can be found in Young and Freedman, chapter 17.3, and you should read it!

With such an absolute scale $k_B T$ (as in the ideal gas law) is a measure of thermal energy at the atomic scale; whereas RT is measure at the molar (macroscopic) scale. At room temperature $T \approx 300$ K, $k_B T \approx \frac{1}{40}$ eV.

[Refs.: (1) Mandl Chap. 1.2, (2) Bowley and Sanchez Chap. 1.2, (3) Zemansky Chap. 1.]

Free telescope This page, when rolled into a tube, makes a telescope with 1 : 1 magnification.

Chapter 3

The second law of thermodynamics

"In this house, we obey the laws of thermodynamics!" (Homer Simpson)

"The law that entropy always increases, holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations – then so much the worse for Maxwell's equations. If it is found to be contradicted by observation – well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation." (Sir Arthur Stanley Eddington, The Nature of the Physical World, 1927)

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3.1 Introduction

The basic observations leading to the second law are remarkably simple:

- When two systems are placed in thermal contact they tend to come to equilibrium with each other the reverse process, in which they revert to their initial states, never occurs in practice.
- Energy prefers to flow from hotter bodies to cooler bodies (and temperature is just a measure of the hotness). It is everyday experience that heat tends to flow from hot bodies to cold ones when left to their own devices. There is a natural direction to spontaneous processes (e.g., the cooling of a cup of coffee)
- Physical systems, left to their own devices, tend to evolve towards disordered states, e.g. the mixing of milk in coffee. The reverse (spontaneous ordering) is not observed in closed systems.

Note: These observations can be used to define a 'direction of time'.

Related to this, it is important to realise that work and heat are simply different forms of energy transfer:

• Work is energy transfer via the macroscopically observable degrees of freedom. In this case the energy is transferred *coherently*.

• Heat is energy transfer between microscopic degrees of freedom. In this case the energy is transferred *incoherently*, the energy is stored in the thermal motion of the molecules of the substance.

The second law says that there is an intrinsic asymmetry in nature between heat and work: extracting <u>ordered motion</u> (i.e. work) from <u>disordered motion</u> (i.e. heat) is hard¹, whereas the converse is easy. In fact the second law says that it is <u>impossible</u> to convert heat completely into work.

We will make these observations more quantitative through the introduction of a new state variable, the so-called **entropy**, S. In classical thermodynamics, entropy 'completes the set' of relevant thermodynamic variables (e.g., for a gas the complete set is (P, V, T, S) - anything else can be expressed in terms of these). However, the underlying deeper meaning of entropy (which is intrinsically a mysterious, deep and subtle concept) will only become clear when we progress to statistical mechanics.

3.2 Heat engines and refrigerators

In order to introduce the concept of entropy it is useful to first consider heat engines and refrigerators.

3.2.1 Heat engines

Heat engines run in cycles. In any one cycle the internal energy of the engines does not change, $\Delta E = 0$, by definition. During a cycle an amount of heat $Q_H > 0$ is absorbed from a hot source (or set of hot sources; e.g., the hot combustion products in a car engine) and the engine does work w > 0 on its surroundings. During this process an amount of heat $Q_C > 0$ has been emitted to a cooler thermal reservoir (or set of cooler reservoirs; e.g., the outside air). This is illustrated in Fig. 3.1.

Experimental observation: We can not make $Q_C = 0$, however hard we try (and engineers have tried very hard!). Even in the absence of frictional or dissipative processes (i.e., even for a reversible engine) we always have $Q_C > 0$.

From the first law we have

$$w = Q_H - Q_C, \tag{3.1}$$

given that $\Delta E = 0$ in one cycle.

¹In his 1848 paper titled 'On an Absolute Thermometric Scale' Kelvin writes: 'In the present state of science no operation is known by which heat can be absorbed, without either elevating the temperature of matter, or becoming latent and producing some alteration in the physical condition of the body into which it is absorbed; and the conversion of heat (or caloric) into mechanical effect is probably impossible, certainly undiscovered.' In a footnote he then goes on to say: 'This opinion seems to be nearly universally held by those who have written on the subject. A contrary opinion however has been advocated by Mr Joule of Manchester; some very remarkable discoveries which he has made with reference to the generation of heat by the friction of fluids in motion, and some known experiments with magneto-electric machines, seeming to indicate an actual conversion of mechanical effect into caloric. No experiment however is adduced in which the converse operation is exhibited; but it must be confessed that as yet much is involved in mystery with reference to these fundamental questions of natural philosophy.' Beautiful – TG.



Figure 3.1: Illustration of flow of work and heat in a heat engine.



Figure 3.2: Processes in the Otto cycle.

We define the **efficiency** of the heat engine as

$$\eta_E = \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H} < 1.$$
(3.2)

Example:

An example can be found in Q1 of Example Sheet 3. Let us here look at another one, the so-called Otto cycle, an idealization of a standard gasoline engine in a car.

The process is illustrated in Fig. 3.2. The compression stroke $a \to b$ and the expansion stroke $c \to d$ are done such that they are adiabatic (no heat enters or leaves), so heat enters and leaves only during the constant-volume (isochoric) processes $b \to c$ and $d \to a$.

It is easy to calculate η_E for this reversible Otto cycle if the working substance is an ideal gas. The specific heat at constant volume, C_V , is then independent of temperature, this is useful when looking at the processes $b \to c$ and $d \to a$. We find

$$Q_H = \int_{T_b}^{T_c} C_V dT = C_V (T_c - T_b)$$
(3.3)

as well as

$$Q_C = -\int_{T_d}^{T_a} C_V dT = C_V (T_d - T_a).$$
(3.4)



Figure 3.3: Illustration of the processes in a refrigerator.

Thus

$$\eta_E = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_d - T_a}{T_c - T_b}.$$
(3.5)

For an adiabatic process in an ideal gas we have $PV^{\gamma} = const$, see Q1 of Example Sheet 2, and the ideal gas law PV = nRT. These two equations give

$$TV^{\gamma-1} = \text{const} \tag{3.6}$$

for adiabatic processes on ideal gas (you should check this!). Thus, for the two adiabatic processes $c \to d$ and $a \to b$, we have

$$T_d V_1^{\gamma - 1} = T_c V_2^{\gamma - 1}, T_a V_1^{\gamma - 1} = T_b V_2^{\gamma - 1}.$$
(3.7)

Subtracting these equations from each other we have

$$(T_d - T_a)V_1^{\gamma - 1} = (T_c - T_b)V_2^{\gamma - 1}$$
(3.8)

Substituting into Eq. (3.5) we find

$$\eta_E = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = 1 - \frac{T_a}{T_b} = 1 - \frac{T_d}{T_c},\tag{3.9}$$

where in the last two equations we have used Eq. (3.7).

Note: For the Otto cycle it is easy to see $T_c > T_b > T_a$ and $T_c > T_d > T_a$ (convince yourself of this!), hence $\eta_E < 1 - \frac{T_a}{T_c}$ (again convince yourself that this is true!). We will comment on this later when we discuss Carnot engines.

3.2.2 Refrigerators

Refrigerators are heat engine run in reverse. I.e., we supply work to pump heat from a cooler to a hotter body. The quantities w, Q_H and Q_C of the heat engine (see above) all change sign and become W, q_H and q_C , as illustrated in Fig. 3.3.

The first law now reads:

$$W = q_H - q_C.$$
 (3.10)

Examples of such machines are standard refrigerators, air-conditioners, and heat pumps. These are all essentially the same, but they have different purposes. Refrigerators and air-conditioners are used for cooling (e.g., the refrigerators cabinet, or a room), whereas the heat pump is used to heat (e.g., a room or a building). We now tailor the definition of efficiency to the purpose. In general:

$$\eta = \frac{\text{desired output}}{\text{necessary input}}.$$
(3.11)

(Note: Whereas the fact that $Q_C \neq 0$ is an unavoidable nuisance for a heat engine, the fact that $q_C \neq 0$ means that refrigerators and heat pumps actually work!)

• For engines: desired output = w; necessary input = Q_H , hence

$$\eta_E = \frac{w}{Q_H} = \frac{Q_H - Q_C}{Q_H}.$$
(3.12)

• For refrigerators: desired output $= q_C$; necessary input = W, hence

$$\eta_R = \frac{q_C}{W} = \frac{q_C}{q_H - q_C}.\tag{3.13}$$

• For heat pumps: desired output $= q_H$; necessary input = W, hence

$$\eta_P = \frac{q_H}{W} = \frac{q_H}{q_H - q_C}.$$
(3.14)

We note: $\eta_E < 1$ always (you should understand why), $\eta_R > 1$ usually, and $\eta_P > 1$ always (you should understand why). The quantities η_R and η_P (which can be greater than one) are sometimes called 'coefficients of thermal performance' because students are worried by 'efficiencies' greater than one. Having a heat pump, as we have defined it would be pointless, if it had $\eta_P < 1$. If we have such heat pump we would not used it, instead we would just use an electric heater instead (efficiency of exactly one)!

Important remark:

Real engines are optimized to perform forward or backwards, they are not reversible in the technical sense (there is friction, processes are not quasistatic). Thus relative sizes of W, Q_H and Q_C will depend on the direction. However for idealized, reversible engines only the signs will change, and we have

$$\eta_P = \frac{1}{\eta_E}$$
 (for reversible engines/pumps). (3.15)

[Refs.: (1) Mandl 5.2, (2) Bowley and Sanches 2.3, (3) Zemansky 6.1-6.5.]

3.3 The second law of thermodynamics

There are two classic statements of the second law of thermodynamics.

<u>Kelvin-Planck statement:</u>

It is impossible to construct an engine which, operating in a cycle, produces no effect other



Figure 3.4: Kelvin-violating (left) and Clausius-violating (right) engines.

than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Clausius statement:

It is impossible to construct a refrigerator which, operating in a cycle, produces no effect other than the transfer of heat from a cooler body to a hotter one.

They are seemingly different statements, both generalized from everyday experience. Note the careful wording:

- Of course it is possible to think of processes which convert heat into work (expansion of a hot gas in a piston) or which pass heat from a cool to a hot body (real fridges) but in these examples *other things change as well* (the gas ends up cooler; you have an electricity bill to pay).
- The bit about 'operating in a cycle' is crucial, it ensures that the engine itself is unchanged by the process.
- Neither of the two statements (Kelvin-Planck and Clausius) is implied by the by the first law, energy would still be conserved in the processes disallowed by the second law. The exclusions by the second law are something genuinely different.

Equivalence of the two statements:

The two statements of the second law look very different, but they do in fact imply each other, as we will now show².

Kelvin violated implies Clausius violated

Consider a hypothetical Kelvin-violating engine \bar{K} , as shown in the left-hand panel of Fig.

²Before we do this, here a little trivia on basic logic (you can skip this footnote if you like, I just added it for fun – TG). Suppose we have two statements, A and B, each of which can either be true or false. When we say 'A implies B' (written as $A \Rightarrow B$) we mean the following: 'If A is true then B must be true'. In order to show that $A \Rightarrow B$ it is sufficient to show that the statement 'B is false' implies that 'A is false', i.e. $\neg B \Rightarrow \neg A$, where $\neg A$ stands for 'not A'. Saying that A is equivalent to B (written as $A \Leftrightarrow B$) means $A \Rightarrow B$ and $B \Rightarrow A$. Sometimes we say 'B is true if and only if A is true', or 'A is true iff B is true' (with a double 'ff' in 'iff') to indicate that A and B are equivalent. In order to demonstrate that $A \Leftrightarrow B$ it is sufficient to show $\neg A \Leftrightarrow \neg B$.



Figure 3.5: Construction to show that violating the Kelvin statement implies violating the Clausius statement.



Figure 3.6: Construction to show that violating the Clausius statement implies violating the Kelvin statement.

3.4. Now hook this engine up with regular (i.e., legal) refrigerator R, as shown in Fig. 3.5. This generates an 'illegal' refrigerator in the sense of the Clausius statement (see right-hand panel of Fig. 3.5).

Clausius violated implies Kelvin violated

Now consider a hypothetical Clausius-violating refrigerator \overline{C} , as shown in the right-hand panel of Fig. 3.4. Combine this with a 'legal' engine, E, as shown in Fig. 3.6. This creates an 'illegal' engine in the sense of the Kelvin statement.

Thus we have shown the equivalence of the two statements of the second law.

[Refs.: (1) Mandl 2.1; (2) Bowley and Sanchez 2.2; (3) Zemansky 6.6-6.8]

3.4 Carnot cycles and Carnot engines

3.4.1 Background

In order to be realised in the real world, any reversible processes which involves a change of temperature from an initial value to a final value would require an infinite number of heat reservoirs at temperatures infinitesimally close to each other in order to keep everything quasi-static. This does not sound very plausible. However, there is a special form of heat engine which only relies on two reservoirs: a hot one at temperature T_H , and a cold one at $T_C < T_H$. Reversible engines with only two such reservoirs will play a very important role in later on in this course. We may wonder, e.g.,

- (i) What is the maximum η_E that can be achieved for a given T_H and T_C ?
- (ii) What are the characteristics of such maximally efficient engines?
- (iii) Of what effect is the nature of the working substance in such maximally efficient engines?

These questions were all answered by Sadi Carnot, and heat engines of this type are known as 'Carnot engines', or the 'Carnot cycle'.

3.4.2 Carnot engines and Carnot's theorem

Definition:

A Carnot engine is a reversible engine acting between only two heat reservoirs. That means that all processes are either isothermal (heat transfer at a constant temperature) or adiabatic (no heat transfer).

Carnot's theorem:

A reversible engine operating between two given given reservoirs is the most efficient engine that can operate between those reservoirs.

We will prove this below. Before we do this, let us re-phrase the theorem. Carnot's theorem says that a reversible engine is the most efficient engine which can operate between two reservoirs.

Much is made of the fact that the Carnot engine is the most efficient engine. Actually, this is not mysterious. First, if we specify only two reservoirs, then all it says is that a reversible engine is more efficient than an irreversible engine, which isn't all that surprising (no friction...) Second, we will see that the efficiency of a Carnot engine increases with the temperature difference between the reservoirs. So it makes sense to use only the hottest and coldest heat baths you have available, rather than a whole series of them at intermediate temperatures. But the independence of the details of the engine is rather deeper, and has far-reaching consequences.

<u>Proof of Carnot's theorem:</u>

The construction used to prove the theorem is illustrated in Fig. 3.7. The green engines/pumps are Carnot (reversible), and the brown ones are irreversible.

Assume there is an engine E which is more efficient than a Carnot engine, i.e. $\eta_E > \eta_C$. The Carnot engine is reversible, and so it can be run as a pump, see left-hand panel of Fig. 3.7. Since $\eta_E > \eta_C$, we have

$$\frac{W}{Q'_H} > \frac{W}{Q_H},\tag{3.16}$$

i.e. $Q_H > Q'_H$. From the first law

$$W = Q'_H - Q'_C = Q_H - Q_C. ag{3.17}$$



Figure 3.7: Left: Construction to prove Carnot's theorem. Right: Construction used to prove that all reversible engines operating between two reservoirs have the same efficiency, η_C .

We conclude

$$Q_H - Q'_H = Q_C - Q'_C. (3.18)$$

Because of $Q_H > Q'_H$ these quantities are both positive. But this means that a net amount of heat, $Q_H - Q'_H = Q_C - Q'_C > 0$ is pumped from the colder reservoir to the hotter reservoir by the combined system. This violates the Clausius statement.

Corollary of Carnot's theorem:

Any reversible engine working between two heat reservoirs has the same efficiency as any other, irrespective of the details of the engine.

Proof:

Consider a Carnot engine, C, maximising the efficiency for two given reservoirs, and another reversible engine, E, operating between the same two reservoirs. Its efficiency is $\eta_E \leq \eta_C$, as C is the most efficient engine for these two reservoirs. We want to show that $\eta_E = \eta_C$, so assume that η_E is strictly smaller than η_C , and construct a contradiction.

So assume $\eta_E < \eta_C$. Run the engine in reverse, and connect it to a Carnot engine, as shown in the right-hand panel of Fig. 3.7. We have

$$\eta_E = \frac{W}{Q_H''} < \frac{W}{Q_H} = \eta_C. \tag{3.19}$$

This implies $Q''_H > Q_H$. From the first law we have $W = Q_H - Q_C = Q''_H - Q''_C$, and so it follows

$$Q_H - Q''_H = Q_C - Q''_C, (3.20)$$

and both of these quantities are negative. Thus, $Q''_H - Q_H = Q''_C - Q_C > 0$. This means that the combined system pumps heat from the cold reservoir to the hot reservoir, which is in violation of Clausius' statement. So we have the desired contradiction. This completes the proof of the corollary.

This is a remarkable (and deep) result. It means that, for two reservoirs with temperatures T_H and T_C , any reversible engine has the same efficiency, and that this efficiency is a function


Figure 3.8: The Carnot cycle for an ideal gas.

of the temperatures of the two reservoirs only, $\eta_C = \eta_C(T_H, T_C)$. In particular the efficiency is independent of working substance, e.g., the working substance could be an ideal gas, a real gas, a paramagnet, etc. We can evaluate the efficiency for any substance and we would always obtain the same result. So we choose the simplest possible substance, an ideal gas.

3.4.3 Calculating the efficiency of a Carnot cycle

Consider a cycle as shown in Fig. 3.8:

- $a \rightarrow b$: isothermal compression in contact with a reservoir at temperature T_C ; heat Q_C emitted;
- $b \rightarrow c$: adiabatic compression (no reservoirs; no heat flow);
- $c \to d$: isothermal expansion in contact with reservoir at temperature T_H , heat Q_H absorbed;
- $d \rightarrow a$: adiabatic expansion.

The first law states

$$dQ = dE - dW = dE + PdV \tag{3.21}$$

for reversible process. For the ideal gas, we have E = E(T) and so dE = 0 along an isotherm. Hence $dQ = nRT \frac{dV}{V}$ along isotherms. Therefore we have

$$Q_C = -\int_a^b nRT_C \frac{dV}{V} = nRT_C \ln \frac{V_a}{V_b}$$
(3.22)

along $a \to b$ (convince yourself that this is of the right sign!), and

$$Q_H = \int_c^d nRT_H \frac{dV}{V} = nRT_H \ln \frac{V_d}{V_c}$$
(3.23)

along $c \to d$.

The efficiency is then

$$\eta_{CE} \equiv 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} \frac{\ln(V_a/V_b)}{\ln(V_d/V_c)}.$$
(3.24)

Next we use that $TV^{\gamma-1} = const$ for adiabatic processes on an ideal gas (with $\gamma = C_P/C_V$ as usual). For the two adiabatic processes $b \to c$ and $d \to a$ we therefore have

$$T_{C}V_{b}^{\gamma-1} = T_{H}V_{c}^{\gamma-1}$$

$$T_{C}V_{a}^{\gamma-1} = T_{H}V_{d}^{\gamma-1}.$$
(3.25)

From this we conclude $(V_a/V_b)^{\gamma-1} = (V_d/V_c)^{\gamma-1}$, i.e.

$$\frac{V_a}{V_b} = \frac{V_d}{V_c}.$$
(3.26)

Substituting this into Eq. (3.24) we find

$$\eta_{CE} = 1 - \frac{T_C}{T_H}.$$
(3.27)

This is the efficiency of a Carnot engine with an ideal gas as a working substance. Using the above corollary we conclude that Eq. (3.27) holds for **all** Carnot engines operating between these two reservoirs.

Using the definition of efficiency, Eq. (3.24) we can further derive an important general relation, the so-called

Carnot relation

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H},\tag{3.28}$$

applicable to Carnot engines.

In the following, we will discuss several examples involving heat engines.

Example 1:

A power station contains a heat engine operating between two reservoirs, one comprising steam at 100°C and the other comprising water at 20°C. What is the maximum amount of electrical energy which can be produced for every Joule of heat extracted from the steam?

Solution:

The maximum w comes from a Carnot engine. We have $Q_H - Q_C = w$ and $Q_H/T_H = Q_C/T_C$. Hence

$$w = Q_H \left(1 - \frac{T_C}{T_H} \right).$$

Insert $Q_H = 1J$, $T_C = 293K$, $T_H = 373K$ and obtain

$$w = 1J \times \left(1 - \frac{293K}{373K}\right) = 0.21J. \tag{3.29}$$

Example 2:

A refrigerator operating in a room at 20°C has to extract heat at a rate of 500 W from the cabinet at 4 °C to compensate for the imperfect insulation. How much power must be supplied to the motor if its efficiency is 80% of the maximum possible?

Solution:

To make our lives a little bit easier we will operate with energy and heat transferred per second, and indicate this by a 'dot', i.e. \dot{W} , \dot{q}_H , etc. The minimum \dot{W}_{min} comes from a Carnot refrigerator. We have

$$W_{min} = \dot{q}_H - \dot{q}_C, \tag{3.30}$$

as well as

$$\frac{\dot{q}_H}{T_H} = \frac{\dot{q}_C}{T_C}.\tag{3.31}$$

hence

$$\dot{W}_{min} = \dot{q}_C \left(\frac{T_H}{T_C} - 1 \right).$$

Insert $\dot{q}_C = 500$ W, $T_C = 277$ K, $T_H = 293$ K and find

$$\dot{W}_{min} = 500 \text{W} \times \frac{16}{277} = 28.9 \text{W}.$$
 (3.32)

But the real refrigerator works at 80% of maximum efficiency, so we have $\dot{W}_{real} = \dot{W}_{min}/0.8 = 36.1$ W.

A few things to think about: Do you know how a real refrigerator works? What is the common working substance used? Can efficiency of a refrigerator (as defined above) be greater than one?

[Refs.: (1) Mandl 5.2; (2) Bowley and Sanchez 2.3; (3) Zemansky 7.1-7.4]

3.5 The thermodynamic temperature scale*

We have already seen how to define temperature based on the properties of an ideal gas, see Sec. 2.6.2. Essentially you do the following: take water to the triple point, and put it in thermal equilibrium with a container of volume V, and with n moles of an ideal gas in it. Call the pressure you measure P_{triple} . Now to define the temperature of something else, put that something else in contact with the same container of n moles of an ideal gas, and with volume V. You will measure a different pressure. The ideal-gas temperature of the 'something' is then defined as $T = T_{\text{triple}} P/P_{\text{triple}}$. The parameter T_{triple} sets the scale, and it is, by convention, set to $T_{\text{triple}} = 273.16$ K.

Now this whole process relies on the properties of the ideal gas. We now want to define a temperature scale which does not depend on the properties of a specific working substance.

To this end we use the properties of the Carnot cycle. We know that <u>any</u> Carnot engine operating between two fixed reservoirs will have the sam efficiency <u>regardless of the working substance</u> of the engine:

$$\eta_{\text{Carnot}} = 1 - \frac{Q_C}{Q_H},\tag{3.33}$$

where Q_H and Q_C are the amounts of heat extracted per cycle from the hot reservoir and rejected into the cold reservoir, respectively. It was Kelvin's idea to use this principle to define a temperature scale: Supposed you have a system A of which you would like to determine the temperature. Use this system as one of the reservoirs of a Carnot engine. For the other reservoir use a system, B, in thermal equilibrium with water at the triple point. Then measure the amounts of heat flowing out of/into systems A and B in one cycle of the Carnot engine. Then define

$$\Theta_A = \frac{|Q_A|}{|Q_B|} \Theta_{\text{triple}}.$$
(3.34)

In other words this definition of Θ_A can be written as

$$\Theta_A = \Theta_{\text{triple}} \left(1 - \eta(A, B) \right), \qquad (3.35)$$

where $\eta(A, B)$ is the efficiency of Carnot engine running between A and B.

Again, Θ_{triple} is a parameter setting the overall scale, but other than that we have not used any properties of any working substance, only the properties of a generic Carnot engine. Given a heat bath at a reference temperature (e.g. a very large triple-point cell) we can use the efficiency of a Carnot engine working between it and another body to label that other body's temperature.

If we use the ideal gas temperature scale, then we know

$$\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H} \tag{3.36}$$

for a Carnot engine operating between reservoirs with absolute temperatures T_C and T_H . This was Kelvin's idea in 1848, and it is referred to as a 'thermodynamic temperature scale'. The word 'thermodynamic' here indicates that one does not use the properties of a particular working substance, but only those of general Carnot engines. And these in turn are derived from the laws of thermodynamics.

We can make this argument more formal. Say we have an arbitrary temperature scale, ϑ , such that

$$\theta_1 > \theta_2 \Leftrightarrow \text{body 1 is hotter than body 2.}$$
 (3.37)

Now look at three thermal baths of temperatures $\theta_C < \theta_I < \theta_H$ in this arbitrary scale. Construct two Carnot engines, one operating between θ_H and θ_I , the other between θ_I and θ_C , as shown on the left in Fig. 3.9. We construct these engines such that the heat transferred into the intermediate heat bath is of the same magnitude as the heat taken out of that heat bath by the other (this is labelled Q_I in the figure). Now, the efficiencies of these two engines are

$$\eta_{HI} = 1 - \frac{Q_I}{Q_H},$$

 $\eta_{IC} = 1 - \frac{Q_C}{Q_I}.$
(3.38)

Given the universality of the efficiencies of Carnot engines, <u>any</u> reversible engine between these reservoirs would have the same efficiencies, regardless of their working substances. So these efficiencies can only depend on temperature:

$$\eta_{HI} = 1 - f(\theta_I, \theta_H)$$

$$\eta_{IC} = 1 - f(\theta_C, \theta_I),$$
(3.39)

with some unknown function $f(\cdot, \cdot)$.

Next, we look at the construction on the left-hand-side of the figure as a whole. Effectively, the composite system (made of the two engines we have discussed) is a reversible engine operating between Q_C and Q_H . That engine must then have efficiency

$$\eta_{HC} = 1 - f(\theta_C, \theta_H). \tag{3.40}$$

Now, assume we use some different temperature scale, θ . Then we have $\theta_C = \theta(T_C)$ and $\theta_H = \theta(R_H)$. The mapping between θ and T is assume to be one-to-one. The efficiency of the Carnot engine can then be expressed in terms of θ_C and θ_H , let's say

$$\eta_{\text{Carnot}} = 1 - f(\theta_C, \theta_H), \qquad (3.41)$$



Figure 3.9: Construction used to deduce properties of the thermodynamic temperature scale.

where $f(\theta_C, \theta_H)$ is an unknown function. Looking at Carnot engines working in series we will now show of what form $f(\theta_C, \theta_H)$ must be.

From the processes within the compound engine on the left we also have

$$w_1 = Q_H - Q_I = [1 - f(\theta_I, \theta_H)]Q_H, \qquad (3.42)$$

and

$$w_2 = Q_I - Q_C = [1 - f(\theta_C, \theta_I)]Q_I = [1 - f(\theta_C, \theta_I)]f(\theta_I, \theta_H)Q_H.$$
 (3.43)

Combine these two equations, and find

$$w_1 + w_2 = [1 - f(\theta_C, \theta_I) f(\theta_I, \theta_H)] Q_H.$$
(3.44)

Hence, the efficiency of the composite engine is

$$\eta_{\text{composite}} = \frac{w_1 + w_2}{Q_H} = 1 - f(\theta_C, \theta_I) f(\theta_I, \theta_H).$$
(3.45)

This must be identical to $\eta_{HC} = 1 - f(\theta_C, \theta_H)$, see Eq. (3.40). This leads to

$$f(\theta_C, \theta_H) = f(\theta_C, \theta_I) f(\theta_I, \theta_H).$$
(3.46)

From this one has

$$\ln[f(\theta_C, \theta_H)] = \ln[f(\theta_C, \theta_I)] + \ln[f(\theta_I, \theta_H)], \qquad (3.47)$$

and thus

$$\frac{\partial}{\partial \theta_C} \ln[f(\theta_C, \theta_H)] = \frac{\partial}{\partial \theta_C} \ln[f(\theta_C, \theta_I)].$$
(3.48)

This is only possible if $f(\cdot, \cdot)$ is of the form $f(\theta_1, \theta_2) = g(\theta_1)h(\theta_2)$. Now insert this into Eq. (3.45), and get

$$g(\theta_C)h(\theta_H) = g(\theta_C)h(\theta_I)g(\theta_I)h(\theta_H).$$
(3.49)

From this we get

$$g(\theta) = \frac{1}{h(\theta)},\tag{3.50}$$

and thus $f(\cdot, \cdot)$ must be of the form

$$f(\theta_1, \theta_2) = \frac{g(\theta_1)}{g(\theta_2)}.$$
(3.51)

We find

$$\eta_{\text{Carnot}} = 1 - \frac{g(\theta_1)}{g(\theta_2)} \tag{3.52}$$

for any Carnot engine operating between θ_1 and θ_2 . The function g is at this point still arbitrary, it is determined by our choice of temperature scale, θ . Or vice versa, any choice of g defines a temperature scale, θ .

The absolute Kelvin scale corresponds to a linear function $g(\theta) = \theta$,

Kelvin scale :
$$\eta_{\text{Carnot}} = 1 - \frac{\theta_1}{\theta_2}.$$
 (3.53)

Comparison with Eq. (3.36) shows that the absolute Kelvin scale θ (defined by $g(\theta) = \theta$) must be proportional to the ideal-gas absolute temperature, i.e. $\theta = \alpha T$, where T is the absolute ideal-gas temperature and α a constant. Clearly $\alpha = 1$ if we define $\theta_{\text{triple}} = T_{\text{triple}} = 273.16$ K. This is in fact the convention Kelvin chose.

[Refs.: (1) Bowley and Sanchez 2.3-2.4; (2) Zemansky 7.5]

3.6 Entropy and maximum-entropy principle

3.6.1 Clausius' Theorem

The extremely important result which we now prove is the following theorem.

Clausius' Theorem

If a system is taken through a cycle, the algebraic sum of the heat added weighted by the inverse of the temperature at which it is added, can never be greater than zero,

$$\oint \frac{dQ}{T} \le 0 \ . \tag{3.54}$$

The equality holds if the process is reversible, i.e.

$$\oint \frac{dQ^{\text{rev}}}{T} = 0 . \tag{3.55}$$

Proof:

We follow Blundell and Blundell, Concepts in Thermal Physics, Oxford University Press. The theorem can be derived from the second law as follows:

Consider a Carnot engine, C, operating between a heat reservoir at temperature T_0 and a second system at temperature T_i . We consider a cyclic process. In each cycle the temperature



Figure 3.10: Construction used to prove Clausius' Theorem.

of the second system goes through a sequence of temperatures, T_1, T_2, \ldots, T_N , this is where the label T_i comes from in Fig. 3.10. In the time element of the cycle during which the system is at T_i and amount of heat dQ_i is transferred from the Carnot engine to the system at T_i , at the same time C does an amount of work dW_i^C . Using the first law the amount of heat the Carnot engine extracts from the reservoir at T_0 must then be $dW_i^C + dQ_i$. At the same time we assume that the system T_i does an amount of work dW_i on the environment during this part of the cycle.

Our strategy is to prove that $\sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0$, and we will then take the limit $N \to \infty$ to obtain Clausius' Theorem.

For the Carnot engine we know that during the time interval i:

$$\frac{\text{heat to reservoir at } T_i}{T_i} = \frac{\text{heat from reservoir at } T_0}{T_0},$$
(3.56)

i.e.

$$\frac{dQ_i}{T_i} = \frac{dQ_i + dW_i^C}{T_0}.$$
(3.57)

From this we find

$$dW_i^C = dQ_i \left(\frac{T_0}{T_i} - 1\right). \tag{3.58}$$

Of course the whole setup in Fig. 3.10 looks very suspicious, from the figure it seems that what the system does in any one cycle is to extract heat from T and to convert it fully into work. This is forbidden by the second law (Kelvin's statement). So some of the quantities in the figure must be negative. More precisely

total work produced per cycle =
$$\sum_{i=1}^{n} (dW_i^C + dW_i),$$
 (3.59)

and this quantity cannot be positive. So

$$\sum_{i=1}^{N} d(W_i^C + dQ_i) \le 0, \tag{3.60}$$

where we have used $\sum_i dW_i = \sum_i dQ_i$. Using relation (3.57) we find

$$T_0 \sum_{i=1}^{N} \frac{dQ_i}{T_i} \le 0, \tag{3.61}$$

and so (since $T_0 > 0$):

$$\sum_{i=1}^{N} \frac{dQ_i}{T_i} \le 0.$$
(3.62)

Taking the limit $N \to \infty$, we replace the sum by an integral and obtain

$$\oint \frac{dQ}{T} \le 0, \tag{3.63}$$

keeping in mind that we are operating a cyclic process.

If the process is reversible, we have

$$\oint \frac{dQ}{T} = 0. \tag{3.64}$$

To demonstrate this, reverse all arrows in Fig. 3.10, i.e. all quantities change sign. The total work done per cycle is then

total work produced per cycle =
$$-\sum_{i=1}^{n} (dW_i^C + dW_i).$$
 (3.65)

Using the second law we require

$$-\sum_{i=1}^{n} (dW_i^C + dW_i) \le 0, \tag{3.66}$$

which leads to

$$-\sum_{i=1}^{N} \frac{dQ_i}{T_i} \le 0.$$
(3.67)

This, together with $\sum_{i=1}^{N} \frac{dQ_i}{T_i} \leq 0$ means that

$$\sum_{i=1}^{N} \frac{dQ_i}{T_i} = 0. ag{3.68}$$

This completes the proof.

Remark:

Clausius' theorem is easily verified for Carnot cycles, since for these heat only enters or leaves at one of two temperatures. One has

$$\oint_{\text{Carnot}} \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0, \qquad (3.69)$$

where we have used Eq. (3.28) for the second equal sign.

3.6.2 Entropy and the maximum-entropy principle

Definition and function-of-state property

We are now in a position to introduce the concept of <u>entropy</u>. For a given system, the change in entropy for an infinitesimal <u>reversible</u> change is defined by

$$dS = \frac{dQ}{T}.$$
(3.70)

It follows from Clausius' theorem (which in turn was derived from the second law) that S is a function of state.

<u>Proof:</u>

We have seen that

$$\oint \frac{dQ}{T} = 0 \tag{3.71}$$

for all reversible processes. Now consider an initial state, i, and a final state f of a system, and two reversible paths from i to f. Call these paths A and B. What we need to show is that the integral $\int_i^f dS$ does not depend on the path. We use a standard argument: go from i to f using path A, and then back from f to i using the reversed path of B. This defines a cycle, so the total change of entropy is zero along the cycle. Get

$$0 = \oint dS = \int_{\text{path A}} dS - \int_{\text{path B}} dS \tag{3.72}$$

and so

$$S(\text{state } f) - S(\text{state } i) = \int_{\text{path A}} dS = \int_{\text{path B}} dS.$$
(3.73)

 \implies The entropy S is a function of state.

Maximum-entropy principle

We have introduced dS = dQ/T for reversible processes, and seen that $\oint dS = 0$ if all processes along the cycle are reversible. What about other processes? By considering a cycle consisting of one reversible and one irreversible process (see Fig. 3.11), we can show that in general,

$$dQ \le TdS. \tag{3.74}$$

To see this, consider Fig. 3.11. From the reversible path we have

$$S_2 - S_1 = \int_1^2 \frac{dQ^{\text{rev}}}{T}.$$
 (3.75)

What can we say about an irreversible process between the same endpoints? Clearly the entropy change is the same (that's what we mean by saying entropy is a function of state.) But if we consider a cycle involving an <u>irreversible</u> process from 1 to 2 and a reversible process to return to 1, we have a cycle for which Clausius's theorem holds:

$$\oint \frac{dQ}{T} < 0 \tag{3.76}$$



Figure 3.11: Construction used to show $dS \ge \frac{dQ}{T}$.

Decomposing $\oint \frac{dQ}{T} = \int_1^2 \frac{dQ^{\text{irrev}}}{T} + \int_2^1 \frac{dQ^{\text{rev}}}{T}$ we find

$$\int_{1}^{2} \frac{dQ^{\text{irrev}}}{T} < \int_{1}^{2} \frac{dQ^{\text{rev}}}{T} = \int_{1}^{2} dS.$$
(3.77)

From this we conclude

$$dQ \le TdS. \tag{3.78}$$

Summary:

If an amount of heat dQ is supplied to a system from a source at temperature T, then the change in the entropy of the system satisfied the inequality

$$dS \ge \frac{dQ}{T}.\tag{3.79}$$

The equality applies if the process is reversible.

Isolated systems: If a system is thermally isolated dQ = 0. This means that

$$dS \ge 0$$
 for thermally isolated systems (3.80)

 \implies The entropy of an isolated system cannot decrease.

This is an alternative statement of the second law. Note: Any system plus its surroundings (in thermodynamics deliberately called by the somewhat grandiose title 'the universe') forms an isolated system. Hence we have another statement:

The entropy of the universe never decreases.

What this means is that any decrease in the entropy of a system must be at least compensated by an increase in the entropy of its surroundings. We can now turn to the

Maximum-entropy principle

An isolated system at equilibrium must be in the state of maximum entropy.

'Proof':

This can be seen as follows: For thermally isolated systems we have $dS \ge 0$ as seen above. In equilibrium state functions do not change, and so we have dS = 0. Hence it is clear that the entropy of an isolated system increases as an equilibrium is approached. It reaches a constant and maximum value when equilibrium is achieved.

Example:

Gas particles expand from volume V_0 to $2V_0$ in an adiabatically isolated container.

Remark:

The more disordered the system, the greater the entropy. This will become more clear (clearer ?) later when we define entropy from microscopic principles. The increase of entropy in every natural irreversible process measures the increase of disorder, or randomness in the universe, associated with that process.

Another remark:

In the next section, we will exploit the fact that entropy is a state function (process independent) when we calculate the entropy change for an irreversible process by considering a reversible process with the same initial and final states. This is the key idea in most questions on entropy calculations. Make sure you understand it, then exploit it when you do the problems on the example sheets.

[Refs.: (1) Bowley and Sanchez 2.5,2.7; (2) Zemansky 8.1-8.2, 8.8-8.9]

3.6.3 Examples involving entropy changes

We will now look at a few prototypical examples of processes involving changes of entropy. These demonstrate (among other things) that, in general,

- the entropy of any system increases when it is heated, and
- the entropy of gas increased when it expands at constant temperature.

A common theme (which we will explore in much more detail later) is that an increase in entropy means an increase in disorder. We will see that the entropy of the universe always increases during spontaneous changes (typical example are the flow of heat from a hotter to a cooler body and the free expansion of a gas). In these examples the total entropy increases, although that of parts of the system may decrease.

Heat flow from hotter to colder bodies is irreversible, and reversible processes must involve heat flow between bodies at the same temperature or only infinitesimally different. The entropy change of the system

$$dS_{\rm system} = \frac{dQ^{\rm rev}}{T} \tag{3.81}$$

must be exactly balanced by that of the heat bath

$$dS_{\rm reservoir} = -\frac{dQ^{\rm rev}}{T} \tag{3.82}$$

so that $dS_{\text{universe}} = 0$.

For adiabatic process no heat flows dQ = 0. Thus, $dS = dQ^{\text{rev}}/T$ and dS = 0 for any reversible, adiabatic process. We say a process is <u>isentropic</u> if it is adiabatic and reversible.

In summary:

- $\Delta S_{\text{universe}} > 0$ for spontaneous changes
- $\Delta S_{\text{universe}} = 0$ for reversible changes, during which

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

- Spontaneous changes are always irreversible
- Isentropic change \Leftrightarrow reversible, adiabatic changes, dS = 0.

Example 1:

Two identical blocks of metal, one at 100 °C and the other at 0 °C are put in thermal contact. Derive the total entropy change when equilibrium is re-established. (You may assume that the heat capacity, C, of each block is constant over this temperature range, and you may neglect volume changes.)

Solution:

Clearly heat will flow from hotter to cooler body until they have the same temperature. By conservation of energy this will be 50 °C. The heat transfer occurs so as to maximise that entropy. So, if dQ is transferred from the hot body at T_H to the cold one at T_C

$$dS_C > \frac{dQ}{T_C}, \quad dS_H > -\frac{dQ}{T_H}, \tag{3.83}$$

and

$$dS_{\text{total}} = dS_H + dS_C > \left(\frac{1}{T_C} - \frac{1}{T_H}\right) dQ > 0.$$
(3.84)

Thus, the entropy decrease of the hot block is more than compensated by the entropy increase of the cold block \implies the spontaneous heat flow is associated with a net (overall) entropy increase.

In order to calculate ΔS_{total} we use the following strategy: we cannot calculate ΔS for irreversible process, so we must find a reversible process that takes us from the same initial to the same final end point. Then, since ΔS is independent of the actual process (you should be able to say why is this so), this will suffice. For heating or cooling of the blocks this would involve a quasistatic process of bringing the blocks into contact with an infinite sequence of heat baths at infinitesimally increasing or decreasing temperature, so that the temperature difference between the heat bath and the block is always negligible and the entropy change is zero.

$$\Delta S = \int_{1}^{2} \frac{dQ^{\text{rev}}}{T},\tag{3.85}$$

where $dQ^{\text{rev}} = CdT$. But if C = const,

$$\Delta S = C \int_{1}^{2} \frac{dT}{T} = C \ln \frac{T_2}{T_1}.$$
(3.86)

Thus, in our case of two identical blocks

$$\Delta S_{\text{total}} = \Delta S_C + \Delta S_H = C \ln \frac{T_f}{T_C} + C \ln \frac{T_f}{T_H} = C \ln \frac{T_f^2}{T_C T_H}.$$
(3.87)

Inserting the values $T_H = 373$ K, $T_C = 273$ K, $T_f = 323$ K,

$$\Delta S_{\text{total}} = C \ln \frac{(323K)^2}{373K \times 273K} = 0.024\text{C}.$$
(3.88)

Note: $\Delta S_{\text{total}} > 0$, as required; and that the unit of entropy = unit of heat capacity = J K⁻¹.

Example 2:

Two identical blocks of metal, one at 100 °C and the other at 0 °C are brought into thermal contact. What is the maximum amount of work w that can be extracted from the hot block in the absence of other heat sinks, expressed as a fraction of the total heat loss Q_H of the hot block?

Solution:

Clearly, we can't just extract heat from the hot block an turn it all into work, since this would violate the second law. In this process $\Delta S_H < 0$. We need to add at least enough heat Q_C to the cold block so that $\Delta S_C > 0$ just balances ΔS_H , i.e. we can make $\Delta S_C + \Delta S_H = 0$. Note the work extracted can always be used to do things which lead to zero entropy change (e.g., raising a weight). Once the two blocks come to the same final temperature T_f no further work can be extracted. From Example 1,

$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_C = C \ln \left(\frac{T_f^2}{T_H T_C}\right) \ge 0.$$
(3.89)

The maximum work possible corresponds to the lowest possible T_f (see equation for work w below). The lowest possible T_f is that for which $\Delta S_{\text{total}} = 0$, viz.

$$T_f = \sqrt{T_H T_C} \approx 319.1 \text{K} = 46.1 \,^{\circ}\text{C}.$$
 (3.90)

(If T_f were any lower $\Delta S_{\text{total}} < 0$ and this isn't allowed by the 2nd law). Now

$$Q_H = C(T_H - T_f), \quad Q_C = C(T_f - T_C).$$
 (3.91)

Hence, by energy conservation, the work extracted is

$$w = Q_H - Q_C = C(T_H + T_C - 2T_f) = C(T_H + T_C - 2\sqrt{T_H T_C}).$$
(3.92)

The efficiency then comes out as

$$\eta = \frac{w}{Q_H} = \frac{T_H + T_C - 2\sqrt{T_H T_C}}{T_H - \sqrt{T_H T_C}} = \frac{(\sqrt{T_H} - \sqrt{T_C})^2}{\sqrt{T_H}(\sqrt{T_H} - \sqrt{T_C})} = 1 - \sqrt{\frac{T_C}{T_H}}.$$
(3.93)

Inserting the values $T_H = 373$ K, $T_C = 273$ K

$$w = \left(1 - \sqrt{\frac{T_H}{T_C}}\right) Q_H = 0.144 Q_H.$$
 (3.94)

i.e., only 14.4% of the heat lost by the initially hot block is available to do work. Note, too, that this maximum efficiency is obtained from a reversible process. [Compare with the corresponding efficiency $\eta = 1 - T_C/T_H = 26.8\%$ for a Carnot engine working between two (infinite) reservoirs at fixed temperatures $T_H = 373$ K, $T_C = 273$ K.]

Example 3 [Heat engines revisited]:

From the law of the non-decrease of entropy, show that the maximum efficiency of a heat engine operating between two (infinite) reservoirs at fixed temperatures T_H and T_C occurs when the engine is reversible.

Solution:

The change in entropy of the total engine

$$\Delta S_{\text{total}} = \Delta S_C + \Delta S_H = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} \ge 0.$$
(3.95)

Hence

$$\frac{Q_C}{Q_H} \ge \frac{T_C}{T_H},\tag{3.96}$$

with equality for $\Delta S = 0$, i.e. for a reversible process. The efficiency is

$$\eta = \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H} \le 1 - \frac{T_C}{T_H},\tag{3.97}$$

with a maximum for equality (i.e., for a reversible engine). This is of course Carnot's theorem, which we have now re-derived from the law of a non-decreasing entropy.

Example 4:

A quantity of n moles of an ideal gas at temperature T_0 is initially confined to half the volume of an thermally insulated container by an insulated partition. The partition is removed without doing any work. What is the ensuing change of entropy?

Solution:

The process is adiabatic, so dQ = 0. However, we recall, this does not imply dS = 0 since this is <u>not</u> a reversible process. Once again we need to find a reversible process to go from same initial to same final point. As we saw earlier (and see, e.g. Q1(b) on Example Sheet 1), this could be an isothermal expansion done reversibly. In such an expansion

$$Q^{\text{rev}} = -W^{\text{rev}} = \int_{1}^{2} P dV = \int_{V_{1}}^{V_{2}} \frac{nRT_{0}}{V} dV = nRT_{0} \ln \frac{V_{2}}{V_{1}}$$
(3.98)

Put $V_2 = 2V_1$ as in this problem

$$\Delta S = \frac{Q^{\text{rev}}}{T_0} = nR\ln 2. \tag{3.99}$$

Note: The logic here is quite subtle - do make absolutely sure you understand the difference between the actual process (with Q = W = 0) and the reversible process for which we are able to calculate ΔS (that process has $Q^{\text{rev}} = -W^{\text{rev}} \neq 0$).

Example 5a: A box of gas is joined by an identical box of the same gas. What is the change in total entropy?

Solution: This is a reversible process (as nothing changes when removing the partition and putting it back). Total entropy change is therefore zero, $\Delta S_{\text{total}} = 0$, where $S_{\text{total}} = S_1 + S_2 = 2S_1$.

The following example is an irreversible process (How?) and the total entropy must increase. Example 5b:

An insulated container is originally divided in half by a partition, and each half is occupied by n moles of two <u>different</u> ideal gases at temperature T_0 . What is the total change in entropy when the partition is removed without doing any work?

Solution:

Since both gases are ideal, they don't interact, each species is oblivious of the other, and ΔS for each is exactly as in Ex. 4 above. Thus

$$\Delta S_{\text{total}} = 2nR\ln 2. \tag{3.100}$$

Note: the total mixing - which we know will happen eventually - is precisely the change that now maximises the entropy, i.e., a clear hint that entropy means disorder. It is obvious that the process is an irreversible one as the situation is quite different from the initial state when putting back the partition after the two gases have mixed.

[Refs.: (1) Mandl 4.3, (2) Bowley and Sanchez 2.8; (3) Zemansky 8.11-8.13]

3.7 The arrow of time

An apparent paradox arises from the second law of thermodynamics:

- Phenomena in the macroscopic world are obviously irreversible.
- But microscopic laws (e.g. Newton's equations, quantum mechanics, Maxwell's equations, ...) are unchanged by replacing t by -t.

Can this paradox be resolved using statistical thermodynamics?

We know that $dS \ge 0$ for isolated systems, and dS > 0 for irreversible processes of such systems. This defines an arrow of time. Eddington stated this as follows (1928):

"Let us draw an arrow arbitrarily. If as we follow the arrow we find more and more of the random element in the state of the world, then the arrow is pointing towards the future; if the random element decreases the arrow points towards the past. $[\ldots]$ I shall use the phrase times arrow to express this one-way property of time which has no analogue in space."

Consider a typical irreversible situation (see Fig. 3.12), the time dependence of the entropy is shown in Fig. 3.13.

Now imagine removing the partition at t = 0, and follow particle trajectories into the past. The fundamental laws of microscopic physics are unchanged under $t \rightarrow -t$, so the same



Figure 3.12: An irreversible process, removal of a barrier separating two sets of identical particles.



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Figure 3.13: Time-dependence of the entropy in the process illustrated in the previous figure.



Figure 3.14: Hypothetical entropy in the past.

uniform distribution would be found at $t = -t_f$ as at $t = +t_f$. This leads to a hypothetical entropy in the past as shown in Fig. 3.14. This looks completely symmetric with respect to time-reversal.

However, starting in the disordered (high-entropy) state at $t = -t_f$ we would never observe the ordered state at later times. If the initial state is one of maximum entropy, then the entropy would remain constant with time.

'Resolution' of the paradox:

So the problem only ever arises if the initial state has an entropy less than the maximum entropy. So one can argue the fact that we see an 'arrow of time' means that the initial state of our universe must have been one of low entropy, i.e. it was very ordered. In our daily physics experience we find that such states need special preparation, e.g. the low-entropy state in the above de-mixing example requires all particles to be on one side of the partition.

Problem:

There is no current theory which would explain a low-entropy early universe. And at this point the paradox is now the cosmologists' problem.

Chapter 4

The mathematical structure of the theory of thermodynamics

"The miracle of the appropriateness of the language of mathematics for the formulation of the laws of physics is a wonderful gift which we neither understand nor deserve."

(Eugene Wigner, 1960)

"Mathematics Is Biology's Next Microscope, Only Better. [...] Those who understand the calculus, ordinary and partial differential equations, and probability theory have a way of seeing and understanding the world, including the biological world, that is unavailable to those who do not.¹" (Joel E. Cohen, 2004)

4.1 Mathematical tools

4.1.1 Differentials

Differentials

Consider a function f = f(x) of one variable. Taylor expanding about a point x then gives

$$f(x + \Delta x) - f(x) = f'(x)\Delta x + \dots$$
(4.1)

where ... stands for higher order terms in Δx . For infinitesimal Δx we write dx, and we introduce df = f(x + dx) - f(x). We then have

$$df = f'(x)dx. \tag{4.2}$$

¹You may wonder why I use this quote in a set of lecture notes for thermal and statistical physics. This is not a course on mathematics, let alone biology, after all. But when Cohen says 'ordinary and partial differential equations', well that's what you learn in physics courses on classical mechanics or electrodynamics, or indeed in third-year nonlinear physics. And when he says 'probability theory', well that's what you discuss in Random Processes, in this course here or in the fourth-year module on advanced statistical physics. The contributions to biology made by those trained in these subjects are tremendous, and much of the progress of modern biology would be impossible without them. Also, I like the title of the paper very much, 'Mathematics Is Biology's Next Microscope, Only Better'. Just brilliant. TG.

If f is a function of multiple variables, x_1, x_2, \ldots , we have the analog expression

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots$$
(4.3)

This is what is called the <u>total differential</u> of f. Next, consider the more general expression

$$du = a_1(x_1, x_2, \ldots) dx_1 + a_2(x_1, x_2, \ldots) dx_2 + \ldots$$
(4.4)

Expressions of this type are also called differentials, but notice the difference compared to Eq. (4.3). The expression in (4.4) is more general, as the functions a_1, a_2, \ldots can be arbitrary. In Eq. (4.3) they have to be the partial derivatives of a common function, f.

Why are these things of interest? Well, consider a particle in classical Newtonian dynamics, moving in a 3-dimensional space, x, y, z. Let the force acting on the particle be

$$\underline{F} = \begin{pmatrix} a_1(x, y, z) \\ a_2(x, y, z) \\ a_3(x, y, z) \end{pmatrix}$$
(4.5)

If the particle is at position (x, y, z) and you move it by $d\underline{r} = \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix}$, then the amount of

work you do is

$$dW = \underline{F} \cdot d\underline{r} = a_1(x, y, z)dx + a_2(x, y, z)dy + a_3(x, y, z)dz.$$
(4.6)

This is obviously a differential of the above general type.

Exact differentials

We can now define what we mean by an \underline{exact} differential. It is a differential of the type described in Eq. 4.3. One has the following

<u>Theorem²</u>

For a differential $du = a_1(x_1, x_2, ...)dx_1 + a_2(x_1, x_2, ...)dx_2 + ...$ the following statements are equivalent:

- (i) There exists a function $f(x_1, x_2, ...)$ such that $a_i(x_1, x_2, ...) = \frac{\partial f(x_1, x_2, ...)}{\partial x_i}$.
- (ii) The integral over *du* along a path in *x*-space only depends on the starting point and the end point, but not on the specifics of the path.
- (iii) The integral of du along closed loops in x-space vanishes, $\oint du = 0$.
- (iv) One has $\frac{\partial a_i}{\partial x_j} = \frac{\partial a_j}{\partial x_i}$ for all combinations i, j.

 $^{^{2}}$ Strictly speaking this holds only on so-called simply connected domains. We will ignore this here, as all domains we are looking at are simply connected.

Definition

A differential which has any of the properties above is called an exact differential. By virtue of the theorem it then has <u>all</u> of the above properties.

This is an extremely important theorem, and somebody should have discussed this with you in earlier courses. It is used everywhere, in classical mechanics, in electrodynamics and here in thermodynamics. Everybody who wants to call themselves a physicist must have gone through the proof in detail at least once. Theorists must remember it forever. If you are not familiar with this then please look it up. Knowing and understanding this is extremely useful for all aspects of your life. I here sketch how this is proved. One does this cyclically.

Remark:

Consider again the force field

$$\underline{F} = \begin{pmatrix} a_1(x, y, z) \\ a_2(x, y, z) \\ a_3(x, y, z) \end{pmatrix}.$$
(4.7)

The condition for $dW = \underline{F} \cdot d\underline{r} = a_1 dx + a_2 dy + a_3 dz$ to be exact then reads (property (iv) in the theorem):

$$\partial_1 a_2 = \partial_2 a_1$$

$$\partial_2 a_3 = \partial_3 a_2$$

$$\partial_3 a_1 = \partial_1 a_3,$$
(4.8)

where I have written $\partial_1 = \frac{\partial}{\partial x}$ and similarly for ∂_2 and ∂_3 . Remembering the definition of the curl, this means

$$\operatorname{curl} \underline{F} = \begin{pmatrix} \partial_2 a_3 - \partial_3 a_2 \\ \partial_3 a_1 - \partial_1 a_3 \\ \partial_1 a_2 - \partial_2 a_1 \end{pmatrix} = \underline{0}.$$
(4.9)

So

$$dW = \underline{F} \cdot d\underline{r}$$
 is exact \Leftrightarrow curl $\underline{F} = \underline{0}$. (4.10)

This is what defines a <u>conservative force</u> in classical mechanics. In this case there is a potential function V(x, y, z) such that $\underline{F} = \nabla V$ (you should understand why this is property (i) in the above theorem, where the convention is to use -V instead of f).

Proof of the theorem:

 $(iii) \Longrightarrow (ii)$

This is almost obvious. No, it is really very obvious. Take two paths both connecting say A and B. Then construct a loop from A to B via one of the paths, then back to A via the other path. The integral along the loop vanishes, but this integral is also the integral along the first path, minus that of the second path.

 $(ii) \Longrightarrow (i)$

Pick a reference point A anywhere in x-space. For any point $B = (x_1, x_2, ...)$ find a path connecting A with that point. Then define $f(x_1, x_2, ...) = \int_A^B du$, where the integral is along the path. The value of $f(x_1, x_2, ...)$ is independent of the path. Choosing a path consisting of segments parallel to the axes, one proves $a_i = \partial_i f$, where I have written ∂_i for $\frac{\partial}{\partial x_i}$.

 $(i) \Longrightarrow (iv)$ This is (almost) obvious. If $a_i = \partial_i f$, then $\partial_j a_i = \partial_j \partial_i f$. But partial derivatives commute, so $\partial_i \partial_i = \partial_i \partial_j$. So $\partial_j a_i = \partial_j \partial_i f = \partial_i \partial_j f = \partial_i a_j$.

 $\underline{(iv)} \Longrightarrow \underline{(iii)}$ This is the hard bit. It would be too long to write this down here. The trick is to consider infinitesimally small loops oriented parallel to the axes, and then to decompose other loops into a collection of such small loops.

The rules of engagement

Notation:

If w = w(u, v) is a function of u and v, the partial derivative of w with respect to u with v held fixed is written as

$$\left(\frac{\partial w}{\partial u}\right)_v = \left.\frac{\partial w}{\partial u}\right|_v \tag{4.11}$$

Both notations means the same thing.

IMPORTANT REMARK:

Partial derivatives appear everywhere in physics. In most contexts we usually do not specify what variables are held constant. In most areas of physics and mathematics we simply write $\frac{\partial f}{\partial x}$ instead of $\left(\frac{\partial f}{\partial x}\right)_y$ when it is obvious that f = f(x, y). E.g., in the wave equation we simply write $\frac{\partial^2 u}{\partial t^2} = c^2 \Delta u$, where $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$. It is here obvious what is being held constant, for example x, y, z are constant in $\frac{\partial^2 u}{\partial t^2}$.

In thermodynamics, where we are often changing variables from one set to another this can be <u>FATAL</u>. It is crucial to <u>ALWAYS</u> specify carefully what is being held constant.

The only exception is that most of the time we deal with a fixed amount of substance, i.e. the number N of molecules involved is constant. We don't always bother to write, e.g. $\left(\frac{\partial E}{\partial S}\right)_{V,N}$. Instead we use the slightly sloppier $\left(\frac{\partial E}{\partial S}\right)_V$, when it is absolutely obvious from context that N is always constant. For some systems this is not the case. It is then again important to specify when N is being held constant, and when not.

Total derivative:

If both u and v change infinitesimally, the corresponding change in w is

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du + \left(\frac{\partial w}{\partial v}\right)_u dv.$$
(4.12)

Basic properties: We have

$$\left(\frac{\partial v}{\partial u}\right)_v = \left(\frac{\partial u}{\partial v}\right)_u = 0, \tag{4.13}$$

and

$$\left(\frac{\partial u}{\partial u}\right)_v = \left(\frac{\partial v}{\partial v}\right)_u = 1. \tag{4.14}$$

Order of derivatives does not matter:

Furthermore, the order in which we take multiple partial derivatives doesn't matter, i.e.

$$\frac{\partial}{\partial v}\Big|_{u}\left(\frac{\partial w}{\partial u}\right)_{v} = \frac{\partial}{\partial u}\Big|_{v}\left(\frac{\partial w}{\partial v}\right)_{u},\tag{4.15}$$

where

$$\frac{\partial}{\partial v}\Big|_{u}\left(\frac{\partial w}{\partial u}\right)_{v} \equiv \left(\frac{\partial}{\partial v}\left(\frac{\partial w}{\partial u}\right)_{v}\right)_{u}.$$
(4.16)

Reciprocals:

If we use u and v as independent variables (w = w(u, v)) we have

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du + \left(\frac{\partial w}{\partial v}\right)_u dv.$$
(4.17)

If we convert w = w(u, v) into u = u(v, w) we have

$$du = \left(\frac{\partial u}{\partial v}\right)_w dv + \left(\frac{\partial u}{\partial w}\right)_v dw.$$
(4.18)

Now consider the case in which v is held constant. We then find

$$dw = \left(\frac{\partial w}{\partial u}\right)_{v} du$$
$$du = \left(\frac{\partial u}{\partial w}\right)_{v} dw$$
(4.19)

We conclude

$$\left(\frac{\partial w}{\partial u}\right)_v = \frac{1}{\left(\frac{\partial u}{\partial w}\right)_v}.$$
(4.20)

 $\frac{\text{Cyclic permutations:}}{\text{If } w = \text{const. we find from Eq. (4.17)}}$

$$\left(\frac{\partial w}{\partial u}\right)_{v} du = -\left(\frac{\partial w}{\partial v}\right)_{u} dv.$$
(4.21)

Taking $\left.\frac{\partial}{\partial v}\right|_w$ of both sides we get

$$\left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w = -\left(\frac{\partial w}{\partial v}\right)_u,\tag{4.22}$$

After multiplying both sides by $\left(\frac{\partial u}{\partial w}\right)_v$ and using the rule for reciprocals, Eq. (4.20)

$$\left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w \left(\frac{\partial v}{\partial w}\right)_u = -1, \tag{4.23}$$

which is not at all obvious. In particular, the factor (-1) is very counter-intuitive!

We can re-write this as

$$\left(\frac{\partial u}{\partial v}\right)_{w} = -\frac{\left(\frac{\partial w}{\partial v}\right)_{u}}{\left(\frac{\partial w}{\partial u}\right)_{v}} = -\frac{\left(\frac{\partial u}{\partial w}\right)_{v}}{\left(\frac{\partial v}{\partial w}\right)_{u}}.$$
(4.24)

Test question:

Does a function f(x, y) exist whose differential satisfies

$$df = -ydx + xdy? \tag{4.25}$$

Answer:

No. In order for -ydx + xdy to be exact, we would need $\partial_y(-y) = \partial_x(x)$, which is obviously not the case. More explicitly, we can prove this as follows:

For any function f one has

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy.$$
(4.26)

So we would need

$$\left(\frac{\partial f}{\partial x}\right)_y = -y,\tag{4.27}$$

and

$$\left(\frac{\partial f}{\partial y}\right)_x = x. \tag{4.28}$$

From (4.27):

$$f(x,y) = -xy + \Phi(y),$$
 (4.29)

with an arbitrary function $\Phi(\cdot)$. This means

$$\left(\frac{\partial f}{\partial y}\right)_x = -x + \frac{d\Phi}{dy},\tag{4.30}$$

which contradicts (4.28). So we should really write

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy,\tag{4.31}$$

as this is <u>not</u> an exact differential.

4.1.2 Legendre transformation

Consider a convex (upward-curved) function y = y(x). This defines a curve in x-y space, see Fig. 4.1. We can draw this curve, if given the functional relationship, y = y(x), say for example $y(x) = x^2$.

Equivalently the curve is described by the set of tangents, drawn as blue lines in the figure. The curve, y = y(x), is the envelope of the set of tangents. So instead of specifying the curve itself, y = y(x), we could specify the set of tangents. How would that work?



Figure 4.1: Legendre transform. Source http://commons.wikimedia.org/wiki/File:Transformada_de_Legendre.png

Well, any particular tangent is specified by its slope, P, and by its intercept, Ψ , see Fig. 4.1. So if the relationship, $\Psi = \Psi(P)$ is known, the set of tangents can be drawn. For any P, start at the point $(x = 0, y = \Psi(P))$ and then draw a straight line with slope P. If you do this for all P would will have drawn the set of tangents, and the curve y = y(x) is obtained as its envelope.

So we have established that knowing $\Psi = \Psi(P)$ is equivalent to knowing y = y(x).

Now, how are $\Psi(P)$ and y = y(x) related?

Well, look again at Fig. 4.1. The tangent through a point (x, y) on the curve has slope

$$P = \frac{y - \Psi}{x - 0},\tag{4.32}$$

if Ψ is the intercept of the tangent. Given that this line is a tangent to the curve, y = y(x), we also have P = y'(x). Now re-arranging this we have

$$\Psi(P) = y - xP \tag{4.33}$$

It remains to specify x and y as a function of P. This is where we need the convexity of the curve, y = y(x). If the curve is convex (upward curved) then any slope appears only at one location, x. So for any given value of P, there is a unique x such that P = y'(x), where y' stands for dy/dx. We write, x = x(P). Inserting into the equation defining the curve, y = y(x), we then also obtain y = y(P).

We can then write the Legendre transform of y = y(x) as

$$\Psi(P) = y(P) - x(P)P. \tag{4.34}$$

Example:

Let us consider the curve, $y(x) = x^2$. We then have y'(x) = 2x. Now for a given P what is the point x, such that y'(x) = P. Well, y'(x) = 2x = P gives

$$x(P) = \frac{P}{2}.\tag{4.35}$$

We then also have

$$y(P) = y(x(P)) = [x(P)]^2 = \left(\frac{P}{2}\right)^2 = \frac{P^2}{4}.$$
 (4.36)

So we find

$$\Psi(P) = y(P) - x(P)P$$

$$= \frac{P^2}{4} - \frac{P}{2}P$$

$$= -\frac{P^2}{4}$$
(4.37)

So we have found that $\Psi(P) = -\frac{P^2}{4}$ is the Legendre transform of y = y(x).

Exercise:

Find the expression defining the inverse Legendre transform of a function, $\Psi = \Psi(P)$.

A nice exposition can be found in C. S. Helrich, Modern Thermodynamics with Statistical Mechanics, Springer, 2009.

4.2 The postulates of thermodynamics*

There are several ways to introduce the theory of thermodynamics:

• Phenomenological:

The theory is built on experimental observations, encoded in the 'laws of thermodynamics'. This is the approach we have taken so far.

• Derived from statistical physics:

In this approach the laws governing macroscopic systems are derived from the microscopic properties of matter. This is the approach we will discuss in the second half of this course (Chapter 5 onwards)

• <u>Axiomatic:</u>

The theory is built on a set of axioms, and all further statements are then derived from these. This is nicely discussed in the book by Callen (Thermodynamics and an introduction to thermostatistics). The axioms are closely related to the phenomenological laws of thermodynamics, but this approach makes the underlying mathematical structures more clear.

So far, we have taken the first approach. It is worth pointing out though that the whole theory of thermodynamics can be based on four axioms (or postulates), as follows. We follow the book by Callen (Herbert B. Callen, Thermodynamics and an introduction to thermostatistics, Wiley):

Postulate 1:

There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the mole number of particles, N_1, N_2, \ldots

Postulate 2:

There exists a function, S, called the entropy, of the extensive parameters of any composite system, defined for all equilibrium states and with following property: The values assumed by the extensive parameters upon removal of an internal constraint are those that maximize the entropy subject to any remaining constraints.

Postulate 3:

The entropy is an extensive quantity, it is additive over the constituent subsystems. The entropy is continuous and differentiable and a strictly increasing function of the internal energy.

Postulate 4:

The entropy of any system is non-negative, and it vanishes for states for which $\frac{\partial U}{\partial S}\Big|_{V,N_1,N_2,\dots} = 0$ (i.e. at zero temperature).

4.3 The fundamental thermodynamic relation

We have the first law for infinitesimal changes

$$dE = dQ + dW \tag{4.38}$$

or, specifically to reversible changes of state

$$dE = dQ^{\rm rev} + dW^{\rm rev}. \tag{4.39}$$

We have already found expressions for dW^{rev} for a variety of thermodynamic systems in Sec. 2.3. Now, after the introduction of entropy, we also have one for $dQ^{\text{rev}} = TdS$. Therefore

$$dE = TdS - PdV. (4.40)$$

This is the FUNDAMENTAL THERMODYNAMIC RELATION (for a fluid), which is valid for <u>all</u> processes between two neighbouring (infinitesimally close) equilibrium states.

Note:

- Eq. (4.40) involves only state variables, so it must be for <u>all</u> changes, whether reversible or not.
- For other systems the term $-PdV = dW^{\text{rev}}$ for a fluid (gas) is to be replaced by the corresponding expression for that system (e.g., σdA for a surface film, $-\mathbf{m} \cdot d\mathbf{B}$ for a paramagnet, etc., as in Sec. 2.3).
- Eq. (4.40) will be used over and over again in this course; it is one of the most important equations we will meet in this course (and you must remember it!)

Summary:

• For <u>all</u> processes we have

$$dE = dQ + dW \tag{4.41}$$

$$dE = TdS - PdV \text{ (for a fluid or gas)}. \tag{4.42}$$

• For <u>reversible</u> processes we have

$$dQ = TdS \tag{4.43}$$

$$dW = -PdV$$
 (for a fluid or gas). (4.44)

• For <u>irreversible</u> processes we have

$$dQ < TdS \tag{4.45}$$

$$dW > -PdV$$
 (for a fluid or gas). (4.46)

[Refs.: (1) Mandl 4.1; (2) Bowley and Sanchez 2.5; (3) Zemansky 8.14.]

4.4 Thermodynamic Potentials

4.4.1 Introduction and definition of the potentials

So far we have encountered various functions of state, for example P, V, T, E, S for a fluid system (gas). We can construct other functions of state by adding combinations of these together.

Four combinations, all with dimensions of energy, play important roles in the theory of thermodynamics. They are

- internal energy: E,
- enthalpy: H = E + PV,
- Helmholtz free energy: F = E TS,
- Gibbs free energy: G = E TS + PV.

For infinitesimal processes we have

- dE = TdS PdV (fundamental thermodynamic relation),
- dH = dE + PdV + VdP = TdS + VdP,
- dF = dE TdS SdT = -PdV SdT,
- dG = dE TdS SdT + PdV + VdP = -SdT + VdP.

This was all expressed for hydrostatic systems. For magnetic systems one has to replace the fundamental relation by

$$dE = TdS - mdB. \tag{4.47}$$

Comparing with dE = TdS - PdV we have the correspondences

$$P \leftrightarrow m, \quad V \leftrightarrow B.$$
 (4.48)

<u>Useful exercise:</u>

Write down the expressions for dH, dF and dG for magnetic systems.

Natural variables for the potentials:

The internal energy E can be thought of, in principle, as a function of any two of the other functions of state, i.e.

$$E = E(V,T), \ E = E(P,T), \ E = E(P,S), \dots$$
 (4.49)

But it is natural to think of E as a function of S and V.

Why?

If we think of E as a function of S and V, i.e. E = E(S, V), then we have

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$
(4.50)

Compare this with the fundamental relation,

$$dE = TdS - PdV. (4.51)$$

We conclude

$$T = \left(\frac{\partial E}{\partial S}\right)_V$$
 and $P = -\left(\frac{\partial E}{\partial V}\right)_S$. (4.52)

 \implies If E = E(S, V) is a known function, the other two functions of state (T and P), can be found by differentiation.

Each potential has its own set of <u>natural</u> independent variables:

$$E = E(S, V), \quad H = H(S, P), \quad F = F(T, V), \quad G = G(T, P).$$
 (4.53)

If any of these potentials is known explicitly in terms of its natural variables, then we have complete information about that system.

Example:

Say the statistical mechanics analysis of a system (see later) delivers F = F(T, V). Then we have

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT.$$
(4.54)

Compare this with dF = -PdV - SdT, and find

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V, \tag{4.55}$$

i.e. we get P = P(T, V) and S = S(T, V). We can then also find the other thermodynamic potentials

$$E = F + TS,$$

$$H = F + PV + TS,$$

$$G = F + PV$$
(4.56)

as functions of T and V.

4.4.2 Thermodynamic potentials and Legendre transforms

We treat this here more as an aside, but the mathematical structure of the theory of thermodynamics contains some intrinsic beauty. The thermodynamic potentials we have introduced are obtained via Legendre transforms. More specifically,

• the Helmholtz free energy, F, is the Legendre transform of E = E(S, V) with respect to S:

$$F = E - TS = E - \left(\frac{\partial E}{\partial S}\right)_V S.$$
(4.57)

• the enthalpy, H, is the Legendre transform of E with respect to V

$$H = E + PV = E - \left(\frac{\partial E}{\partial V}\right)_S V. \tag{4.58}$$

• the Gibbs free energy, G, is the Legendre transform of the internal energy E with respect to the entropy S and the volume V

$$G = E - TS + PV = E - \left(\frac{\partial E}{\partial S}\right)_V S - \left(\frac{\partial E}{\partial V}\right)_S V$$
(4.59)

If you would like to know more about Legendre transforms, then I recommend the following article: 'Making sense of the Legendre transform', R. K. P. Zia, Edward F. Redish, Susan R. McKay, Am. J. Phys. **77** 614 (2009). This is quite advanced, and not course material. Highly recommended as a reference, should you ever need Legendre transforms in the future.

4.4.3 Energy picture and entropy picture*

So far we have seen two state functions, internal energy E and entropy S. And we know 2nd law can be used to predict the state of a thermodynamic system. For example, if a system in isolation can have several possible states with different values of entropy, we know it must in the state with maximum entropy.

We revisit the fundamental thermodynamic relations of Eq. (4.40):

$$dE = TdS - PdV. (4.60)$$



Figure 4.2: Surface defined by the relations E = E(S, V) or S = S(E, V) respectively. We have here written X instead of V, to indicate possible other thermodynamic variables. X can be multi-dimensional, and stands for all other variables collectively, including V. A much better version of this figure can be found in the book by Callen, chapter 5.

In this form it suggest that the *natural* variables in which to express E are S and V, i.e., E = E(S, V), as disussed earlier. Hence

$$T = \left(\frac{\partial E}{\partial S}\right)_V; \quad P = -\left(\frac{\partial E}{\partial V}\right)_S. \tag{4.61}$$

It is also easy to re-express the fundamental relation as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \tag{4.62}$$

where S is a state function, S = S(E, V), and E is a variable. So we have the relations

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E.$$
(4.63)

The equations E = E(S, V) and S = S(E, V) define a surface in U - S - V space, see Fig. 4.2

We have the following two principles:

Maximum-entropy principle:

For a closed system with fixed internal energy (i.e. an isolated system) the equilibrium values of any unconstrained thermodynamic variables are such as to maximise the entropy for the given value of the internal energy.

Minimum-energy principle:

For a closed system with fixed entropy, the equilibrium values of any unconstrained thermodynamic variables are such as to minimise the internal energy for the given value of the entropy.



Figure 4.3: Maximum-entropy principle (see text). A better version of this figure can be found in the book by Callen.



Figure 4.4: Minimum-energy principle (see text). A better version of this figure can be found in the book by Callen.



Figure 4.5: Illustration used for definition of 'availability'.

These are illustrated geometrically in Figs. 4.3 and 4.4.

The equivalence of the two principles can be demonstrated by a physical argument, or by a mathematical proof. We here only give the physics argument, for a more formal proof see the book by Callen, chapter 5.1

Physical argument (also following Callen, chapter 5.1): We show that the entropy could not be maximal in equilibrium if the energy wasn't minimal. So assume the system is in equilibrium but that the energy is not at its the minimum value consistent with a given entropy. In this case we could withdraw energy from the system (as work). The entropy of the system would remain constant. We could then convert the extracted work into heat, and return it to the system. The system would return to its initial energy, but its entropy would have increased. This is not consistent with the maximum-entropy principle. So the maximum-entropy principle implies the minimum-energy principle.

4.5 Available work and interpretation of the potentials

4.5.1 Available work

We now consider the maximum amount of useful work (the so-called 'available work') which can be extracted from a system initially out of equilibrium with its surroundings, which are at temperature T_0 and pressure P_0 . This is schematically shown in Fig. 4.5. There are two factors which limit the available work:

- If the system expands, it must overcome the external pressure (e.g. atmosphere), so an amount of work, $P_0\Delta V$, is not available for useful work.
- If the entropy of the system decreases (as in cooling), the entropy of the surroundings must increase enough to compensate. The system must give heat Q_{out} to the surroundings, where $\Delta S + Q_{\text{out}}/T_0 \ge 0$ or $Q_{\text{out}} \ge -T_0 \Delta S$.

The above means that during a change not all of the internal energy change (decrease) can be converted into useful work. More precisely, of the total energy decrease of the system, ΔE , the amount available to do work is

$$w^{\text{useful}} = (-\Delta E) - Q_{\text{out}} - P_0 \Delta V, \qquad (4.64)$$

where we have used the first law. Using $Q_{\text{out}} \geq -T_0 \Delta S$, we find

$$w^{\text{useful}} \le -\Delta E + T_0 \Delta S - P_0 \Delta V \equiv -\Delta A, \tag{4.65}$$

where we have defined the availability

$$A = E - T_0 S + P_0 V. (4.66)$$

We have

$$w^{\text{useful}} \le -\Delta A,$$
 (4.67)

where equality holds for reversible processes. Such a reversible process maximises the useful work available. (Remark: To cool reversibly with only a single cold reservoir would require the use of a heat engine to extract the heat, rather than the direct transfer depicted in Fig. (4.5.) It is now clear why A is referred to as 'availability'.

Note:

- T_0, P_0 are the temperature and pressure of the surroundings, not those of the system
- For system starting and ending at T_0, P_0 :

$$w^{\text{useful}} \le -\Delta G.$$
 (4.68)

• For system at constant volume and starting and ending at T_0 :

$$w^{\text{useful}} \le -\Delta F.$$
 (4.69)

Example:

What is the maximum useful work that can be obtained by cooling 1 mole of an ideal gas at constant volume from a temperature T to the temperature T_0 of the surroundings?

Solution:

We have $\Delta V = 0$, so

$$w_{\rm max} = -\Delta E + T_0 \Delta S. \tag{4.70}$$

(Note $\Delta S < 0$ for cooling.) For an ideal gas

$$\Delta E = C_V \Delta T = C_V (T_0 - T) < 0 \tag{4.71}$$

as $C_V = \text{const.}$ Also, ΔS will be the same as for a reversible process, $dS = dQ/T = C_V dT/T$ (Ex. 1 in Sec. 3.6.3),

$$\Delta S = C_V \int_T^{T_0} \frac{dT}{T} = -C_V \ln \frac{T}{T_0} < 0.$$
(4.72)

The maximum work is therefore

$$w_{\max} = C_V(T - T_0) - C_V T_0 \ln \frac{T}{T_0}.$$
(4.73)

The rest of the energy is discarded to the surroundings to ensure no overall decrease in entropy. Note:

It is not difficult to prove that the above expression for w_{max} is positive for any $T > T_0$. Try it yourself!

4.5.2 The physical meaning of the potentials

From Eq. (4.40) we conclude that E = const. for process at constant volume and constant entropy. These are not exactly the most common experimental condition (S is not directly measurable), this is why it is useful to introduce the other thermodynamic potentials, which are constant when other sets of variables are held fixed. Note also that a system with constant E, V is usually an isolated system. However, more often than not, we are dealing with a system not in isolation but in thermal contact with its environment. This is another reason that it is more convenient to use other state functions (the thermodynamic potentials) to predict the behaviour of such systems.

More specifically:

(a) Internal energy E:

Piston/cylinder with adiabatic walls:

$$\Delta E = Q + W, \tag{4.74}$$

where Q = 0 given that the system is thermally isolated. I.e. $\Delta E = W$: increase in internal energy = work done on the system.

(b) Helmholtz Free Energy F = E - TS:

System in thermal contact with an environment at temperature T_0 .

Theorem:

In a transformation for which the system starts and ends in equilibrium at temperature T_0 (but intermediate states not necessarily at T_0), the change of free energy of a system is less or equal to the work done on the system.

Proof:

Let a system undergo a transformation from state A to state B. Then

$$Q \le T_0 \Delta S. \tag{4.75}$$

This is because of

$$\Delta S \ge \int \frac{dQ}{T_0} = \frac{Q}{T_0}.$$
(4.76)

Also

$$F_B - F_A = (E_B - T_B S_B) - (E_A - T_A S_A) = (E_B - E_A) - T_0 (S_B - S_A),$$
(4.77)

i.e.

$$\Delta F = \Delta E - T_0 \Delta S \le \Delta E - Q = W. \tag{4.78}$$

In the last equality we have used the first law (you should understand each of the equal signs, and the \leq).

Thus, we have

$$\Delta F \le W,\tag{4.79}$$

with equality only for reversible processes.

You (hopefully) realise that we already proved this above in Sec. 4.5.1, see Eq. (4.69). I know, but it is always good to look at important things several times – TG. You may be concerned by the different signs. If you aren't then, you are probably not paying enough attention. Always convince yourself of all details of the calculations in these notes, including the signs. This is the only way to understand this material in detail. Note that our sign conventions are such that W is the work done on the system, not by the system. The quantity w^{useful} on the other hand is useful work done by the system.

Remark:

If the system is mechanically isolated and held constant temperature, the free energy never increases (mechanically isolated means no work is done on or by the system, so W = 0)

Corollary:

In a mechanically isolated system at a constant temperature, the equilibrium state is the state of minimum free energy, i.e., system evolves until F reaches a minimum.

Interpretation:

F is a function of state, so

$$\Delta F = W^{\text{rev}}.\tag{4.80}$$

This implies $W^{\text{rev}} < W^{\text{irrev}}$. (You should understand how this follows from the function-ofstate property, and how the '<' arises). Note: This is work done <u>on</u> the system. So:

- The maximum amount of work that can be extracted from a system is in a reversible change: $-W^{\text{rev}} > -W^{\text{irrev}}$.
- This maximum amount of work is equal to the decrease in Helmholtz free energy

$$-W^{\rm rev} = -\Delta F. \tag{4.81}$$

- The name 'free' comes about since $-W^{\text{rev}} = -\Delta F$ is the maximum amount of energy available (or <u>free</u>) for doing work.
- We have seen dF = -SdT PdV, so the Helmholtz free energy is constant at constant temperature and volume. It plays a key role in statistical physics. The Helmholtz free energy is the thermodynamic potential of the statistical physicist.

<u>Illustration:</u>

Consider a gas in a cylinder at constant T, with a piston dividing the cylinder in two. See Fig. 4.6. If the piston is released, what is its equilibrium position? <u>Answer:</u>

The equilibrium position must be one of minimum total F. Our system comes in two parts, and the total Helmholtz free energy is

$$F = F_1(T, V_1) + F_2(T, V_2).$$
(4.82)

Consider a small change from equilibrium (but no work done on the whole), i.e., the piston moves a little, then $\delta F = 0$, since the free energy at the equilibrium is at a minimum. We have

$$0 = \delta F = \left(\frac{\partial F_1}{\partial V_1}\right)_T \delta V_1 + \left(\frac{\partial F_2}{\partial V_2}\right)_T \delta V_2 .$$
(4.83)

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Figure 4.6: The equilibrium position of this system, if the piston is released, is one in which both phases are at equal pressure.

But $V_1 + V_2 = \text{constant}$, so $\delta V_1 = -\delta V_2$, i.e.,

$$0 = \left[\left(\frac{\partial F}{\partial V_1} \right)_T - \left(\frac{\partial F}{\partial V_2} \right)_T \right] \delta V_1.$$
(4.84)

As δV_1 is an arbitrary change, we must have

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T = \left(\frac{\partial F_2}{\partial V_2}\right)_T$$
, or $P_1 = P_2$,

according to Eq. (4.55). This is intuitively obvious.

(c) Gibbs free energy G = F + PV = E - TS + PV:

Decrease in Gibbs free energy equal maximum amount of useful work obtainable from a system whose initial and final temperature <u>and</u> pressure are equal to those of a constant environment, see Eq. (4.68).

Theorem:

In a system kept at constant temperature and pressure, G never increases.

Corollary:

For a system kept at constant temperature and pressure, the equilibrium state is the state of minimum Gibbs potential.

Proof:

For T = const. we already have $\Delta W \leq -\Delta F$, i.e. $\Delta W + \Delta F \leq 0$. Note that this is now work done by the system. If the pressure is kept constant, then $\Delta W = P\Delta V$. Then

$$P\Delta V + \Delta F \le 0, \quad \text{or} \quad \Delta G \le 0,$$

$$(4.85)$$

i.e., the system can slowly evolve until G is at the minimum.

Note:

• We have seen dG = -SdT + VdP, so the Gibbs free energy is constant when T and P are fixed. These are the conditions under which phase transitions (melting, boiling) take place. They are also relevant to chemical equilibrium.
(d) Enthalpy H = E + PV:

Consider a system at constant external pressure, P_0 . The work done by the system is then $P_0\Delta V$. From the first law:

$$\Delta E = Q - P_0 \Delta V. \tag{4.86}$$

On the other hand

$$H_B - H_A = E_B - E_A + (P_B V_B - P_A V_A)$$

= $(E_B - E_A) + P_0 (V_B - V_A).$ (4.87)

I.e., we have

$$\Delta H = \Delta E + P_0 \Delta V \quad \Rightarrow \Delta H = Q. \tag{4.88}$$

Example:

Two chemicals in cylinder (test tube) which react when an amount of heat, Q, is supplied. Gas produced by reaction pushes piston back against atmospheric pressure, P_0 . Work done in this process is $P_0\Delta V$. The heat of the reaction, Q, then equals the change in enthalpy, ΔH .

Remark:

Recall also Q3 of Example Sheet 1: heat absorbed at constant pressure is equal to the change in enthalpy, $\Delta Q = \Delta H$ at P = constant. At a phase transition, this heat is referred to as **latent heat**, a concept you heard about in the first-year unit "Gases, Liquids and Solids".

Another remark:

The enthalpy is the thermodynamic potential of the chemist.

<u>Useful exercise:</u>

Earlier we showed that $C_V = \left(\frac{\partial E}{\partial T}\right)_V$. Now show that $C_P = \left(\frac{\partial H}{\partial T}\right)_P$.

Answer:

dH = dQ at constant P (this is a special case of $\Delta H = Q$, or use dH = TdS + VdP = dQ for a reversible change at constant P). Also,

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T \underbrace{dP}_{=0}$$
(4.89)

It follows

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT$$
 at constant *P*. (4.90)

Compare with

$$C_P = \frac{dQ}{dT} \quad \text{at constant} P, \tag{4.91}$$

and we are done.

[Refs.: (1) Mandl 4.4-4.5; (2) Bowley and Sanchez 2.6; (3) Zemansky 10.1-10.3.]

4.6 The approach to equilibrium

We have seen that, for an isolated system, the entropy change will always be greater than or equal to zero. But more than that, we have seen in specific examples that if a change can take place which increases the entropy, it will. A hot and a cold block brought in to contact will exchange heat until they are at the same temperature, and not stop half way. Two gases which are allowed to mix will mix fully, and not just partially. In both cases the final state maximises the entropy with respect to the free parameter - the amount of heat exchanged, or the degree of mixing.

But what about non-isolated systems? Obviously the entropy of the universe increases. But it would be convenient if we could describe what happens by referring only to the system, and not the surroundings. In fact there is a way.

Recall the definition of the availability. If T_0 , P_0 refer to the temperature and pressure of the surroundings, we define

$$A \equiv E - T_0 S + P_0 V. \tag{4.92}$$

Theorem:

During any <u>spontaneous change</u> of a system in contact with surroundings at fixed temperature and pressure, the availability does not increase:

$$\Delta A \le 0. \tag{4.93}$$

Proof:

The proof is easy. We imagine a system in thermal contact with its surroundings at T_0 and at the pressure P_0 of the surroundings. Taking the surroundings and the system together, the entropy will be maximised. Imagine a spontaneous change during which heat Q is absorbed by the system, and the volume of the systems changes by ΔV , so that work $W = -P_0 \Delta V$ is done on the system. From the first law we have $Q = \Delta E + P_0 \Delta V$. The total change of entropy has two parts, ΔS for the system and $-Q/T_0$ for the surroundings (you should think carefully about the sign here!). So

$$\Delta S_{\text{universe}} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0} (T_0 \Delta S - \Delta E - P_0 \Delta V)$$
(4.94)

and we must have $\Delta S_{\text{universe}} \geq 0$. This means

$$\Delta(E - T_0 S + P_0 V) \le 0. \tag{4.95}$$

This completes the proof.

Now, let us look at various scenarios:

(a) For a process with starts and ends at the temperature and pressure of the surroundings, the initial and final availabilities are just the initial and final Gibbs free energy, so any such process minimises G. For spontaneous processes of this type, we have

$$(\Delta G)_{T,P} \le 0,\tag{4.96}$$

and G(T, P) is at its minimum in equilibrium.

(b) For a process with starts and ends at the temperature of the surroundings and which is at constant volume, $\Delta V = 0$ and so $\Delta A = \Delta F$. Such a process minimises the Helmholtz free energy. For spontaneous processes of this type, we have

$$(\Delta F)_{T,V} \le 0 \tag{4.97}$$

Hence F(T, V) is at its minimum at equilibrium.

(c) For isolated systems E and V must be constant, we then have $\Delta A = -T_0 \Delta S$, so a decrease in availability simply means an increase in entropy as it should. We have

$$(\Delta S)_{E,V} \ge 0 \tag{4.98}$$

for all spontaneous changes of this type, i.e., S(E, V) is maximized at equilibrium (maximum-entropy principle).

Summary:

System	$\Delta E = 0$ $\Delta V = 0$	$\Delta T = 0$ $\Delta V = 0$	$\Delta T = 0$ $\Delta P = 0$
Direction of spontaneous processes	$\Delta S \ge 0$	$\Delta F \le 0$	$\Delta G \le 0$
Equilibrium achieved when	$\Delta S = 0$	$\Delta F = 0$	$\Delta G = 0$

[Refs.: Mandl 4.2; (2) Bowley and Sanchez 2.9; Zemansky 15.8.]

4.7 The Maxwell relations

4.7.1 Derivation

The fundamental thermodynamic relation of Eq. (4.40)

$$dE = TdS - PdV \tag{4.99}$$

suggested E = E(S, V) so that

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$
(4.100)

Comparison shows

$$T = \left(\frac{\partial E}{\partial S}\right)_V, \quad -P = \left(\frac{\partial E}{\partial V}\right)_S \tag{4.101}$$

as we have seen before. By taking a further derivative

$$\frac{\partial}{\partial V}\Big|_{S}\left(\frac{\partial E}{\partial S}\right)_{V} = \frac{\partial}{\partial S}\Big|_{V}\left(\frac{\partial E}{\partial V}\right)_{S},\tag{4.102}$$

$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$	⇒	$T = \frac{\partial E}{\partial S}\Big _{V} & \& P = -$	$\left. \frac{\partial E}{\partial V} \right _{S} \Rightarrow$	$\left. \frac{\partial P}{\partial S} \right _{V} = \left\frac{\partial T}{\partial V} \right _{S}$
$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V$	⇒	$S = -\frac{\partial F}{\partial T}\Big _{V} & P = -$	$\frac{\partial F}{\partial V}_T \Rightarrow$	$\frac{\partial P}{\partial T}\Big _{V} = \frac{\partial S}{\partial V}\Big _{T}$
dH=TdS+Vd₽	⇒	$T = \frac{\partial H}{\partial S}\Big _{P} \& V = \frac{\partial}{\partial S}\Big _{P}$	<u>∂H</u> ⊋P _S ⇒	$\left. \frac{\partial V}{\partial S} \right _{P} = \left. \frac{\partial T}{\partial P} \right _{S}$
dG=-SdT+VdP	⇒	$S = -\frac{\boldsymbol{\theta}G}{\boldsymbol{\theta}T}\Big _{P} & \& V = \begin{cases} \mathbf{\theta} \\ \mathbf{\theta} \\ \mathbf{\theta} \\ \mathbf{\theta} \end{cases}$	9 <u>G</u> 9P _T ⇒	$\left. \frac{\partial V}{\partial T} \right _P = \left \frac{\partial S}{\partial P} \right _T$

Figure 4.7: Summary of the Maxwell relations.

we have the first of four Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$
(4.103)

The other three Maxwell relations are derived from the fundamental thermodynamic relations in dF, dG and dH. One finds (you should go through these derivations in detail!)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,\tag{4.104}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P,\tag{4.105}$$

and finally

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{4.106}$$

Remark:

- In all four Maxwell equations, the dependent variables are always one of $\{T, S\}$ and one of $\{P, V\}$. The independent variables are then the other two. We never get terms like $\partial T/\partial S$ or $\partial P/\partial V$ or $\partial/\partial S|_T$ or $\partial/\partial V|_P$].
- We get a minus sign if S and P both occur as variables on the same side of the equation, otherwise there is no minus sign.

4.7.2 An application

As one of many applications of the Maxwell relations, let us discuss how they can be used to express $\left(\frac{\partial E}{\partial V}\right)_T$ in terms of P, V and T. This will ultimately allow us to show that E = E(T) for the ideal gas, i.e. the internal energy of an ideal gas is independent of V. Start from the

fundamental relation dE = TdS - PdV. We have

$$dE = TdS - PdV$$

= $T\left\{\left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT\right\} - PdV$
= $\left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] dV + \left[T\left(\frac{\partial S}{\partial T}\right)_V\right] dT.$ (4.107)

But

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT.$$
(4.108)

It follows

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \tag{4.109}$$

$$\left(\frac{\partial E}{\partial T}\right)_{V} = T \left(\frac{\partial S}{\partial T}\right)_{V} \tag{4.110}$$

Using the first of these two relations and the second Maxwell relation in Fig. 4.7, we find

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P.$$
(4.111)

So if we know the equation of state (an equation relating p, V and T), we can compute how E depends on V.

Example: The ideal gas Here PV = RT (for one mole). Hence,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} = \frac{P}{T}.$$
(4.112)

It follows

$$\left(\frac{\partial E}{\partial V}\right)_T = T\frac{P}{T} - P = 0. \tag{4.113}$$

So E is not an explicit function of V (only of T) for an ideal gas, E = E(T).

[Refs.: (1) Mandl 4.4-4.5; (2) Bowley and Sánchez 2.6, E.1-E.2; (3) Zemanksy 40.5.]

4.8 Heat capacities and calculating entropy

For a thermodynamic system, we can typically determine its equation of state and heat capacities from experimental measurements. But how do we determine other physical quantities such as entropy? We will now demonstrate how the Maxwell relations are very useful for this purpose.

By definition, a heat capacity $C_y \equiv dQ^{\text{rev}}/dT$, depends on the process, since Q^{rev} is not a state variable. We use C_y for heat capacity and c_y for specific heat capacity (i.e., per mole or unit mass). As usual the subscript y stands for quantities held constant during the process.

Since $dQ^{\text{rev}} = TdS$ by the second law, we have

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P \tag{4.114}$$

for the heat capacity at constant pressure, and

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V \tag{4.115}$$

for the heat capacity at constant volume.

If we think of S as a function of T and V, S = S(T, V), we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV.$$
(4.116)

Using the Maxwell relation in Eq. (4.104) we have

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV.$$
(4.117)

From this, the entropy can be obtained by integration if C_V and the equation of state is known. First example: Entropy of the ideal gas We have PV = RT (one mole), and C_V =const. Then

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V},\tag{4.118}$$

for one mole of an ideal gas. It follows

$$S(T,V) = C_V \ln T + R \ln V + \text{constant.}$$
(4.119)

Second example: Entropy of an elastic string

Given the heat capacity C_l at constant length l and the equation of state (a relation between string tension Γ , temperature T and length l) $\Gamma = \Gamma(T, l)$, the entropy can be determined using Maxwell relations.

To do this, one proceeds as follows: The work done on the string by stretching is

$$dW = \Gamma dl, \tag{4.120}$$

and the fundamental thermodynamic relation for a string is

$$dE = TdS + \Gamma dl. \tag{4.121}$$

We will use the Maxwell relations derived from the Helmholtz free energy. We have

$$dF = d(E - TS) = -SdT + \Gamma dl.$$
(4.122)

Comparing with the general differential form

$$dF = \left(\frac{\partial F}{\partial T}\right)_l dT + \left(\frac{\partial F}{\partial l}\right)_T dl.$$
(4.123)

we find

$$-S = \left(\frac{\partial F}{\partial T}\right)_l, \quad \Gamma = \left(\frac{\partial F}{\partial l}\right)_T. \tag{4.124}$$

Take the second order derivative and using the fact that

$$\frac{\partial^2 F}{\partial l \partial T} = \frac{\partial^2 F}{\partial T \partial l} \tag{4.125}$$

we have the corresponding Maxwell relation,

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial \Gamma}{\partial T}\right)_l.$$
(4.126)

The heat capacity at constant length is, using dQ = TdS,

$$C_l = \left(\frac{dQ}{dT}\right)_l = T\left(\frac{\partial S}{\partial T}\right)_l \tag{4.127}$$

where we take the entropy S(l,T) as a function of l and T. The differential form of entropy is, in general

$$dS = \left(\frac{\partial S}{\partial T}\right)_l dT + \left(\frac{\partial S}{\partial l}\right)_T dl.$$
(4.128)

Therefore, the differential entropy is given by, using the Maxwell relation and the equation for heat capacity,

$$dS = \frac{C_l}{T} dT - \left(\frac{\partial \Gamma}{\partial T}\right)_l dl.$$
(4.129)

If $\Gamma(l, T)$ and C_l are known, the above equation can be used to determine the entropy. For a specific example, see Q2 of Example Sheet 6.

Remark:

Instead of Eq. (4.116), we can also start from S = S(T, P). Then

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP.$$
(4.130)

Using the appropriate Maxwell relation (you should understand this in detail!) one finds

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP.$$
(4.131)

This can then again we used to find the entropy, assuming C_P and the equation of state are known.

4.9 Open systems and phase equilibrium conditions

4.9.1 Open systems and chemical potential

Up to now we have mostly deal with <u>closed systems</u>, where no matter enters or leaves, i.e., N = const. Let us now generalise our approach to open systems, i.e. to cases where matter can

be exchanged with the surroundings. This situation can for example be useful in describing mixtures of substances, or mixtures of phases of the same substances, as we will see.

We need to extend the fundamental thermodynamic relations of Eq. (4.40) for a hydrostatic system,

$$dE = TdS - PdV \tag{4.132}$$

to include the energy change due to adding or subtracting particles. The extension reads

$$dE = TdS - PdV + \mu dN, \tag{4.133}$$

where the new intensive variable μ is referred to as the chemical potential. The quantity μ is the energy required to add a single particle to the system.

The internal energy is now a function of three variables, E = E(S, V, N) and we have a new thermodynamic relation, in addition to the original two:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}.$$
(4.134)

Rearranging Eq. (4.133) we find

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN,$$
(4.135)

i.e., S = S(E, V, N), and

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}.$$
(4.136)

Similarly, we have the following relations for the other thermodynamic potentials of an open system:

$$dF = -SdT - PdV + \mu dN \tag{4.137}$$

$$dG = -SdT + VdP + \mu dN \tag{4.138}$$

$$dH = TdS + VdP + \mu dN, \tag{4.139}$$

The chemical potential is given by partial derivatives as follows:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial H}{\partial N}\right)_{S,P}.$$
(4.140)

Theorem:

 $G = \mu N$

Proof:

This simple theorem can be easily proved by using the fact that G is extensive, i.e., $G = g(T, P) \cdot N$ together with Eq. (4.140), $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$.

4.9.2 Equilibria between phases

We now discuss the conditions for the coexistence of two phases of a given substance. Consider the entropy for each of the phases as a function of its internal energy, volume and particle number, namely $S_1 = S_1(E_1, V_1, N_1)$ for phase 1 and $S_2 = S_2(E_2, V_2, N_2)$ for phase 2. The total entropy of the whole system is the sum of the two

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2),$$

if we ignore the small boundary contributions (involving small numbers of particles of both phases at the phase boundary). Each of the phases is an open system. But the whole system (the two phases together) is an isolated system; its total entropy is maximum at equilibrium.

This can be used to show that:

All intensive thermodynamic variables of the two phases at equilibrium must be equal respectively, namely

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2.$$
 (4.141)

Proof:

This can be proved by considering a small change in the system as whole and using the maximum-entropy condition dS = 0. For details, see Q2 of Example Sheet 7.

[Refs.: (1) Mandl 5.3; (2) Bowley and Sánchez 2.5-2.6, E.3; (3) Zemansky and Dittman 10.6, 10.8.]

4.10 The Clausius-Clapeyron equation*

We now turn our attention to situations where two phases of a given substance co-exist (e.g., ice and water at 0^{0} C; for which if no heat is exchanged with the surroundings, the mixture will persist indefinitely). In general, different phases have different internal energies, different entropies, different densities, etc. In Section 4.9.2 (and Q2 of Example Sheet 7) we have proved that temperatures and pressures of the two phases at equilibrium are equal respectively. We wish to find the equation of coexistence curve of the two phases.

We saw above in Section 4.6 that at constant T and P the Gibbs free energy is minimized. Define g_1 and g_2 to be the 'specific Gibbs free energies' (i.e., per unit mass) for each phase. If the phases have masses m_1 and m_2 ,

$$G = m_1 g_1 + m_2 g_2. \tag{4.142}$$

At equilibrium with T_0, P_0 fixed dG = 0, and so we have

$$g_1\delta m_1 + g_2\delta m_2 = (g_1 - g_2)\delta m_1 = 0, \qquad (4.143)$$

where in the last equation, we have used the fact that total matter is conserved, $\delta m_1 = -\delta m_2$. Therefore, the condition for 2 phases to co-exist at given T_0, P_0 ,

$$g_1 = g_2. (4.144)$$



Figure 11

Figure 4.8: Phase coexistence line.



Figure 4.9: Phase coexistence line and derivation of the Clausius-Clapeyron equation.

In fact this is quite general; it also holds for isolated systems. For most choices of T_0 , P_0 only one phase will exist (e.g., all the water will freeze at all the ice will melt). A typical coexistence curve on a P-T plot is shown in Fig. 4.8

An obvious equation is to ask for the equation of the co-existence line. This is provided by the so-called <u>Clausius-Clapeyron equation</u>: Consider 2 infinitesimally close points a and b on the co-existence curve $g_1 = g_2$, as shown in Fig. 4.9.

$$g_1^{(a)} = g_2^{(a)}, \quad g_1^{(b)} = g_2^{(b)}.$$

So, if dg is the difference in g_1 between points a and b, it is the same for both phases

$$dg_1 = dg_2.$$

But we have dG = -SdT + VdP (see Sec. 4.4.1), so dg = -sdT + vdP with $s \equiv S/m, v \equiv V/m$, i.e.,

$$dg_1 = -s_1 dT + v_1 dP$$

$$dg_2 = -s_2 dT + v_2 dP$$



Figure 4.10: Phase diagram of water.

or $(s_2 - s_1)dT = (v_2 - v_1)dP$. Hence we have the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T\Delta v},$$
(4.145)

where we have used $\Delta S = Q/T$ for an isothermal process, and L = Q is simply the <u>latent heat</u> (per unit mass) of the substance at given P, T. Eq. (4.145) gives the slope the co-existence curve at any point (P, T).

In Fig. 4.10 we show the phase diagram of water. Note: Water is strange in that the solidliquid coexistence curve has a negative slope. This is because ice is less dense than water (putting ice under pressure causes it to melt). Most liquids behave oppositely.

Example:

At what temperature does water boil at the top of Mt. Everest? Input data: pressure at top of Everest is 0.36 atm; the density of water vapour at 100 °C is 0.598 kg m⁻³ and the latent heat is 2.257×10^3 J g⁻¹).

Answer:

The change in volume of a mass m of water is well approximated by volume of vapour phase alone (since it is about 10^3 less dense than liquid)

$$\Delta v = v_g - v_l \approx v_g = \frac{m}{\rho_g}$$

Hence

$$\frac{dP}{dT} = \frac{L}{T\Delta v} \approx \frac{L\rho_g}{mT_0} = \frac{2.257 \times 10^6 \text{ J kg}^{-1} \times 0.598 \text{ kg m}^{-3}}{373 \text{ K}} = 3.62 \times 10^3 \text{ Pa K}^{-1}.$$

Hence, by linear extrapolation $\Delta P/\Delta T = 3.62 \times 10^3$ Pa K⁻¹. Use given data $\Delta P = -0.64$ atm and 1 atm = 1.013×10^5 Pa,

$$\Delta T \approx -\frac{0.64 \times 1.013 \times 10^5}{3.62 \times 10^3} \text{ K} \approx -17.9 \text{ K},$$

i.e., the boiling point at the top of Mt. Everest is about 355 K or 82 °C. Notice that the difference between the two temperatures 373 and 355 K is (relatively) small, hence the linear extrapolation made is valid.

[Refs.: (1) Mandl 8.1-8.4; (2) Bowley and Sánchez 11.1,11.4,11.5; (3)Zemansky 11.3-11.5.]

4.11 Limitations of classical thermodynamics

The theory we have studied so far, classical thermodynamics, has several limitations:

- It does not produce specific numerical values for observable quantities. Instead it establishes relationships between those observables.
- In certain situations effects are seen which cannot be described by classical thermodynamics. Examples are systems near a critical point (phase transition). For example, the density of a fluid may no longer be spatially uniform, even though the system is in thermal equilibrium. This non-uniformity is due to <u>statistical fluctuations</u>. These are not accounted for by classical thermodynamics.

Chapter 5

The statistical basis of thermodynamics

"Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the same work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously."

(David Goodstein, States of Matter)

"If we wish to find in rational mechanics an a-priori foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy." (J.W. Gibbs).

5.1 Introduction

Our approach so far has been phenomenological. The theory of thermodynamics, as we formulated it, is based on empirical observations (i.e., observations from experiments), encoded in the laws of thermodynamics. In particular we have no microscopic basis for any of these observations, we have not attempted to derive them from first principles. Take for example the notion of entropy, as we have defined it. It is at this point entirely unclear how this concept is related to the underlying dynamics of systems at the microscopic level. Our view has so far been limited to a purely macroscopic perspective. We have established relations between macroscopic quantities (such as pressure, volume, internal energy, etc), these are properties of large (formally infinite) thermodynamic systems. We will now dig deeper and consider the details of the microscopic world.

In particular we will focus on two topics: (a) foundation of statistical mechanics and (b) application to isolated systems.

So far, we have only calculated the entropy changes but never the absolute value. The classical theory of thermodynamics leaves important questions unanswered, e.g.,

- What really is entropy?
- Why does entropy increase?

• Can we deduce equation of state of real thermodynamic systems from first principles?

The statistical theory, we are about to develop, addresses these. In particular, we have already mentioned that that entropy is 'a measure of disorder', but what exactly does that mean? How do we measure disorder? As we will see there is a deep connection between entropy, uncertainty and information theory.

5.2 The distinction between macrostates and microstates

5.2.1 Macrostates

A <u>macrostate</u> of a thermodynamic system is described by a few thermodynamic variables, such as P, V, T and E, S etc. for a gas system. These quantities are the measure of collective behaviour of a system of many particles, but not the behaviour of any individual constituent of that system. Macroscopic properties pertain to bulk features of a system composed of many constituents. A macrostate is the current disposition of the system defined in terms of macroscopic variables.

5.2.2 Microstates

A <u>microstate</u>, on the other hand, pertains to properties of the individual constituents of a system. For a single particle, we cannot speak of pressure, temperature of volume in a thermodynamic sense. But we can specify its physical state of motion. A microstate of a system is specified by the physical states of <u>all</u> of the system's constituents, not just by the bulk properties of the system.

In classical mechanics, the state of a single particle is specified by its position, \underline{r} , and momentum \underline{p} . For a system composed of N particles a micro-state is the specified by the positions and momenta of all N particles, i.e.

$$(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_N)$$

Since each of these vectors has three components, the combined vector has 6N entries. It lives in a 6N-dimensional space, the so-called phase space of the N-particle system.

In quantum mechanics, we use wavefunctions to describe the physical state of a single particle. Wavefunctions are usually specified by a set of quantum numbers. For example, a state of an electron in hydrogen atom is specified by a set of quantum numbers (n, l, m, σ) , where n is the principle quantumnumber, l the angular momentum quantum number, m the z-component of angular momentum, and finally $\sigma = \pm 1/2$ is its spin quantum number. Notice that quantum states are discrete, i.e., the parameters (n, l, m, σ) are discrete numbers, in contrast to the classical micro-states which are described by continuous variables, \underline{r}_i and p_i .

For a quantum particle moving in a box, its state is a plane-wave specified by three discrete components of its momentum $\underline{p} = (p_x, p_y, p_z)$ together with its spin σ . We will discuss this in details later. For a system of N quantum particles in a box, the collection of all quantum numbers

$$(\underline{p}_1, \underline{p}_2, \dots, \underline{p}_N; \sigma_1, \sigma_2, \dots, \sigma_N)$$



Figure 5.1: Illustration of microstates of a 6×6 arrangement of spin-1/2 particles (see text for details).

is used to specify the micro-states in the so-called independent particle approximation (ignoring the interactions between particles). Later, we will consider a system of N localized spins in a solid, for which a micro-state is specified by a given spin configuration ($\sigma_1, \sigma_2, ..., \sigma_N$).

We notice immediately that the number of micro-states is huge when N is large, both in the classical case and in the quantum case.

5.2.3 Example

Suppose we have a 6×6 checkerboard. Each square of the board represents a localised spin-1/2 particle with two possible spin orientations, one spin-up marked by X and the other spin-down marked by O. Any particular configuration of this up and down spins corresponds a micro-state. Many different patterns are possible, such as those shown in Fig. 5.1. In fact, it is easy to compute how many micro states there are. We have N = 36 spins, and each spin can be in one of two states. So the total number of micro-states for this system is $\Omega = 2^N = 2^{36} \approx 7 \times 10^{10}$.

If we want to specify the macro state of the system, we are not interested in the state of each and every particle, but only in the bulk properties. A macro state for this system is characterised by the total number of, say, up-spins n_{\uparrow} (the number of down-spins is then $N - n_{\uparrow}$, where N = 36 in our checkerboard example).

We immediately see that there are many micro states which belong to the same macro state. For example, if the macrostate is "13 up-spins", then we can pick those 13 spins arbitrarily among the total of 36 spins. There are many possibilities to do that, some of these are illustrated in Fig. 5.2.

How many possible such microstates are there for a given macrostate? This is just the common combinatorial problem of splitting a group of N identical objects into two smaller groups n_{\uparrow} and $(N - n_{\uparrow})$ without caring about the ordering in each group. The number of ways of doing this is

$$\frac{N!}{n_{\uparrow}!(N-n_{\uparrow})!}.\tag{5.1}$$

In our example, N = 36 and $n_{\uparrow} = 13$, so the total is 2.31×10^9 . Similarly for $n_{\uparrow} = 15$ there are only 5.57×10^9 ways, whereas for $n_{\uparrow} = 18$ there are 9.08×10^9 ways (this is the maximum for this case).



Figure 5.2: Illustration of 3 different microstates all belonging to the macro state '13 up-spins'.

Note: the numbers N!/[n!(N-n)!] are called the binomial coefficients, and are often written as either

$$C_N^n$$
 or $\binom{N}{n}$. (5.2)

They appear in the binomial expansion

$$(a+b)^{N} = \sum_{n=0}^{N} C_{N}^{n} a^{N-n} b^{n}, \qquad (5.3)$$

and in Pascal's triangle.

See Q3 of Example Sheet 7 for more examples of microstates of various systems.

5.3 A crash course in probability theory

5.3.1 Motivation

We can imagine the dynamics of a typical thermodynamic system to evolve quickly from one microstate to the next on a very short time scale. In statistical physics we are not interested in the exact state of each and every constituent of the system. This is because evaluating this would require us to solve the microscopic equations of motion (say Newton's equations) for all N particles of the system, this could lead to 10^{23} coupled differential equations, solving these is simply not realistic.

We therefore move away from this approach and ask questions at a slightly more coarsegrained level. For example, we may ask, how likely it is to observe a given microstate. We do not care so much when exactly the system is in particular microstate, but just how much time it spends in each of them on average. In this sense, we are looking for a <u>statistical</u> description of the mechanics of the underlying dynamics, hence the name <u>statistical mechanics</u> or statistical physics.

5.3.2 Models with discrete microstates

Suppose we have a thermodynamic system which can be in one of Ω microstates at any one time. We label these by $i = 1, ..., \Omega$. In equilibrium the system will 'hop' from one microstate to the next on a very fast timescale. Say p_i is the probability to find the system in state i at

any one time. Imagine for example, we took a photograph of the system (on a microscopic scale) at a random time, the quantity p_i tells us how likely it is that this photograph shows the system in state i.

The probability distribution, $\{p_i\}$, has the following properties:

- $p_i \ge 0$ for all i
- $\sum_{i=1}^{\Omega} p_i = 1.$

We can then imagine physical properties associated with each of the microstates. These are typically macroscopic quantities, such as an energy, or a magnetisation. If microstate i is associated with an energy ε_i for example, then the mean energy of the system is

$$\langle \varepsilon \rangle = \sum_{i=1}^{\Omega} p_i \varepsilon_i. \tag{5.4}$$

More generally, if f is a function that assigns an observable value to each microstate i, and if the value of f in state i is written as f_i , then the expected value of f (also known as expectation value, average value or mean value) is defined as

$$\langle f \rangle = \sum_{i} p_i f_i. \tag{5.5}$$

The above normalisation condition, $\sum_i p_i = 1$ can for example be written as $\langle 1 \rangle = \sum_i p_i \times 1 = 1$. We can also ask how much the value of f fluctuates from one micostate to the next. To this end we define the variance of f:

$$\sigma^2 = \left\langle f^2 \right\rangle - \left\langle f \right\rangle^2 = \sum_i p_i f_i^2 - \left(\sum_i p_i f_i\right)^2.$$
(5.6)

Exercise:

It should be clear to you

- that $\sigma^2 = \sum_i p_i (f_i \overline{f})^2$, if we abbreviate $\overline{f} = \langle f \rangle$,
- why a vanishing variance, $\sigma^2 = 0$, means that $f_i = \langle f \rangle$ for all *i*, i.e. all microstates have the same associated value f_i , independent of *i* (and that value is then trivially the average $\langle f \rangle$).

You can derive these from the above properties and definitions. If this is not clear to you, please revise basic probability theory.

Common probability distributions over discrete states, include

- the geometric distribution, $p_i = (1 \lambda)\lambda^i$, where $0 < \lambda < 1$ is a parameter and $i = 0, 1, 2, \ldots$,
- the Poisson distribution $p_i = e^{-\lambda} \frac{\lambda^i}{i!}$, where $\lambda > 0$ is a parameter and $i = 0, 1, 2, \ldots$,
- the binomial distribution, $p_i = \binom{m}{i} \lambda^i (1-\lambda)^{m-i}$, where the integer m, and $\lambda > 0$ are parameters, and where i = 0, 1, ..., m.

Exercise:

Check the normalisation property for each of these, and compute $\langle i \rangle = \sum_{i} p_{i} i$.

5.3.3 Models with continuous states

The situation is slightly more complicated for systems with continuous degrees of freedom (continuous microstates). Take for example a single particle in a box, with position \underline{r} and momentum \underline{p} . Now imagine that this (classical) particles bounces around in a container, a small box maybe, at high speed. If you take a picture at a random moment in time, you will essentially find the particle at a random position, and with momentum pointing in a random direction. How do we describe the statistics of such a system?

We now need to introduce a probability density in phase space. The phase space of this particle is 6-dimensional, and we write $\rho(\underline{r}, \underline{p})$ for the probability density in phase space. That is, if $d^3r d^3p$ is an infinitesimal 6-dimensional volume element in phase space, located at the point (\underline{r}, p) , then the probability to find the particle in that volume element in phase space is

$$\rho(\underline{r}, p)d^3rd^3p. \tag{5.7}$$

So $\rho(\underline{r}, p)$ is a probability density per unit volume in phase space. It has the following properties

- $\rho(\underline{r}, p) \ge 0$ (the density can never be negative any any point)
- $\int d^3r d^3p \ \rho(\underline{r}, p) = 1$ (normalisation of the probability distribution).

We have here written $\int d^3r d^3p \dots$ for the 6-dimensional integral $\int dx \int dy \int dz \int dp_x \int dp_y \int dp_z \dots$, where $\underline{r} = (x, y, z)$ and $\underline{p} = (p_x, p_y, p_z)$.

If $f(\underline{r}, \underline{p})$ is an observable for this single particle, then the definition of the expected value of f (or average value of f, or 'the mean of f') is now

$$\langle f \rangle = \int d^3r d^3p \ \rho(\underline{r}, \underline{p}) f(\underline{r}, \underline{p}), \qquad (5.8)$$

and the variance is

$$\sigma^{2} = \left\langle f^{2} \right\rangle - \left\langle f \right\rangle^{2} = \int d^{3}r d^{3}p \ \rho(\underline{r},\underline{p}) \left(f(\underline{r},\underline{p}) - \overline{f} \right)^{2}, \tag{5.9}$$

where we have abbreviated $\overline{f} = \langle f \rangle$.

Exercise:

If the second equality in Eq. (5.9) is not completely obvious to you, then please make sure you derive it.

Common probability distributions with continuous states include the following examples (with one continuous variable, x):

- the exponential distribution, $\rho(x) = \lambda e^{-\lambda x}$, where $\lambda > 0$ is a parameter, and where $x \ge 0$,
- the Gaussian distribution, $\rho(x) = (2\pi\sigma^2)^{-1/2} \exp\left(-(x-\mu)^2/(2\sigma^2)\right)$, where σ^2 and μ are parameters, and where $-\infty < x < \infty$.

Exercise:

Check the normalisation property for the first example (exponential distribution), and to compute $\langle x \rangle$. The corresponding calculations for the Gaussian distribution are not that easy.

5.4 Ensemble view and the ergodic hypothesis

5.4.1 Time average and ensemble average

As discussed earlier, classical thermodynamics describes macroscopic systems (i.e., systems with a very large number of constituents) in terms of a few thermodynamic variables, such as P, V, T, E etc. But we know such systems are really made of individual particles (classical or quantum), and a microscopic description would be in terms of the underlining states of all particles. Hence we need a bridge between the microstate and macrostate description. This bridge is provided by statistical mechanics.

As the atoms interact the microstates change very rapidly (maybe 10^{35} times/second). We can in principle take two approaches in averaging:

(a) Time average:

Suppose X is some observed macroscopic quantity (i.e., a state variable) e.g., internal energy E, we could take a time average over some (long) time τ :

$$X_{\text{observable}} = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} X(t) dt.$$
 (5.10)

At equilibrium, this quantity is independent of t_0 , provided we make the time-window over which we average long enough (the length of this window is τ). Formally, we take the limit $\tau \to \infty$, and obtain

$$\langle X \rangle \equiv X_{\text{observable}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} X(t) dt.$$
 (5.11)

But, this notion of time-average is impossible to compute in practice even though it is what we actually measure in an experiment.

(b) Ensemble average:

An <u>ensemble</u> is a collection of a large number of independent copies of a given system, each in one of the allowed microstates. Let Ω be the number of microstates consistent with a given macrostate, and let ν be the total number of copies of the system in the ensemble. Clearly, if $\nu \gg \Omega$, the number of copies of the *i*-th microstates is simply $\nu_i = p_i \nu$, where p_i is the probability to find any one copy in microstate *i*. If we use $\alpha = 1, 2, \dots, \nu$ to label the copies and $i = 1, 2, \dots, \Omega$ to label the microstates, the ensemble average is defined as

$$\langle X \rangle = \frac{1}{\nu} \sum_{\alpha=1}^{\nu} X_{\alpha} = \frac{1}{\nu} \sum_{i=1}^{\Omega} \nu_i X_i = \sum_{i=1}^{\Omega} p_i X_i.$$
 (5.12)

We have here written X_{α} for the value of the observable of copy α in the ensemble.

The idea of taking an ensemble average is clearly much easier in practice than the much more complicated time-averaging, provided we know the probabilities p_i .

Three major types of ensembles which are used in statistical mechanics:

(i) the <u>microcanonical ensemble</u> pertains to isolated systems (i.e., at fixed E, V, N); the copies in the ensemble are isolated.

- (ii) the <u>canonical ensemble</u> pertains to systems in contact with a heat bath (i.e., at fixed T, V, N).
- (iii) the grand canonical ensemble pertains to systems in contact with a reservoir with which they can exchange both heat and particles (i.e., at fixed T, V, μ).

Definition: Ergodic systems

In mathematics a dynamical system is called <u>ergodic</u>, broadly speaking, if the long-time average of an observable over a trajectory is equal to the (ensemble-) average over all states of the system. We will not enter the exact mathematical details here, but be slightly more sloppy, and use the word ergodic to indicate systems for which 'time-average=ensemble average'.

5.4.2 Microcanonical ensemble and postulate of equal a-priori probabilities

Let us start by considering an isolated system, i.e., the so-called microcanonical ensemble. We consider a large number of independent copies of the system. Each one of them is a completely isolated system. The big question now is how to weight the various microstates, i.e., how to find p_i , the probability to find any one of the copies in microstate *i*. In order to find out, we should really solve the equations of motion for the whole macroscopic system, i.e. for a system of $\approx 10^{23}$ atoms or so, an impossible task.

Instead we make the following assumption

The Postulate of equal a-priori probabilities:

A macroscopic isolated system with an exactly known energy samples every permissible microstate with equal probability.

In other words, all microstates of a system, consistent with applied macroscopic constraints, are equally probable.

Remark:

It is important to be clear about what we mean by 'permissible microstate' and 'consistent with applied macroscopic constraints'. This refers to constraints imposed by the fact that the system is isolated. In particular the total energy of the system is fixed. Additionally, in a fluid system for example the volume would be fixed as the system is isolated. Similarly, the total number of particles in the system is fixed. This will become more clear in the example below.

Further remark and definition of statistical weight:

If the number of accessible microstates is Ω , then the postulate of equal a-priori probabilities states that the probability of finding the system in any one of the accessible microstates is

$$p_i = \frac{1}{\Omega},\tag{5.13}$$

The quantity $\Omega = \Omega(E, V, N)$, i.e. the total number of microstates allowed within the constraints is referred to as the statistical weight. Note that we have normalization

$$\sum_{i=1}^{\Omega} p_i = \Omega \cdot \frac{1}{\Omega} = 1.$$
(5.14)

The above principle of equal a-priori probabilities together with the assumption that ergodicity

holds in thermodynamic systems leads to the so-called ergodic hypothesis:

Ergodic hypothesis (Boltzmann 1871):

Over a long period, all accessible microstates of an isolated system are equally probable. I.e. the time spent by the system in any region of phase space of accessible microstates is proportional to the volume of that region.

5.4.3 First Example

Let us consider a system composed of N = 100 quantum particles, each of which can be in one of two quantum states, with energy levels 0 and 1eV respectively. How many microstates are there for this system? Well, each particle can be in one of two states, so the total number of combinations is 2^{100} . This is the total number of all microstates.

Let us now consider the macrostate with total energy E = 50 eV. This means that exactly 50 must be in the 1eV energy level, and the other 50 in the ground state. How many microstates are there that are consistent with this constraint? The answer is

$$\Omega \left(E = 50 \text{eV}, N = 50 \right) = \begin{pmatrix} 100\\ 50 \end{pmatrix} = \frac{100!}{50!50!}.$$
(5.15)

What could the microscopic dynamics of such a system look like, if it is isolated? Well, the total energy is fixed, so at any moment in time 50 particles must be in the upper energy level, and the other 50 in the ground state. But the precise microstate may change from time to time, one particle may drop down from the 1eV state to the ground state, and at the same time another particle is excited to the upper state. The ergodic hypothesis and the principle of equal a-priori probabilities state that all of the above 100!/(50!50!) microstates are equally probably in this process. I.e., provided we observe the system for long enough, all microstates with total energy 50eV will be observed equally often. If we take a snapshot of the system at a random time, we will observe each such microstate with probability

$$p_i = \frac{1}{\left(\begin{array}{c} 100\\50\end{array}\right)}.\tag{5.16}$$

This is intuitively plausible as none of these states distinguishes itself from any of the others, why would one of them carry a higher probability than another? Note however that microstates with a total energy not equal to 50eV are never observed in this process (we have assumed that the system is started with 50eV, otherwise it makes no sense to consider the macrostate with this total energy).

5.4.4 Second example

We now consider a simple harmonic oscillator, with the equation of motion $\ddot{x} = -\omega^2 x$. We write x for the position of the particle, and $p = m\dot{x}$ for its momentum. The energy of the system is then specified by the following function

$$H_1(x,p) = \frac{p^2}{2m} + \frac{1}{2m\omega^2 x^2} .$$
 (5.17)

kinetic energy potential energy



Figure 5.3: Energy shell in phase space of a simple harmonic oscillator. The thick black line is $H_1(x, p) = E$, the grey shell marks the set of all microstates with $E \leq H(x, p) \leq E + \Delta E$.

We here use the notation H_1 to indicate the total energy (kinetic+potential). The use of the letter 'H' is in-line with the theory of Hamiltonian dynamics, the subscript '1' indicates a single-particle system. We will frequently refer to 'H' as <u>the Hamiltonian</u> of the system. (Note: you should understand in detail that $H_1(x, p)$ as given above is the total energy of a simple harmonic oscillator. If this is not absolutely clear to you, please go and revise your first year dynamics course.)

Now let's consider such an harmonic oscillator as fixed energy E. What is the number of 'accessible' microstates. First of all, the term 'number' is misleading here, as microstates are not discrete. This classical oscillator has a continuous phase space, spanned by the variables x and p. So it makes no sense to talk of a 'number' of accessible microstates. But, the set of accessible microstates defines a continuous set in x-p space, and we what we can specify is the volume of all microstates that are accessible.

So say we demand that the energy of the oscillator be between E and $E + \Delta E$. What geometric object do the microstates form that are accessible within this constraint. Well, the total energy is $H_1(x, p) = p^2/(2m) + \frac{1}{2}m\omega^2 x^2$, and demanding

$$E \le H_1(x, p) \le E + \Delta E \tag{5.18}$$

hence constrains the microstates to an elliptic shell in x - p space, see Fig. 5.3. (It should be absolutely clear to you why $H_1(x, p) = E$ defines an ellipse for a fixed E. It it is not then please revise your basic geometry.)

Now, what is the phase space density $\rho(x, p)$ for this system in the microcanonical ensemble? Recall that $\rho(x, p)dxdp$ is the probability to find the system in a small volume of size dxdp around the point x and p (see Sec. 5.3.3). The ergodic hypothesis asserts that all allowed microstates are equally probable, so the phase space density must be constant within the energy shell, and zero everywhere else. We have

$$\rho(x,p) = \begin{cases}
\frac{1}{\Gamma(E)} & \text{if } E \leq H_1(x,p) \leq E + \Delta E, \\
0 & \text{else,}
\end{cases}$$
(5.19)

where the quantity $\Gamma(E)$ is the volume of the energy shell around E in x - p space, i.e.

$$\Gamma(E) = \int \int_{E \le H_1(x,p) \le E + \Delta E} 1 \, dx dp \tag{5.20}$$

[Refs.: (1) Mandl 2.1-2.2; (2) Bowley and Sánchez 4.1]

5.5 The statistical basis of entropy

We are now in a position to make a connection between the microscopic world, and the second law of thermodynamics. Now that we have introduced the concept of a set of microstates corresponding to a given macrostate, we can re-formulate the second law as follows:

Re-formulation of the second law:

The macroscopic equilibrium of an isolated system is the macrostate with the highest number of microstates. Given the ergodic hypothesis, it is the most likely macrostate to be observed.

Example:

Consider a system of N fair dice. For starters let us just consider N = 2. There are 36 possible microstates, $(1, 1), (1, 2), \ldots, (5, 6), (6, 6)$, and if the two dice are thrown each of these 36 states appears with the same probability, $p_i = 1/36$. When we talk about macrostates, we are not interested in the outcome for each die, but only in the bulk result, for example the sum of the two numbers. These will be in the range from 2 to 12. Which one of these 11 macrostates is the most likely one? Well, it is the one with a sum of 7, as there are 6 microstates corresponding to a sum of 7. For comparison there is only one microstate that corresponds to a sum one 2, and similarly only one microstate corresponding to macrostate 12.

Now consider a system of N dice. There will then be 6^N microstates, and the macrostate with the most microstates will be the one with a sum of 3.5N. If you shake a big bag of a large number of dice, the most likely sum of numbers is 3.5N. In fact if N is very large, this will be the outcome by an overwhelming probability.

See also http://people.virginia.edu/~lz2n/mse305/notes/StatThermo.pdf.

Statistical interpretation of the spontaneous increase of entropy:

In earlier chapters we have seen that spontaneous processes in isolated systems (for example following the removal of constraints) lead to an increase in entropy. We can now interpret this microscopically. The system will initially be in the macrostate corresponding to the highest number of accessible microstates. 'Accessible' here means accessible in the situation before the constraints are lifted. When the constraints are removed, additional microstates become accessible, and the system reacts. It's macrostate will change and the new macrostate will be the one with the highest number of accessible microstates <u>after</u> the constraints have been removed. It is clear that this new number of accessible microstates must be higher than the number of microstates that were accessible before the constraint is removed.

We can now provide a statistical basis of entropy.

Boltzmann's definition of entropy:

The entropy of the macrostate of a thermodynamic system is proportional to the logarithm of the number of accessible microstates that correspond to this macrostate:

$$S = k \ln \Omega. \tag{5.21}$$

The quantity k is, for the moment, just an arbitrary constant, with units of energy per Kelvin. We will later see why it is the same Boltzmann constant appearing for example in the ideal gas equation, $PV = Nk_BT$ (where N is the number of particles, not moles).

Motivation for the logarithm:

You may ask why S is proportional to the logarithm of the number of accessible microstates, and not simply equal to Ω . The reasoning is simple. We want entropy to be additive, i.e. if we combine two separate systems into one, we want $S = S_1 + S_2$. If the number of microstates accessible by the first system is Ω_1 , and that by system 2 is Ω_2 , then the combined system will have $\Omega = \Omega_1 \Omega_2$ microstates. Hence $S \propto \ln \Omega$ is a sensible definition.

The second law of thermodynamics has become a statistical statement: Classically, the system is evolving from a macrostate of lower entropy to one of higher entropy. Statistically, it is evolving from less probable to more probable macrostates, that is from macrostates corresponding to smaller numbers of microstates to those corresponding to larger numbers of microstates.

Note:

The Boltzmann constant, k_B , has dimension of entropy. One has $k_B = R/N_A \approx 1.381 \times 10^{-23}$ J K⁻¹ $\approx 8.617 \times 10^{-5}$ eV K⁻¹. $k_BT \approx \frac{1}{40}$ eV for T = 300 K, room temperature.)

Together with the thermodynamic relations involving entropy S = S(E, V, N) discussed earlier, we now have the following basis for the statistical mechanics of isolated systems:

$$S = k_B \ln \Omega, \tag{5.22}$$

where

$$\Omega = \Omega(E, V, N) \tag{5.23}$$

is the total number of microstates of the system consistent with a given macrostate (E, V, N). Other thermodynamic quantities are calculated using the relations derived from the fundamental thermodynamic relations, e.g.,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}
\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}.$$
(5.24)

The first one of these is the equation E = E(T, V) for the internal energy, and the second relation gives the equation of state.

Therefore, the key to the microcanonical ensemble approach, i.e., to the statistical physics of isolated systems, is to find the statistical weight $\Omega(E, V, N)$. All other physical properties can then be obtained via the above relations.

We will apply this approach to paramagnet of spin-1/2 system in Sec. 5.6, where it is relative easy to count the statistical weight $\Omega(E, V, N)$. Furthermore, the second relation in Eq. (5.24) gives a precise definition of temperature for an isolated system, from microscopic point of view, namely, if we can find the statistical weight $\Omega(E, V, N)$ of the system as a function of its energy, then we can find its temperature.

[Refs.: (1) Mandl 2.3; (2) Bowley and Sánchez 4.1, 4.5.]

5.6 Example the ideal spin-half paramagnet

5.6.1 Simple model - basic setup

We will now try to evaluate Ω for a simple model system. Hence, the corresponding physics essentially becomes a counting problem. Consider a system of the following type: (i) constituents are localised at fixed sites (e.g., crystalline solids); (ii) the particles are assumed to be independent (i.e., they not to interact with each other); (iii) each particle has a set of energy levels $\epsilon_0, \epsilon_1, \epsilon_2, \cdots$.

The most basic scenario is a system, in which each particle has just two energy levels, e.g., the ideal spin-1/2 paramagnet. Paramagnetism arises when some of the atoms in a crystal have a resultant magnetic dipole moment, associated with electron orbital angular momentum or electron spin (or both).

Spins reside at the sites of a lattice, at each of N sites we have an atom with spin S = 1/2. According to quantum mechanics, the z-component of each spin has only two possible values: $S_z = -1/2$ for the down-state (\downarrow) and $S_z = 1/2$ for the up-state (\uparrow). Each spin has a magnetic moment $-\mu$ (\downarrow) or μ (\uparrow). It is here important not to confuse the magnetic moment, μ , with the chemical potential, also μ . The total magnetic moment of the system is then

$$m = n_{\uparrow}\mu + n_{\downarrow}(-\mu) = (n_{\uparrow} - n_{\downarrow})\mu = (2n_{\uparrow} - N)\mu$$
(5.25)

where n_{\uparrow} = number of spin-up atoms and n_{\downarrow} = number of spin-down atoms. Obviously, $n_{\uparrow} + n_{\downarrow} = N$.

We will neglect interaction between the spins. In an external magnetic field **B** the energy of a magnetic dipole $\underline{\mu}$ is $-\underline{\mu} \cdot \underline{B}$ (see e.g. Grant and Phillipps). Hence, in our case the total energy of the system is

$$E = n_{\uparrow}(-\mu B) + n_{\downarrow}(\mu B) = -(2n_{\uparrow} - N)\mu B = -mB.$$
(5.26)

5.6.2 Microstates and macrostates

Macrostates for this system can be characterized by their total magnetic moment m (i.e., equivalently by the number of up-spins, see Eq. (5.25)). In order to specify a microstate, on the other hand, we have to know the state (up/down) of each and every spin.

For N = 3 we have 4 macrostates (you should understand why) and $2^3 = 8$ microstates (you should understand why). They are the following:

$$\begin{array}{ll} m &= 3\mu & \uparrow\uparrow\uparrow \\ m &= \mu & \uparrow\uparrow\downarrow, \uparrow\downarrow\uparrow, \downarrow\uparrow\uparrow \\ m &= -\mu & \uparrow\downarrow\downarrow, \downarrow\uparrow\downarrow, \downarrow\downarrow\uparrow \\ m &= -3\mu & \downarrow\downarrow\downarrow \end{array}$$

So we have $\Omega(m = 3\mu) = \Omega(m = -3\mu) = 1$, and $\Omega(m = \mu) = \Omega(m = -\mu) = 3$.

More generally, we can ask how many microstates there are for a given macrostate for a system of N spins. Such a system will have 2^N microstates in total, but they correspond to different macrostates. So we ask:

Question:

How many microstates for a given macrostate (N, n_{\uparrow}) ?

Answer:

We have to choose n_{\uparrow} objects out of a total of N objects, there are

$$\Omega(N, n_{\uparrow}) = \frac{N!}{n_{\uparrow}! (N - n_{\uparrow})!}$$
(5.27)

possibilities to do this. This is the number of microstates of given n_{\uparrow} , i.e. the number of microstates corresponding to the macrostate (N, n_{\uparrow}) . If we sum over all n_{\uparrow} we must recover the total number of microstates, 2^N , of this system. If we don't, then we have made a mistake. So let's check:

$$\sum_{n_{\uparrow}=0}^{N} \Omega(N, n_{\uparrow}) = \sum_{n_{\uparrow}}^{N} \frac{N!}{n_{\uparrow}! (N - n_{\uparrow})!} = 2^{N}.$$
(5.28)

Phew. You should by the way understand the last equal sign in this calculation, if you do not, then you need to revise the binomial expansion¹.

The quantity $\Omega(N, n)$ is shown as a function of n/N for different N in Fig. 5.4, normalized to 1 at the peak. See also Example Sheets 7 and 8.

Example:

Suppose we have $N = 10^{23}$ spins, and a total energy of E = 0 in an external magnetic field, $B \neq 0$. How many accessible microstates are there?

Answer:

The macrostate is one with zero total energy, so half of the spins must be in the 'up' state, the other half in the 'down' state. So $n_{\uparrow} = N/2$. The number of accessible microstates is hence

$$\Omega(E=0, B, N=10^{23})) = \frac{N!}{[(N/2)!]^2} \approx 10^{3 \times 10^{22}} \text{ for } N = 10^{23}.$$
 (5.29)

Compare: Number of protons and neutrons in the Universe: $\sim 10^{80}$.

5.6.3 Stirling approximation

Before we continue, let us introduce an important approximation, frequently used in the context of counting microstates.

Stirling approximation:

For large enough n we have

$$n! = \sqrt{2\pi n} n^n e^{-n} \left[1 + \frac{1}{12n} + \dots \right], \text{ valid for } n \gg 1.$$
 (5.30)

In logarithmic form this can be written as

$$\ln n! \approx n \ln n - n + \frac{1}{2} \ln(2\pi n) + \dots$$
 (5.31)

¹I realise that I have been saying 'You should understand the equal sign in Eq. (...)' on several occasions now. Generally, you should make sure that you understand every equal sign in these lecture notes.



Figure 5.4: Number of microstates in a paramagnet with N spins, as a function of the re-scaled number of up-spins, n/N $(n = n_{\uparrow})$. Curves are normalised to 1 at the peak.

[If you check this carefully, I have already ignored the 1/(12n) term in the above direct representation]. In textbooks you will also find $\ln n! \approx n \ln n - n$, with the $\ln(2\pi n)$ -term omitted. This makes sense in the limit of large n, as $\ln n$ is then much smaller than n or $n \ln n$. It really depends on how accurately you want to approximate the factorial, i.e. how many orders of sub-leading terms you want to include.

5.6.4 Paramagnet - the thermodynamic limit

Back to the problem with the paramagnet. Let us consider B = 0 (zero external magnetic field). In this case all microstates have the same energy (zero) and, following the ergodic hypothesis, they are equally likely. This is just like our checkerboard example in Sec. 5.2. We can ask

Question:

If we take a 'photograph' of the system at a random time, how likely is it to observe a given total magnetisation, m (equivalently, a given number of up-spins, n_{\uparrow})?

Answer:

Given that all 2^N microstates are equally likely in absence of an external field, the probability to find the system in a state with exactly n_{\uparrow} up-spins is $\Omega(N, n_{\uparrow})/2^N$. So we need to study the shape of $\Omega(N, n)$ as a function of n.

Crude argument (thermodynamic limit for beginners): In order to determine the shape of $\Omega(N, n)$ it is best to consider the logarithm

$$\ln \Omega(N,n) = \ln(N!) - \ln(n!) - \ln[(N-n)!].$$
(5.32)

Let us look at $\Omega_{\text{max}} = \Omega(N, N/2)$. We use the Stirling approximation to arrive at

$$\ln \Omega_{\max} = \ln \Omega(N, N/2) = \ln \left[\frac{N!}{[(N/2)!]^2} \right]$$

$$\approx N \ln N - N - 2 \left[\frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \right] = N \ln 2.$$
(5.33)

You should make sure you understand each and every equal sign in this expression.

This means that $\Omega(N, N/2) \approx 2^N$, i.e. <u>all</u> 2^N microstates are concentrated around n = N/2. So if you pick one of the 2^N microstates at random, you will with overwhelming probability have picked one with $n_{\uparrow} = N/2$ up-spins, i.e. a state in which half of the spins are up, and the other half down.

Important: This is not because these microstates are favoured in any way, it is just because they outnumber all other states by a huge margin.

To say the same thing in different words, look at the following inequalities (you should understand why each of the '<' holds):

$$\Omega(N, N/2) < \Omega(N) < N \cdot \Omega(N, N/2).$$
(5.34)

Since all terms are positive, we can take logs

$$\ln \Omega(N, N/2) < \ln \Omega(N) < \ln \Omega(N, N/2) + \ln N$$
(5.35)

But $\ln N \ll \ln \Omega(N, N/2) \approx N \ln 2$ (because of $N \gg \ln N$), hence $\ln \Omega(N)$ is 'squeezed' by $\ln \Omega(N, N/2)$ from below and from above, so it must be approximated by it in the limit $N \gg 1$:

$$\ln \Omega(N) \approx \ln \Omega(N, N/2). \tag{5.36}$$

These result mean that the average over <u>all</u> microstates can be replaced by only looking at those with n = N/2. In the sum over all microstates, you only have to consider those with n = N/2. It is quite common in statistical mechanics to find such examples where sums can, to a very good approximation, be replaced by their largest term - it is always a consequence (as here) of the very sharply peaked nature of the function in the sum.

More refined argument (thermodynamic limit for professionals):

A more refined argument can be developed as follows. As N increases the function $\Omega(N, n)$ is more and more sharply peaked around its maximum at n = N/2, see Fig. 5.4. In the limit $N \gg 1$ the curve is very well approximated by a Gaussian

$$\Omega(N,n) \approx \sqrt{\frac{2}{\pi N}} 2^N \exp\left[-\frac{(n-N/2)^2}{N/2}\right], \quad N \gg 1,$$
(5.37)

as the keen and ambitious will show in a challenge question on example sheet 7 (the proof is again based on the Stirling approximation). Recall the standard Gaussian

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\langle x \rangle)^2/(2\sigma^2)}.$$
(5.38)

So we here have $\langle n \rangle = N/2$ and $\sigma = \sqrt{N}/2$ and $\sigma/\bar{n} = 1/\sqrt{N}$, namely, relative magnitude of fluctuations is proportional to $1/\sqrt{N}$, a standard result for large systems ². As N increases the curve will be more and more sharply peaked around the maximum. In fact the peak is really very very sharp for realistic system sizes. For example, for a macroscopic sample with $N = 10^{24}$ we have $\sigma/\langle n \rangle = 10^{-12}$.

So we see that for macroscopic systems, the macroscopic (thermodynamic) properties are extremely sharply defined, all you will ever see is the most likely behaviour, which occurs with overwhelming probability. Statistical fluctuations are so rare that they are imperceptible. Next, we discuss the thermodynamics of spin paramagnet using the statistical mechanics formulas discussed earlier.

5.6.5 The thermodynamics of the isolated ideal spin-1/2 paramagnet in an external magnetic field

We now consider the case $B \neq 0$. The key question is to determine the internal energy and magnetization as a function of temperature.

In this case the work term dW = -PdV is replaced by dW = -mdB. The fundamental thermodynamic relation is

$$dE = TdS - mdB \tag{5.39}$$

or

$$dS = \frac{1}{T}dE + \frac{m}{T}dB.$$
(5.40)

Hence, once we have computed S = S(E, B, N), we can use with

$$\left(\frac{\partial S}{\partial E}\right)_{B,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial B}\right)_{E,N} = \frac{m}{T}.$$
 (5.41)

to find the temperature and total magnetisation, m. This is the thermodynamic magnetisation, so the average over all accessible microstates.

Now, if the system is isolated, E is fixed, and hence, since $E = (N - 2n_{\uparrow})\mu B$ from Eq. (5.26), n_{\uparrow} is fixed. The number of accessible microstates at fixed energy is hence $\Omega = \Omega(n_{\uparrow}, B, N)$, and so the Boltzmann entropy is

$$S(E(n_{\uparrow}), B, N) = k_B \ln \Omega(n_{\uparrow}, B, N)) = k_B \ln \left[\frac{N!}{n_{\uparrow}!(N - n_{\uparrow})!}\right]$$
(5.42)

with

$$n_{\uparrow} = \frac{1}{2} \left(N - \frac{E}{\mu B} \right). \tag{5.43}$$

We use the Stirling approximation again to for $\ln N!$, $\ln n!$, $\ln(N-n)!$, and find

$$S = k_B \Big\{ N \ln N - N - [n_{\uparrow} \ln n_{\uparrow} - n_{\uparrow}] - [(N - n_{\uparrow}) \ln(N - n_{\uparrow}) - (N - n_{\uparrow})] \Big\},$$
(5.44)

i.e.,

$$S = k_B [N \ln N - n_{\uparrow} \ln n_{\uparrow} - (N - n_{\uparrow}) \ln(N - n_{\uparrow})].$$
(5.45)

²The $N^{-1/2}$ behaviour is ultimately a consequence of the central limit theorem.

Temperature:

We find

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{B,N} = \left(\frac{\partial S}{\partial n_{\uparrow}}\right)_{N} \left(\frac{\partial n_{\uparrow}}{\partial E}\right)_{B,N},\tag{5.46}$$

which reduces to

$$\frac{1}{T} = k_B [-\ln n_{\uparrow} - 1 + \ln(N - n_{\uparrow}) + 1] \left(-\frac{1}{2\mu B}\right), \qquad (5.47)$$

i.e.,

$$\frac{1}{T} = \frac{k_B}{2\mu B} \ln \frac{n_\uparrow}{n_\downarrow},\tag{5.48}$$

where $n_{\downarrow} = N - n_{\uparrow}$.

A few interesting observations:

- We always have T > 0 since n_↑ > n_↓ (there will always be more spins aligned along B than against it);
- $T = \infty$ for $n_{\uparrow} = n_{\downarrow};$
- T = 0 for $n_{\downarrow} = 0$.
- We can solve for Using the fact that N = n_↑ + n_↓ we can find say n_↑ as a function of T from Eq. (5.48). We can then use Eq. (5.26) to find the energy E as a function of temperature:

$$E = -N\mu B \tanh \frac{\mu B}{k_B T}.$$
(5.49)

For details, see Example Sheet 8.

Magnetisation:

We also find

$$\frac{m}{T} = \left(\frac{\partial S}{\partial B}\right)_{E,N} = \left(\frac{\partial S}{\partial n_{\uparrow}}\right)_{N} \left(\frac{\partial n_{\uparrow}}{\partial B}\right)_{E,N},\tag{5.50}$$

and hence

$$\frac{m}{T} = k_B \left[-\ln n_{\uparrow} + \ln(N - n_{\uparrow})\right] \left(\frac{E}{2\mu B^2}\right),\tag{5.51}$$

or

$$\frac{m}{T} = -\frac{k_B E}{2\mu B^2} \ln \frac{n_\uparrow}{n_\downarrow}.$$
(5.52)

Combining this with Eq. (5.48) we find

$$m = -\frac{k_b E}{2\mu B^2} \cdot 2\mu B k_B = -\frac{E}{B}, \quad \text{or } E = -mB,$$
(5.53)

as required.

Important remark:

As discussed above we obtain the energy as a function of T in explicit form for this example (you will work this out on problem sheet 8). Together with E = -mB, this gives us the magnetic moment, m, as a function of T. This is a remarkable result, derived from first principles (Boltzmann entropy), it produces an actual <u>quantitative</u> prediction. Recall that we said that thermodynamics does not generate specific numbers, but only relations between quantities.

5.7 Information entropy and the principle of maximal ignorance

5.7.1 The method of Lagrange multipliers

We follow the book by Boas (Mathematical methods in the physical sciences), Sec. 9.

Often one has to solve maximisation (or minimisation) problems with constraints. Take the following example:

Maximise the function $f(x, y) = (x - y)^2$ under the constraint $x^2 + y^2 = 1$.

Here, the variables, x and y are coupled through the constraint $x^2 + y^2 = 1$, they are not independent.

For this particular example, we can use a trick. We can write $x = \cos t$ and $y = \sin t$, the constraint is then automatically fulfilled. We then only need to worry about the minimisation of f, written as a parametric function of t:

$$g(t) \equiv f(x(t), y(t)) = (\cos t - \sin t)^2 = 1 - 2\sin t \cos t.$$
 (5.54)

The extremisation is then easy, take dg/dt = 0, and find

$$-2(\cos t)^2 + 2(\sin t)^2 = 0, \qquad (5.55)$$

i.e. $\cos t = \pm \sin t$. Using $x = \cos t$ and $y = \sin t$, we find that the extrema occur at the four points $(x, y) = (\pm 1/\sqrt{2}, \pm 1/\sqrt{2})$. Of these two are maxima, and two are minima, and it is easy to work out which are which (can you do that?).

But, in this example we are lucky, we were able to express x and y in parametric form as a function of t. This was because the constraint had a very special form (the unit circle). What do we do for less convenient constraints?

<u>General problem</u>: Find the maximum (or minimum) values of the function f(x, y) when x and y are related by the constraint $\phi(x, y) = 0$.

Solution:

Given that x and y are related through the constraint, the function f is really only a function of one of the two variables, say x. To find extrema we have to set df/dx = 0, i.e. df = 0. This can be written as

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0.$$
(5.56)

The quantities dx and dy are here not independent due to the constraint. In fact given that $\phi(x, y) = 0$ we have

$$d\phi = \left(\frac{\partial\phi}{\partial x}\right)_y dx + \left(\frac{\partial\phi}{\partial y}\right)_x dy = 0$$
(5.57)

Multiplying both sides of Eq. (5.57) by λ and subtracting this from Eq. (5.56) we have

$$\left[\left(\frac{\partial f}{\partial x}\right)_{y} + \lambda \left(\frac{\partial \phi}{\partial x}\right)_{y}\right] dx + \left[\left(\frac{\partial f}{\partial y}\right)_{x} + \lambda \left(\frac{\partial \phi}{\partial y}\right)_{x}\right] dy = 0$$
(5.58)

This is true for all λ , so we can choose λ as we wish. Specifically we will make the choice $\lambda = -\frac{\left(\frac{\partial f}{\partial y}\right)_x}{\left(\frac{\partial \phi}{\partial y}\right)_x}$. Then we get

$$\left(\frac{\partial f}{\partial x}\right)_{y} + \lambda \left(\frac{\partial \phi}{\partial x}\right)_{y} = 0,$$

$$\left(\frac{\partial f}{\partial y}\right)_{x} + \lambda \left(\frac{\partial \phi}{\partial y}\right)_{x} = 0.$$

$$(5.59)$$

These two equations can now be solved, together with $\phi(x, y) = 0$ to give x, y and λ .

Example:

Let's take our example from above. We have $f(x, y) = (x - y)^2$ and $\phi(x, y) = x^2 + y^2 - 1$. So the two equations in (5.59) read

$$2(x - y) + 2\lambda x = 0 -2(x - y) + 2\lambda y = 0.$$
 (5.60)

Subtracting these off each other gives

$$(x - y)(2 + \lambda) = 0, (5.61)$$

i.e. x = y, or $\lambda = -2$. For $\lambda = -2$ we conclude 2(x - y) - 4x = 0 (using $2(x - y) + 2\lambda x = 0$), i.e. -2(x + y) = 0, so x = -y. So again we find $x = \pm y$, and the constraint $x^2 + y^2 = 1$ leads to the same four points as above, i.e.,

$$(1/\sqrt{2}, 1/\sqrt{2}), (-1/\sqrt{2}, -1/\sqrt{2}), (1/\sqrt{2}, -1/\sqrt{2}), (-1/\sqrt{2}, 1/\sqrt{2}).$$
 (5.62)

Two of these are maxima, the other two minima.

Remark:

The above equations (5.59) are exactly the equations we obtain if we construct the function

$$F(x, y, \lambda) = f(x, y) + \lambda \phi(x, y), \qquad (5.63)$$

with two independent variables x and y, and if we then extremise this with respect to x, y and λ (the extermination with respect to λ gives $\partial_{\lambda}F(x, y, \lambda) = 0$, i.e. $\phi(x, y) = 0$, so exactly the constraint subject to which we optimise x and y.)

The variable λ is called the Lagrange multiplier.

This can be generalised to problems with multiple variables, x_1, x_2, \ldots, x_M :

Method of Lagrange multipliers:

To find the minimum (or maximum) values of $f(x_1, x_2, ...)$ when $x_1, x_2, ...$ are related by a constraint $\phi(x_1, x_2, ...) = 0$ construct the function

$$F(x_1, x_2, \dots, x_M, \lambda) = f(x_1, \dots, x_M) + \lambda \phi(x_1, \dots, x_M)$$
(5.64)

and set all partial derivatives to zero

$$\frac{\partial F}{\partial x_1} = \frac{\partial F}{\partial x_2} = \dots = \frac{\partial F}{\partial x_M} = 0.$$
(5.65)

Solve these equations together with the constraint $\phi(x_1, \ldots, x_M) = 0$ to get x_1, \ldots, x_M .

5.7.2 Shannon entropy

Consider the situation in which one of M events may occur, label them i = 1, ..., M. Each event, i, happens with known probability p_i , where $\sum_i p_i = 1$. Until one of the event actually happens, the information provided by the occurrence of the event is missing. We will call this the 'missing information'.

Now, how much information do we gain, when an event actually happens? Say the event occurs with a high probability, it is a frequent event. The occurrence of such an event will provide only a relatively small amount of information (say 'rain in Manchester'). The extreme case is an event that occurs with absolute certainty ($p_i = 1$), for example 'England beaten by Germany in football penalty shoot-out'. The actual occurrence of such an event provides no information at all, since we knew from that start that this would happen. A rare event however provides a non-zero amount of information.

Let us formalise this. We wish to define a measure I(p) of the information we gain when an event which occurs with probability p actually occurs. We require the following properties of $I(\cdot)$:

- It has to be monotonic, the information gained from the occurrence of an event increases the less frequent the event is: $I(p_2) > I(p_1)$ if $p_2 < p_1$.
- I(p) is a continuous function of p, it is non-negative (i.e., $I(p) \ge 0$) and we have I(p = 1) = 0 (no information gained if the event is certain).
- The probability that two indistinct events *i* and *j* happen independently is $p_i p_j$, and the information gained by this needs to be equal to the sum of information gained by each of the two events. I.e., we require $I(p_1p_2) = I(p_1) + I(p_2)$.

It turns out that, up to an overall multiplicative factor, the only mathematical function with these properties is the negative logarithm, so we define the 'missing information' of an event which occurs with probability p_i as

$$I(p_i) = -\ln p_i. \tag{5.66}$$

The <u>average</u> information provided by an event is then given by by the average over all events, i.e. by the so-called

Shannon entropy:

$$I(\{p\}) = -\sum_{i} p_{i} \ln p_{i}.$$
(5.67)

5.7.3 The microcanonical ensemble

We can now return back to the micro canonical ensemble, and the principle of equal a-priori probabilities. It can be derived from the following

Principle of maximum Gibbs entropy:

For a given set of constraints let p_i be the probability that a thermodynamic system is found

in the accessible microstate i. The $\{p_i\}$ are then such as to maximise the Gibbs entropy³

$$S = -k_B \sum_{i} p_i \ln p_i.$$
(5.68)

Application to the micro canonical ensemble:

Let us consider an isolated thermodynamic system. If we restrict the allowed states $i = 1, \ldots, \Omega$ to those with the given energy, we have no constraints on the $\{p_i\}$ other than $\sum_{i=1}^{\Omega} p_i = 1$. So we have the following maximisation problem:

Maximise $S = -k_B \sum_i p_i \ln p_i$ under the constraint $\sum_i p_i = 1$.

We solve this using the method of Lagrange multipliers. The constraint can be written as $\phi(p_1, p_2, \ldots) = 0$, if we introduce $\phi(p_1, p_2, \ldots) = \sum_i p_i - 1$. So we construct

$$F(p_1, p_2, \dots, \lambda) = -\sum_i p_i \ln p_i + \lambda \left(\sum_i p_i - 1\right)$$
(5.69)

Taking $\frac{\partial F}{\partial p_j}$ for a fixed j gives

$$-k_B \ln p_j - k_B + \lambda = 0 \tag{5.70}$$

[To understand this, consider a concrete value of j, say j = 3. In the above sums over i you can then ignore all terms other than the one with i = 3. We have used the fact that $\frac{d}{dp}[p \ln p] = \ln p + p \times (1/p) = \ln p + 1$.]

From Eq. (5.70) we conclude that $p_j = \exp((\lambda/k_B) - 1)$ for all j, i.e. in particular that all p_j must be identical. Given the normalisation, this leaves

$$p_j = \frac{1}{\Omega} \tag{5.71}$$

for all $j = 1, ..., \Omega$. This is of course the micro canonical ensemble as we have discussed it above.

So we have shown that the principle of equal a-priori probabilities over accessible microstates follows from the principle of maximum 'missing information' (or maximum uncertainty). If we know nothing about the probability distribution over allowed microstates other than that it is normalised, then the distribution which maximises the uncertainty is that of the microcanonical ensemble.

Nice, innit?

³Compared to the Shannon entropy the Gibbs entropy contains an additional factor k_B . The Shannon entropy comes from information theory, and has no relation to thermodynamics. It is dimensionless. The Boltzmann constant in the Gibbs entropy is required to make the Gibbs entropy, obtained from maximisation as explained in the text, agree with the thermodynamic entropy. Given that both entropies only differ by a constant factor, it does not make a difference which one of the two one maximises. If one is maximised so is the other.

5.8 Density of states and correspondence between classical and quantum mechanical statistical weight

As discussed in Sec. 5.5, the Boltzmann entropy relies on a counting of the microstates accessible by a given system. A microstate of a quantum system is specified by a set of discrete quantum numbers. Therefore, in principle, there is no ambiguity in counting the total number of the microstates Ω in Quantum Mechanics. We have seen an example in Sec. 5.6, where we have counted the microstates explicitly.

In a classical system, the same can not be said as a microstate is specified by the continuous variables $\underline{r}_i, \underline{p}_i, i = 1, 2, \dots, N$. So it is not clear how to 'count' microstates, and how to define the Boltzmann entropy.

We will now try to resolve this issue.

5.8.1 Qualitative argument:

A classical state $(\underline{r}, \underline{p})$ makes no sense quantum-mechanically, as position and momentum cannot be specified sharply simultaneously. The uncertainty principle imposes the limit

$$\Delta x \Delta p_x \ge \frac{\hbar}{2},\tag{5.72}$$

and similarly for the other components.

This suggests that each microstate takes requires a phase space volume proportional to \hbar^3 , one factor of \hbar for each dimension. Each microstate effectively corresponds to a cell of a size proportional to \hbar^3 in phase space. A more detailed analysis of simple model systems (see below) shows that the precise phase space volume is given by h^3 , where

$$h = 6.626 \times 10^{-34} \,\mathrm{m}^2 \,\mathrm{kg \, s^{-1}},\tag{5.73}$$

is Planck's constant.

This defines a <u>unique correspondence</u> between the classical and quantum mechanical calculations of the total number of the microstates Ω .

For a single particle the 'number' of accessible microstates is hence

$$\Omega = \frac{1}{h^3} \int d^3r d^3p, \qquad (5.74)$$

where

$$d^3p = dp_x dp_y dp_z, (5.75)$$

where where the integral is over the volume in phase space allowed within externally applied constraints. In the example of the harmonic oscillator, this could be a given energy shell, see Eq. (5.20).

5.8.2 Quantum mechanical density of states

Let us consider a single quantum particle confined to the space $0 \le x \le L$, i.e. a box with sides of length L. The stationary Schrödinger equation then reads

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = 0, \qquad (5.76)$$

for $0 \le x \le L$. Following e.g. Mandl (see appendix B) or indeed the Ashcroft and Mermin book on solid state physics we apply periodic boundary conditions, i.e. $\Psi(x + L) = \Psi(x)$. This makes it possible to consider travelling wave solutions. Solutions are of the form

$$\Psi(x) = A \exp(ikx) \tag{5.77}$$

where $k = \frac{2\pi}{L}n$, and where $n = 0, \pm 1, \pm 2, \ldots$ is the corresponding quantum number. The above wave functions (plane wave solutions) are the eigenfunctions of the momentum operator. The quantum mechanical momentum of these eigenfunctions (of the momentum operator) is given by

$$p = \hbar k = \frac{h}{L} n_x, \tag{5.78}$$

where $h = 2\pi\hbar$. On the *p*-line these states are lined up in sequential order with a distance of h/L. The number of these states within a momentum interval Δp is hence given by $L\Delta p/h$, so one state per $L\Delta p/h$.

Going to three dimensions, the number of quantum states within a phase space volume $L_x L_y L_z \Delta p_x \Delta p_y \Delta p_z$ is hence $\frac{L_x \Delta p_x}{h} \times \frac{L_y \Delta p_y}{h} \times \frac{L_z \Delta p_z}{h}$. This motivates the above statement

$$\Omega = \frac{1}{h^3} \int d^3x d^3p. \tag{5.79}$$

A very similar argument can be derived from the usual boundary condition, $\Psi(x = 0) = \Psi(x = L) = 0$, for a quantum particle in a potential well (with infinite potential outside the box). See e.g. this set of notes here http://www.sfu.ca/~boal/445lecs/445lec24.pdf. This can also be found in various textbooks, see again Mandl for example.

You can find more on the density of states in quantum systems in the Britney Spears guide to semiconductor physics:

http://britneyspears.ac/physics/dos/dos.htm

[Refs.: (1) Mandl 2.4; Mandl, Appendix B; (2) Bowley and Sánchez 2.9.]
Chapter 6

The statistical physics of non-isolated systems: Boltzmann distribution and canonical ensemble

"His line of thought may be called my first love in science. No other has ever thus enruptured me or will ever do so again." (Erwin Schrödinger about Boltzmann)

"I don't believe that atoms exist!" "Have you seen one?" (Ernst Mach)

"Whoever rejects faith in the reality of atoms ... will find it difficult to advance physical knowledge." (Max Planck)

6.1 Recap: constant-energy distribution (a.k.a. microcanonical ensemble)

This distribution applies to isolated systems, E, V, N fixed. In practice we assume that the energy lies in the range E to $E + \delta E$. The system is isolated, so the postulate of equal a-prior probabilities can be directly applied: system equally likely to be found in any of its accessible microstates:

$$p_i = \begin{cases} \frac{1}{\Omega} & \text{if } E < E_i < E + \Delta E, \\ 0 & \text{else,} \end{cases}$$
(6.1)

where Ω is the statistical weight of the macrostate specified by E, V, N.

This is the constant energy (or <u>microcanonical</u>) distribution.

Disadvantage:

Inconvenient for calculations, not very flexible.

But, very useful as a starting point for deriving the Boltzmann distribution.



Figure 6.1: Construction used to derive the Boltzmann distribution.

6.2 Derivation of the Boltzmann distribution

Consider a system S in contact with a heat reservoir R at temperature T as shown in Fig. 6.1. The system and the reservoir together $({}^{\circ}R + S')$, form an isolated system with fixed energy E_0 . Heat can be exchanged between S and R, but R is so large that its temperature remains T if heat is exchanged. We now ask: What is the probability p_i that the system S is in a particular microstate with energy E_i ?

The total number of microstates of the combined system is

$$\Omega = \Omega_R \times \Omega_S. \tag{6.2}$$

Now, let us consider a specific microstate i of the system S, and say that S has energy E_i in that state. How many microstates of the <u>combined</u> system are now accessible? Well, the state of S has been fixed, but R can take any of its microstates, provided that that R has energy $E_0 - E_i$. Recall that the combined system is isolated and has total energy E_0 , and we have fixed that of S to be E_i .

So the number of accessible microstates of the combined system is now

$$\Omega = \Omega_R (E_0 - E_i) \times 1, \tag{6.3}$$

where $\Omega_R(E_0 - E_i)$ is the number of microstates of the reservoir with energy $E_0 - E_i$.

Thus, the probability p_i of S being in a state with energy E_i depends on the number of microstates of R with energy $E_0 - E_i$,

$$p_i = p_i(E_i) = \frac{\Omega_R(E_0 - E_i)}{\Omega_{R+S}(E_0)} = \frac{\text{number of microstates of } (S+R) \text{ with } S \text{ in state } i}{\text{total number of microstates of } (S+R)}.$$
 (6.4)

Now, use the Boltzmann relation $S = k_B \ln \Omega$ from the previous chapter:

$$\Omega_R(E_0 - E_i) = \exp\left[\frac{1}{k_B}S_R(E_0 - E_i)\right].$$
(6.5)

If R is a good reservoir it must be much bigger than S, so $E_i \ll E_0$. So, let's Taylor expand around E_0 :

$$S_R(E_0 - E_i) = S_R(E_0) - E_i \left[\left(\frac{\partial S_R}{\partial E} \right)_{V,N} \right]_{E=E_0} + \cdots .$$
(6.6)

But, from the thermodynamic relations involving partial derivative of $S_{,,}$

$$\left(\frac{\partial S_R}{\partial E}\right)_{V,N} = \frac{1}{T}.$$
(6.7)

Thus,

$$S_R(E_0 - E_i) = S_R(E_0) - \frac{E_i}{T} + \dots$$
 (6.8)

This gives

$$p_i \propto \Omega_R(E_0 - E_i) = \exp\left[\frac{1}{k_B}S_R(E_0 - E_i)\right] \approx \exp\left[\frac{S_R(E_0)}{k_B} - \frac{E_i}{k_BT}\right],\tag{6.9}$$

i.e. we have found

$$p_i = \text{const.} \times e^{-E_i/(k_B T)}.$$
(6.10)

We have used that $S_R(E_0)$ is a constant, independent of the microstate *i* of the system *S*. The constant in Eq. (6.10) is labeled 1/Z by convention, i.e.

$$p_i = \frac{1}{Z} e^{-E_i/(k_B T)}.$$
(6.11)

The quantity Z is then determined from the overall normalisation, all microstates

$$\sum_{i} p_i = 1. \tag{6.12}$$

This means

$$Z = \sum_{i} e^{-E_i/(k_B T)},$$
(6.13)

where sum on i runs over all distinct microstates i of the system S.

We have thus derived the

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-E_i/(k_B T)}, \quad Z = \sum_i e^{-E_i/(k_B T)}.$$
 (6.14)

The quantity Z is called the <u>partition function</u> of the system S (Boltzmann called this 'Zustandssumme' in German, roughly 'sum over states', hence the letter Z). As we will see later, partition function Z is very useful because all other thermodynamic quantities can be calculated through it. Keep in mind that Z = Z(T, V, N) is a function in particular of temperature.

<u>Remark:</u>

The Boltzmann distribution gives the probability that a system, when placed in contact with a heat reservoir at temperature T, is in a particular state. This is also known as the <u>canonical ensemble</u>.

Remark 2:

It is very common to introduce the notation

$$\beta = \frac{1}{k_B T},\tag{6.15}$$

this is often referred to as the 'inverse temperature' in statistical physics. The Boltzmann distribution then becomes

$$p_i = \frac{1}{Z} e^{-\beta E_i}, \quad Z = \sum_i e^{-\beta E_i}.$$
 (6.16)

Remark 3 (important!):

It is important to emphasize also that the index i labels the microstates of N-particles and E_i is the total energy. For example, a microstate for the case of an spin-1/2 paramagnet of N independent particles is a configuration of N spins (up or down):

$$i = (\uparrow, \uparrow, \downarrow, \dots, \downarrow). \tag{6.17}$$

For a gas of N molecules, however, i represents a set of values of positions and momenta as

$$i = (\mathbf{r_1}, \mathbf{r_2}, \dots, \mathbf{r_N}; \mathbf{p_1}, \mathbf{p_2}, \dots, \mathbf{p_N}),$$

as discussed in Sec. 5.2.

For (classical) systems with continuous states:

Single-particle partition function:

$$Z_1 = \int \frac{d^3 r d^3 p}{h^3} e^{-\beta H_1(\underline{r},\underline{p})}$$
(6.18)

For an N-particles system with distinguishable particles the N-particle particle function is:

$$Z_N = \int \frac{d^{3N} p d^{3N} r}{h^{3N}} e^{-\beta H_N(\underline{r}_1, \underline{p}_1, \dots, \underline{r}_N, \underline{p}_N)}.$$
(6.19)

We will discuss the case of indistinguishable particles below.

[Ref.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.1-5.2]

6.3 Derivation from maximum-entropy principle

In Sec. 5.7 we have introduced the Gibbs entropy of an ensemble

$$S = -k_B \sum_{i} p_i \ln p_i.$$
(6.20)

We will now show that the Boltzmann distribution maximises this entropy under the constraint of a fixed average energy.

So consider the following maximisation problem:

Find the $\{p_i\}$ such that $S = -k_B \sum_i p_i \ln p_i$ is maximal, given the constraints:

(i) $\sum_{i} p_i = 1$ (normalisation), and

(ii) $\sum_{i} p_i E_i = E$. Here E is then given value of the average energy.

Solution:

We use the method of Lagrange multipliers. Define

$$F(\{p_i\},\lambda_1,\lambda_2) = -k_B \sum_i p_i \ln p_i + \lambda_1 \left(\sum_i p_i - 1\right) + \lambda_2 \left(\sum_i p_i E_i - E\right).$$
(6.21)

Taking $\frac{\partial}{\partial p_i}$ of this object, and setting this to zero, we find:

$$-k_B (\ln p_i + 1) + \lambda_1 + \lambda_2 E_i = 0.$$
(6.22)

Re-arranging this gives

$$p_i = e^{\frac{\lambda_1}{k_B} - 1} e^{\frac{\lambda_2 E_i}{k_B}} \tag{6.23}$$

It is here important to keep in mind that λ_1 and λ_2 are Lagrange multipliers, they enforce the constraint, but they do not depend on *i*. The quantity λ_2 in the first exponential can be used to enforce normalisation (the above constraint (i)). So we have

$$p_i = \frac{e^{\frac{\lambda_2 E_i}{k_B}}}{Z},\tag{6.24}$$

where $Z = \sum_{j} e^{\frac{\lambda_2 E_j}{k_B}}$. This is already looking good, as p_i depends on E_i through an exponential. It remains to relate λ_2 to temperature.

To do this keep in mind that λ_2 is the Lagrange multiplier enforcing $\sum p_i E_i = E$ for the given value of E (constraint (ii)).

Using this, we have

$$S = -k_B \sum_{i} p_i \ln p_i$$

$$= -\frac{k_B}{Z} \sum_{i} e^{\lambda_2 E_i/k_B} \left(\frac{\lambda_2}{k_B} E_i - \ln Z\right)$$

$$= -\lambda_2 \underbrace{\frac{1}{Z} \sum_{i} E_i e^{\lambda_2 E_i/k_B}}_{=\langle E \rangle} + \underbrace{\frac{k_B}{Z} \ln Z}_{=Z} \underbrace{\sum_{i} e^{\lambda_2 E_i/k_B}}_{=Z}.$$

$$= -\lambda_2 E + k_B \ln Z.$$
(6.25)

Next we use

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \tag{6.26}$$

to find the identification

$$-\lambda_2 = \frac{1}{T}.\tag{6.27}$$

Thus we have

$$p_i = \frac{1}{Z} e^{\frac{\lambda_2 E_i}{k_B}} = \frac{1}{Z} e^{-\frac{E_i}{k_B T}},$$
(6.28)

i.e. the Boltzmann distribution.

6.4 The partition function

Although the partition function, $Z = \sum_i e^{-\beta E_i}$, is initially introduced as a relatively innocent normalization constant, its usefulness is much deeper than that. Loosely speaking all thermodynamic quantities of a system in thermal equilibrium at temperature T can be computed if its partition function is known, just in the same way that all thermodynamic information of an isolated system (at fixed E, N, V) is contained in $\Omega(E, N, V)$. For a system in thermal equilibrium everything is know (i.e., can be derived) when Z is known. Keep in mind that this means Z = Z(T, N, V) for a hydrostatic system, or Z = Z(T, N, B) for a magnetic system, etc..

Above we say that everything 'can be derived' once Z is known. But I haven't told you how this is done in practice. So here we go.

6.4.1 Expected internal energy

The expected internal energy of the system is calculated as the average $\langle E \rangle = \sum_i p_i E_i$, i.e.

$$\langle E \rangle = \frac{1}{Z} \sum_{i} E_i e^{-E_i/k_B T} = \frac{\sum_{i} E_i e^{-\beta E_i}}{\sum_{j} e^{-\beta E_j}}$$
(6.29)

Fact:

$$\langle E \rangle = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_{V,N}.$$
 (6.30)

Proof:

$$-\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_{V,N} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{i} e^{-\beta E_{i}}$$
$$= -\frac{1}{Z} \sum_{i} \left(-E_{i} e^{-\beta E_{i}}\right)$$
$$= \frac{1}{Z} \sum_{i} E_{i} e^{-\beta E_{i}}, \quad \text{q.e.d.}$$
(6.31)

Exercise:

Show that

$$\langle E \rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}.$$
 (6.32)

[You must do this in detail!]

6.4.2 Entropy

We have

$$S = -k_B \sum_{i} p_i \ln p_i. \tag{6.33}$$

This can either be accepted as a postulate (see the section on information theory), or you can derive it as the entropy of an ensemble, see e.g. Mandl, Chapter 2.5. For the Boltzmann distribution we have (repeating the same calculation we did already above):

$$S = -k_B \sum_{i} p_i \ln \frac{e^{-\beta E_i}}{Z}$$

= $-k_B \sum_{i} p_i (-\beta E_i - \ln Z)$
= $k_B \beta \sum_{i} p_i E_i + k_B \ln Z \sum_{i} p_i$
= $k_B \beta \langle E \rangle + k_B \ln Z$ (6.34)

where we have used the definition $\langle E \rangle = \sum_i p_i E_i$ and normalization condition $\sum_i p_i = 1$. Rearrange the above equation

$$k_B T \ln Z = -(\langle E \rangle - TS), \qquad (6.35)$$

i.e.,

$$TS = \langle E \rangle + k_B T \ln Z. \tag{6.36}$$

So if we know Z we can compute S.

6.4.3 Energy fluctuations

We have seen above how the average energy of a system can be found in the canonical ensemble:

$$\langle E \rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V}.$$
 (6.37)

From $\langle E \rangle$ we can then also calculate the heat capacity

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = k_B \beta^2 \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{N,V}.$$
(6.38)

Make sure you understand all equalities in these expressions <u>in detail</u>. See also example sheet 9.

The quantity $\langle E \rangle$ is the typical ('average') energy, but there are fluctuations as the system moves from one microstate to the next in the canonical ensemble. We now ask how large these energy fluctuations are. In fact we show that they are negligibly small in the thermodynamic limit, $N \gg 1$.

So we consider the variance

$$\sigma^2 = (\Delta E)^2 \equiv \langle E^2 \rangle - \langle E \rangle^2. \tag{6.39}$$

Clearly

$$\langle E^2 \rangle = \frac{\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2} \right)_{N,V}.$$
 (6.40)

(again make sure you understand all of these equal signs in detail).

Hence, (all derivatives in the followings are at constant N, V)

$$(\Delta E)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(-\frac{1}{Z} \frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta}\right) = \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{N,V}$$
$$= -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{N,V} = -\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} \frac{dT}{d\beta} = k_B T^2 \langle C_V \rangle.$$

or (see also example sheet 9)

$$(\Delta E)^2 = \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{N,V} = k_B T^2 C_V.$$
(6.41)

It is important that you go through this calculation <u>step by step</u> with a pencil and a piece of paper, and that you understand all equalities. You should do this for all (!) calculations in these notes. Unfortunately I know of no other way of acquiring a good and thorough understanding of the material.

Remark:

For a macroscopic system we typically have $\langle E \rangle \propto N k_B T$, and $C_V \propto N k_B$, hence

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N}k_BT}{Nk_BT} = \frac{1}{\sqrt{N}}.$$

So, if $N \approx 10^{24}$, $\Delta E/\langle E \rangle \approx 10^{-12}$, an unobservably tiny number! So, for most normal macroscopic systems the fluctuations are totally negligible and we can forget the notation $\langle \rangle$, and write $\langle E \rangle \rightarrow E$, etc., and there is no real difference between an isolated system of fixed energy E and one in contact with a heat bath at the same temperature $T = (\partial E/\partial S)_{N,V}$. Remark:

A notable exception occurs near critical points, where the distinction between two phases disappears. Near critical points fluctuations may not be negligible. This can sometimes be observed as 'critical opalescence' where the meniscus between the liquid and gas phases disappears, and the mixture becomes milky-looking and opaque as it scatters light.

[Ref.: (1) Mandl 2.5]

6.4.4 The connection with thermodynamics

As discussed above, energy fluctuations are essentially negligible in macroscopic systems. The probability that the system has a given energy has a sharp spike at the average energy, you practically always find that the system's energy is equal to the average. So for all practical purposes the energy of a <u>macroscopic</u> body in contact with a heat bath is completely determined (by the temperature of that heat reservoir).

 \Rightarrow The most probable value of the energy, the mean value and the classical thermodynamic energy are indistinguishable.

So from now on we identity the average energy, $\langle E \rangle$, with the thermodynamic energy of a macroscopic system.

From Eq. (6.35) we then have

$$TS = E + k_B T \ln Z, \tag{6.42}$$

$$F = E - TS = -k_B T \ln Z, \tag{6.43}$$

where $F \equiv E - TS$ is the Helmholtz free energy. Hence we have the so-called

Bridge equation:

$$F(T, V, N) = -k_B T \ln Z(T, V, N).$$
 (6.44)

This equation formally makes the connection between statistical physics and thermodynamics. It is sometimes called the 'bridge equation', as it provides a bridge between the microscopic and the macroscopic description of a system

The other thermodynamic quantities can then calculated by partial derivatives of F, as explained in the earlier chapters. We said earlier that F(T, V, N) contains the full information about a thermodynamic system. It is now clear that Z(T, V, N) contains the same information, hence the importance of the canonical partition function. Everything else follows by differentiation.

<u>Cute observation:</u>

Compare $F(T, V, N) = -k_B T \ln Z(T, V, N)$ for the canonical ensemble with $S(E, V, N) = k_B \ln \Omega(E, V, N)$ for the microcanonical ensemble. So the partition function, Z(T, V, N), in the canonical ensemble is what the statistical weight, $\Omega(E, V, N)$, is in the microcanonical ensemble. Beautiful, isn't it?

The power of going microscopic:

The results we have derived provide a powerful algorithm to calculate thermal quantities for any microscopic model. If you are not impressed and amazed by this, then you probably haven't understood it. Following the steps below we can derive all thermodynamic quantities for any microscopic system. If you don't find this impressive, well, then I am afraid, I can't help you.

- Label microstates, i, and find E_i , for example from Schrödinger's equation.
- As a function of temperature (and V, N) calculate the partition function

$$Z = \sum_{i} e^{-E_i/k_B T}.$$
 (6.45)

• Find

$$F = -k_B T \ln Z. \tag{6.46}$$

• Use thermodynamics to find quantities of interest from F, e.g.,

$$E = -\left(\frac{\partial \ln Z_N}{\partial \beta}\right)_{N,V} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N},$$
$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N},$$
$$C_V = T \left(\frac{\partial S}{\partial T}\right)_{V,N} = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N},$$

or

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V},\tag{6.47}$$

etc etc.

Now, clearly, the difficult part is to compute Z in the first place. Remark:

For magnetic systems the term -PdV is replaced by -mdB; and hence we have for example $m = -(\partial F/\partial B)_{T,N}$ etc. instead of the above relations.

Further comments* 6.4.5

You should now be very annoyed with me!

I promised that we would derive the whole of thermodynamics again from scratch, starting from microscopic considerations. But in Eq. (6.7) we have introduced temperature via the relation $\left(\frac{\partial S_R}{\partial E}\right)_{V,N} = \frac{1}{T}$, which we have taken from thermodynamics. That's not nice, is it? So let me comment on this.

Introduction of temperature

In the above derivation of the Boltzmann distribution the derivative $\left(\frac{\partial S}{\partial E}\right)_{V,N}$ comes up, and we have simply identified this with the (inverse) temperature $\frac{1}{T}$ from thermodynamics. But why should this be so?

Consider again the system R + S made of a reservoir and the actual system S. The combined system has energy E_0 , and let E be the energy of the system S alone. If the combined system is in the macrostate defined by (E_0, E) we have

$$\Omega_{R+S}(E_0, E) = \Omega_R(E_0 - E) \times \Omega_S(E), \qquad (6.48)$$

the product of the number of states R can be in (given that R's energy is $E_0 - E$) times the number of states S can be in, given that S's energy is E.

This expression, $\Omega_{R+S}(E_0, E)$ is a function of E, and macroscopically the observed equilibrium value, E^* of E, will be such that $\Omega_{R+S}(E_0, E)$ is maximised, as maximising Ω_{R+S} is the same as maximising the entropy of R + S. Now at this maximum we have

$$\frac{\partial}{\partial E} \left\{ \Omega_R(E_0 - E) \Omega_S(E) \right\} = 0, \tag{6.49}$$

i.e.,

$$\frac{\partial \Omega_R(E_0 - E)}{\partial E} \Omega_S(E) + \Omega_R(E_0 - E) \frac{\partial \Omega_S(E)}{\partial E} = 0.$$
(6.50)

This on the other hand is the same as

$$-\Omega_R \Omega_S \left[\frac{1}{\Omega_R(E_R)} \frac{\partial \Omega_R(E_R)}{\partial E_R} - \frac{1}{\Omega_S(E)} \frac{\partial \Omega_S(E)}{\partial E} \right] = 0, \tag{6.51}$$

where we have written $E_R = E_0 - E$. From this we then conclude

$$\left(\frac{\partial \ln \Omega_R}{\partial E_R}\right)_{V_R,N_R} = \left(\frac{\partial \ln \Omega_S}{\partial E}\right)_{V_S,N_S} \tag{6.52}$$

This relation determines $E = E^*$. It is the condition for thermal equilibrium derived from microscopic considerations. Macroscopically the condition is $T_R = T_S$. We can now formally define

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}.$$
(6.53)

Then the condition of thermal equilibrium between two systems 1 and 2 is $\beta_1 = \beta_2$. It is at this point clear that the quantity $\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$ must have something to do with the temperature in classical thermodynamics. One knows from everyday experience that systems in thermal contact equilibrate at equal temperature, and we have just shown that $\beta_1 = \beta_2$ in such cases. But the precise connection between β and T is not clear, if we do not want to use the thermodynamic result $1/T = \left(\frac{\partial S}{\partial E}\right)_{V,N}$.

We can develop the formalism of statistical mechanics with $\beta := \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$. Following the steps of Sec. 6.2 we can derive the Boltzmann distribution as

$$p_i = \frac{1}{Z} e^{-\beta E_i} \tag{6.54}$$

with $\beta := \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$, based on the principle of maximising the number of accessible microstates Ω . One does not formally have to introduce $S = k_B \ln \Omega$ do to this, simply write $\Omega = \exp(\ln \Omega)$ and expand $\ln \Omega$ in powers of E_i in Sec. 6.2. See also Mandl, Chapter 2.5. You arrive at $p_i = \frac{1}{Z}e^{-\beta E_i}$ with the formal definition $\beta := \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$.

If we then use this as a starting point and apply it to the ideal gas, we find

$$\beta PV = N,\tag{6.55}$$

where N is the number of particles and where P is defined via Eq. (6.47). We will do this derivation in Sec. 6.7.

Comparing this with $PV = nRT = Nk_BT$ gives

$$\beta = \frac{1}{k_B T}.\tag{6.56}$$

We stress again that the parameter β was – in this context – introduced purely mathematically as $\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$. We have to make a connection with empirical thermodynamics at some point though and this is what we have done, we have identified β with $1/(k_BT)$ using the empirical behaviour of ideal gases.

This means that the connection between microscopic and macroscopic description of the world is

$$\frac{1}{T} = \left(\frac{\partial k_B \ln \Omega}{\partial E}\right)_{V,N}.$$
(6.57)

From classical thermodynamics we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}.$$
(6.58)

This leads to the identification

$$S(E, V, N) = k_B \ln \Omega(E, V, N) \tag{6.59}$$

for a fluid.

Summary:

We have two routes to make the connection:

- Do as we did before: Postulate $S = k \ln \Omega$, and leave the nature of the constant k open. Then derive the Boltzmann distribution using an expansion of S(E), and using $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$. This delivers $p_i = Z^{-1}e^{-E_i/(kT)}$, where it is not clear a-priori that k is the Boltzmann constant. Use this, and the identification $P = -kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$ to study the ideal gas, and compare with the empirically known ideal gas equation (which contains k_B). This leads to the identification $k = k_B$.
- Do not introduce entropy, but derive the Boltzmann distribution using an expansion of $\ln \Omega$ in E. Formally introduce $\beta = \frac{\partial \ln \Omega}{\partial E}$. This leads to $p_i = Z^{-1}e^{-\beta E_i}$. Develop the formalism for the ideal gas using β , and compare with the empirically known ideal gas equation (which contains both T and k_B). This leads to the identification $\beta = 1/(k_B T)$. Then use $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{VN}$ from thermodynamics to make the identification $S = k_B \ln \Omega$.

6.5 The independent-particle approximation: one-body partition function

6.5.1 Systems with independent particles

We can represent a microstate of an N-particle system by specifying the microstates of all particles, e.g.

$$i = (i_1, i_2, \dots, i_N).$$
 (6.60)

This notation indicates that particle 1 is in single-particle state i_1 , particle 2 in state i_2 , etc., (e.g., the spin configurations for a paramagnet).

If there is no interaction between the particles the total energy in the microstate of the N particles is then simply the sum of energies of each particle,

$$E_i = \epsilon_{i_1} + \epsilon_{i_2} + \ldots + \epsilon_{i_N}, \tag{6.61}$$

where ϵ_{i_1} is the energy of particle 1 in state i_1 etc (you should understand why this implies the absence of interactions). The partition function of the N-particle system then given by

$$Z = Z_N = \sum_{i} e^{-E_i/(k_B T)} = \sum_{i_1, i_2, \dots, i_N} \exp\left[-\frac{1}{k_B T}(\epsilon_{i_1} + \epsilon_{i_2} + \dots + \epsilon_{i_N})\right].$$
 (6.62)

If we further assume that N particles are <u>distinguishable</u>, summations over i's are independent of one another. They can then be carried out separately as

$$Z_N = \sum_{i_1, i_2, \dots, i_N} e^{-\epsilon_{i_1}/(k_B T)} e^{-\epsilon_{i_1}/(k_B T)} \cdots e^{-\epsilon_{i_N}/k_B T}$$
$$= \left(\sum_{i_1} e^{-\epsilon_{i_1}/(k_B T)}\right) \left(\sum_{i_2} e^{-\epsilon_{i_2}/(k_B T)}\right) \cdots \left(\sum_{i_N} e^{-\epsilon_{i_N}/(k_B T)}\right).$$
(6.63)

It is important that you understand this step in detail. We notice that in the last equation, the summation in each factor runs over the same complete single-particle states. Therefore, they are all equal,

$$\sum_{i_1} e^{-\epsilon_{i_1}/k_B T} = \sum_{i_2} e^{-\epsilon_{i_2}/k_B T} = \dots = \sum_{i_N} e^{-\epsilon_{i_N}/k_B T}.$$

Hence, the N-particle canonical partition function in the independent-particle approximation is,

$$Z_N = (Z_1)^N, (6.64)$$

where

$$Z_1 = \sum_{i_1} e^{-\epsilon_{i_1}/(k_B T)}$$
(6.65)

is the one-body canonical partition function.

We notice that the index i_1 in the above equation labels *single particle states* and ϵ_{i_1} is the corresponding energy of the single particle, contrast to the index *i* used in earlier sections of this chapter, where *i* labels the microstate of total *N*-particle system and ϵ_i is the corresponding total energy of the system.

6.5.2 Distinguishable and indistinguishable particles

The above analysis are valid for models of solids and paramagnets where particles are localized hence distinguishable.

The case of N indistinguishable particles is more complicated. The fact that the permutation of any two particles in a configuration (i_1, i_2, \ldots, i_N) does not produce a new microstate imposes restrictions on the sum $\sum_i = \sum_{i_1, i_2, \ldots, i_N}$; the number of microstates is hence much reduced and sums over *i*'s are not longer independent of each other. The simple separation method of Eq. (6.63) is invalid.

If there are N indistinguishable particles in the system, then the over counting factor is N! as there are N! permutations for the same microstate (i_1, i_2, \ldots, i_N) . For N indistinguishable particles we hence approximate the partition function as,

$$Z_N \approx \frac{1}{N!} (Z_1)^N. \tag{6.66}$$

Important remark:

It is important to realise that this is an <u>approximation</u>. The overcounting factor of N! only applies to states in which all i_1, i_2, \ldots, i_N are pairwise different. For example if all particles are in the same one-particle microstate, i.e., $i_1 = i_2 = \ldots, i_N$, then there is only one permutation.

The above approximation hence holds only provided the number of single-particle microstates is much larger than the number of particles. It is then very unlikely to find two particles in the same one-particle microstate. The overcounting factor is then consistently given by N!.

Summary:

• N distinguishable particles (models of solids and paramagnets):

$$Z_N = (Z_1)^N; (6.67)$$

• N indistinguishable classical particles (classical ideal gas):

$$Z_N \approx \frac{1}{N!} (Z_1)^N; \tag{6.68}$$

• Either way

$$Z_1 = \sum_{i_1} e^{-\epsilon_{i_1}/k_B T}$$
(6.69)

is the one-body partition function, with ϵ_{i_1} the single-particle energy.

Remark:

Taking the logarithm of the partition function, we have

$$\ln Z_N \begin{cases} = N \ln Z_1, & \text{distinguishable particles;} \\ \approx N \ln Z_1 - \ln N!, & \text{indistinguishable particles,} \end{cases}$$
(6.70)

In both cases

$$E = E_N = -\left(\frac{\partial \ln Z_N}{\partial \beta}\right)_{N,V} = -N\left(\frac{\partial \ln Z_1}{\partial \beta}\right)_{N,V} = NE_1, \tag{6.71}$$

where $E_1 = -\partial \ln Z_1 / \partial \beta$ is the average energy of a single particle. Namely, in the independentparticle approximation, the total internal energy of N particles (distinguishable or indistinguishable) is equal to N times the average energy of a single particle.

6.5.3 Example

Consider a system of two free (independent) particles. Assume that there are only two singleparticle energy levels ϵ_1, ϵ_2 . By enumerating all possible two-body microstates, determine the partition functions Z_2 if these two particle are (a) distinguishable and (b) indistinguishable.

Solution:

(a) We list all four possible microstates of two distinguishable particles in the <u>occupation diagram</u> of Fig. 6.2.

Notice that the second and third microstates are different states as two particles are distinguishable. By definition, the partition function of the two-particle system is given by

$$Z_{2} = \sum_{i} e^{-E_{i}/k_{B}T}$$

= $e^{-2\epsilon_{1}/k_{B}T} + 2e^{-(\epsilon_{1}+\epsilon_{2})/k_{B}T} + e^{-2\epsilon_{2}/k_{B}T}$
= $(e^{-\epsilon_{1}/k_{B}T} + e^{-\epsilon_{2}/k_{B}T})^{2} = Z_{1}^{2},$ (6.72)



Figure 6.2: Occupation diagram of the two-particle two-level system with <u>distinguishable</u> particles discussed in the text.



Figure 6.3: Occupation diagram of the two-particle two-level system with <u>indistinguishable</u> particles discussed in the text.

in-line with the general expression $Z_N = (Z_1)^N$ of Eq. (6.67). Using Eq. (6.29) the average energy of the two-particle system is given by

$$\langle E \rangle = \frac{1}{Z} \sum_{i} E_{i} e^{-E_{i}/(k_{B}T)}$$

$$= \frac{1}{Z_{2}} \left[(2\epsilon_{1})e^{-2\epsilon_{1}/(k_{B}T)} + 2(\epsilon_{1} + \epsilon_{2})e^{-(\epsilon_{1} + \epsilon_{2})/(k_{B}T)} + (2\epsilon_{2})e^{-2\epsilon_{2}/(k_{B}T)} \right].$$
(6.73)

(b) For two <u>indistinguishable</u> particles, there are only three microstates as shown in Fig. 6.3. The corresponding partition function is then given by

$$Z_{2} = \sum_{i} e^{-E_{i}/k_{B}T}$$

= $e^{-2\epsilon_{1}/k_{B}T} + e^{-(\epsilon_{1}+\epsilon_{2})/k_{B}T} + e^{-2\epsilon_{2}/k_{B}T}.$ (6.74)

Notice that this partition function of two identical particles $Z_2 \neq \frac{1}{2!}Z_1^2$ as given by Eq. (7). Only the middle term has same weight as given by $\frac{1}{2!}Z_1^2$. The average energy of the two-particle system is

$$\langle E \rangle = \frac{1}{Z} \sum_{i} E_{i} e^{-E_{i}/k_{B}T} = \frac{1}{Z_{2}} \left[(2\epsilon_{1})e^{-2\epsilon_{1}/k_{B}T} + (\epsilon_{1} + \epsilon_{2})e^{-(\epsilon_{1} + \epsilon_{2})/k_{B}T} + (2\epsilon_{2})e^{-2\epsilon_{2}/k_{B}T} \right].$$

For the case of a two-particle system with three states, see Q1 of Example Sheet 9.

Remarks:

• It is important to note that the sum in Eq. (6.65) runs over all single-particle states i_1 , and not over all different energies. It is possible that different microstates have the same energy, i.e. a given energy level ϵ_{i_1} may be degenerate. Alternatively, we can express

Eq. (6.65) as a sum over distinct energy levels:

$$Z_{1} = \sum_{i_{1}} e^{-\epsilon_{i_{1}}/(k_{B}T)}$$

= $\sum_{\epsilon_{i_{1}}} g(\epsilon_{i_{1}})e^{-\epsilon_{i_{1}}/(k_{B}T)},$ (6.75)

where $g(\epsilon_{i_1})$ is the degeneracy factor of energy level ϵ_{i_1} .

- The one-body partition function Z_1 is a useful quantity for determining N-particle partition function in the independent-particle approximation. However, it is important to keep in mind that Z_1 itself has no physical meaning as temperature is undefined for a single-particle system.
- Even if we ignore interaction completely (i.e., in the independent-particle approximation) and restrict to classical mechanics, many-body effects still appear for N identical particles as demonstrated by the 1/N! factor.
- Eq. (6.67) is invalid in the low temperature limit where quantum effects dominate (e.g., a significant portion of particles of a quantum gas are in the zero-momentum state: the Bose-Einstein condensation). A proper way to tackle the problems of identical particles is to introduce occupation-number configurations and to use the so-called grandcanonical ensemble. A third-year course (*Bose and Fermi gases*) will discuss this subject in detail.

[Ref.: (1) Mandl 7.1]

6.6 Further simple examples of partition function calculations

In this section, we discuss a few examples of systems of non-interacting particles, and show how to compute their partition functions.

6.6.1 The ideal spin-1/2 paramagnet

Only two energy states for each spin, $i_1 = \uparrow, \downarrow$, with energies

$$\epsilon_{\uparrow} = -\mu B, \quad \epsilon_{\downarrow} = +\mu B, \tag{6.76}$$

where μ is the magnetic moment of one spin particle and B is the magnetic field. The one-body partition function is therefore

$$Z_1 = \sum_{k_1} e^{-\epsilon_{k_1}/(k_B T)} = e^{\mu B/(k_B T)} + e^{-\mu B/(k_B T)} = 2\cosh(\mu B/(k_B T)).$$
(6.77)

The partition function for the N spins (distinguishable particles) is

$$Z_N = [2\cosh(\mu B/(k_B T))]^N.$$
 (6.78)

6.6.2 A simple model for a one-dimensional solid

The model consists of M independent harmonic oscillators, each with energy

$$H_1(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \qquad (6.79)$$

where ω is the angular frequency. The state of a classical particle is specified by i = (x, p)and the sum becomes integral

$$\sum_{i} = \frac{1}{h} \int dx dp,$$

as discussed in Sec. 5.8.2. The one-body partition function is therefore given by

$$Z_{1} = \frac{1}{h} \int dx dp \, e^{-H_{1}(x,p)/(k_{B}T)}$$

$$= \frac{1}{h} \int_{-\infty}^{\infty} dp e^{-p^{2}/(2mk_{B}T)} \int_{-\infty}^{\infty} dx e^{-m\omega^{2}x^{2}/(2k_{B}T)}$$

$$= \frac{1}{h} \sqrt{2\pi m k_{B}T} \sqrt{\frac{2\pi k_{B}T}{m\omega^{2}}}$$

$$= \frac{2\pi k_{B}T}{h\omega},$$
(6.80)

where we have used the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad a > 0.$$
(6.81)

The partition function of M oscillators (distinguishable) is

$$Z_M = (Z_1)^M = \left(\frac{2\pi k_B T}{h\omega}\right)^M.$$
(6.82)

6.6.3 Classical ideal gas of N particles in a volume V

In this case, the single particle energy is

$$H_1(\mathbf{r}, \mathbf{p}) = \epsilon(p) = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2).$$
 (6.83)

The one-body partition function is

$$Z_1 = \frac{1}{h^3} \int d^3r d^3p \, e^{-\beta H_1(p)}.$$
(6.84)

As the energy $\epsilon(p)$ is r independent, the integral over real space produces a factor of volume V and the integral over momentum is,

$$\int d^3 p \, e^{-\beta p^2/(2m)} = \left(\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/(2m)} \right) \left(\int_{-\infty}^{\infty} dp_y e^{-\beta p_y^2/(2m)} \right) \left(\int_{-\infty}^{\infty} dp_z e^{-\beta p_z^2/(2m)} \right)$$
$$= \sqrt{2\pi m/\beta} \cdot \sqrt{2\pi m/\beta} \cdot \sqrt{2\pi m/\beta}$$
$$= (2\pi m/\beta)^{3/2}, \tag{6.85}$$

where we have again used the Gaussian integral formula given above. The one-body partition function is

$$Z_1 = V \left(\frac{2\pi m/\beta}{h^2}\right)^{3/2} \tag{6.86}$$

and the partition function for a classical ideal gas of N identical molecules in a volume V is

$$Z_N = \frac{1}{N!} Z_1^N = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}.$$
 (6.87)

6.6.4 Einstein model of a one-dimensional solid

Revisit the example in Sec. 6.6.2 above, but now consider the oscillators are quantum mechanical. A single quantum oscillator has energies

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, 3, \dots$$
(6.88)

The one-particle partition function is

$$Z_{1} = \sum_{n=0,1,2,\cdots} e^{-\epsilon_{n}/(k_{B}T)}$$

$$= e^{-\hbar\omega/(2k_{B}T)} \sum_{n=0,1,2,\cdots}^{\infty} e^{-\hbar\omega n/(k_{B}T)}$$

$$= e^{-\hbar\omega/(2k_{B}T)} \frac{1}{1 - e^{-\hbar\omega/(k_{B}T)}}$$

$$= \frac{1}{2\sinh(\hbar\omega/(2k_{T}))}.$$
(6.89)

We have used the geometric series,

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x},\tag{6.90}$$

which you remember from primary school, and which you must remember for the rest of your life.

The partition function of M quantum oscillators is

$$Z_M = (Z_1)^M = \frac{1}{[2\sinh(\hbar\omega/2k_BT)]^M}.$$

We will see later the thermodynamics of quantum oscillators reduces to the classical one in the high temperature limit but is completely different in the low temperature limit.

In the next sections, we will discuss how to calculate energy, entropy and other thermodynamic quantities from partition functions.

[Ref.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.1-5.2]

We have calculated the partition functions Z_N for a number of very basic systems in this section. as described above it is then straightforward to calculate other thermodynamic quantities. In the rest of the chapter we will do just that for a number of model systems. We will also discuss the physical implications of our results.

[Refs.: (1) Mandl 2.5; (2) Bowley and Sánchez 5.3-5.6.]

6.7 Example: The classical ideal gas

Now it is time to revisit the ideal gas we discussed often in thermodynamics. We hinted before that it would be a challenging problem using microcanonical ensemble approach. We will show that this is not the case using canonical ensemble approach.

Note:

The calculation in this section is based on a classical approach. We will repeat the same calculation quantum mechanically in Sec. 6.8.

In Eq. (6.87) we have calculated the partition function of classical ideal gas of N identical molecules at fixed temperature T in a volume V

$$Z_N = \frac{1}{N!} Z_1^N = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}.$$
 (6.91)

Hence, using Stirling approximation, $N! \approx (N/e)^N$,

$$\ln Z_N = N \ln \left[e \frac{V}{N} \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \right]$$
(6.92)

Now we follow the standard calculations of canonical ensemble to obtain other thermodynamic quantities. The Helmholtz free energy is obtained from Eq. (6.44)

$$F = -\frac{1}{\beta} \ln Z_N = -\frac{1}{\beta} N \left[\frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) + \ln \frac{V}{N} + 1 \right].$$

$$(6.93)$$

Note:

Had we not included the 1/N! factor in Z_N , the second term in Eq. (6.93) would be $\ln V$ instead of the intensive quantity $\ln(V/N)$ (you should convince yourself of that!), and F would not be extensive as required.

The equation of state is obtained using the definition of pressure in Eq. (6.47):

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{1}{\beta}N \cdot \frac{1}{V}.$$
(6.94)

With the identification $\beta = \frac{1}{k_B T}$ we therefore obtain the familiar formula

$$PV = Nk_BT. (6.95)$$

The entropy is calculated using Eq. (6.47), and we find

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_B N \left(\frac{3}{2}\ln\frac{2\pi m k_B T}{h^2} + \ln\frac{V}{N} + \frac{5}{2}\right),\tag{6.96}$$

which can be compared with Q2(a) of Example Sheet 5

$$S = k_B N \left(\frac{3}{2} \ln \frac{T}{T_0} + \ln \frac{V}{V_0}\right) + \text{const.}$$

$$(6.97)$$

Eq. (6.96) is referred as Sackur-Tetrode equation. It gives the <u>absolute</u> value of the entropy of a gas at a given temperature T. See Q2 of Example Sheet 11 for more details. Apart from the factor m of atomic mass, it is the same for every substance. At high enough temperature and low enough densities <u>all</u> substances behave as ideal gases, and so the Sackur-Tetrode formula can be checked experimentally. Good agreement is found.

The internal energy of an ideal gas can be calculated by partial derivative of the log of the partition function (you should understand how exactly, and why), or simply from F = E - TS. We have

$$E = F + TS = \frac{3}{2}k_BNT, \tag{6.98}$$

which is independent of volume V as expected. The heat capacity at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}k_B N.$$
(6.99)

<u>Note:</u>

The entropy S of Eq. (6.96) has the wrong low-T behavior as $S \to -\infty$ in the limit $T \to 0$, in conflict with the third law which states $S \to 0$ in the limit $T \to 0$. There are two reasons for the problem:

- (a) We have ignored interactions between particles when calculating partition function Z_N ; these interactions are responsible for the particles condensing into liquids or forming solids at low temperature.
- (b) We have also ignored quantum effects (significant at low temperature) when we considered the properties of indistinguishable particles by assuming particles are in different single-particle states (hence the over-counting factor is simple N!). The quantum effects of many particles in the zero-momentum state is responsible for the Bose-Einstein condensation.

Inclusion either of the above two effects will result correct low temperature behavior for the entropy. More detailed discussion for validity of the classical Z_N above is given by Mandl 7.3.

6.8 Translational energy of molecules: Quantum treatment

In Sec. 6.7 we have calculated the one-body partition function and the energy for the translational motion of N particles (i.e., an ideal gas), using an approach based on classical mechanics. In this section we now repeat this calculation using quantum mechanics. We will see that Z_1 is the same as in the classical calculation

Consider a single free particle (acted on by no forces, potential V = 0), contained in a box of lengths L_x, L_y, L_z . Its wave function $\psi = \psi(x, y, z)$ satisfies the free Schrödinger equation inside the box

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z).$$

We assume the box is impenetrable so that ψ vanishes everywhere on the boundaries of the box and outside it. The Schrödinger equation with this boundary condition is easily seen to be satisfied by the solution

$$\psi(x, y, z) = \begin{cases} A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right), & \text{inside the box;} \\ 0, & \text{outside the box,} \end{cases}$$

where $n_x, n_y, n_y = 1, 2, \dots$, and where A is a normalization constant. (If you do not understand why this is the appropriate wave function, please revise your quantum physics.)

The corresponding energy eigenvalues are (you should understand why) $E = \epsilon_{n_x, n_y, n_z}$, with

$$\epsilon_{n_x,n_y,n_z} = \left[\left(\frac{n_x \pi}{L_x} \right)^2 + \left(\frac{n_y \pi}{L_y} \right)^2 + \left(\frac{n_z \pi}{L_z} \right)^2 \right] \frac{\hbar^2}{2m} \equiv \frac{\hbar^2 k^2}{2m}, \tag{6.100}$$

where $k^2 = k_x^2 + k_y^2 + k_z^2$ and $k_x = n_x \pi/L_x$, $k_y = n_y \pi/L_y$ and $k_z = n_z \pi/L_z$. Hence, the one-particle partition function for this free translational motion is

$$Z_{1}^{t} = \sum_{n_{x}=1}^{\infty} \sum_{n_{y}=1}^{\infty} \sum_{n_{z}=1}^{\infty} e^{-\beta \epsilon_{n_{x}, n_{y}, n_{z}}}.$$

This sum can be further evaluated only in the limit $k_B T \gg \hbar^2 \pi^2 / 2mL^2$, i.e., when the thermal energy per degree of freedom is large compared to the spacing between energy levels. For L = 1cm, $m = m_H$ (hydrogen mass), we have an energy-level spacing of $\hbar^2 \pi^2 / 2mL^2 \approx 2 \times 10^{-18}$ eV, a truly tiny energy, and for all attainable temperature the condition $k_B T \gg \hbar^2 \pi^2 / 2mL^2$ is always satisfied. Thus, for all macroscopic boxes and even at the lowest temperature ever reached, we can replace the sums by integrals. Putting $n_x = k_x L_x / \pi$, etc., we replace

$$\sum_{n_x=1}^{\infty} \cdots \to \int_0^\infty \frac{L_x}{\pi} dk_x \cdots,$$

etc. We rewrite Z_1 as

$$Z_{1}^{t} = \frac{L_{x}}{\pi} \frac{L_{y}}{\pi} \frac{L_{z}}{\pi} \int_{0}^{\infty} dk_{x} \int_{0}^{\infty} dk_{y} \int_{0}^{\infty} dk_{z} e^{-\beta\epsilon(k)} = \frac{V}{8\pi^{3}} \int d^{3}k e^{-\beta\epsilon(k)}$$

where $V = L_x L_y L_z$ and $\epsilon(k) \equiv \hbar^2 k^2 / 2m$, and where the d^3k integral is over the entire 3dimensional k-space (hence the extra factor of 1/8).

So we are left with

$$Z_1^t = \frac{V}{(2\pi)^3} \int d^3k e^{-\beta\epsilon(k)}, \quad \epsilon(k) \equiv \frac{\hbar^2 k^2}{2m}.$$
 (6.101)

This is a Gaussian integral, and so it can be evaluated. We introduce spherical coordinates via

$$d^3k = k^2 \ dk \ \sin\theta \ d\theta \ d\phi. \tag{6.102}$$

After integrating out the angles we rewrite Eq. (6.101) as

$$Z_1^t = \int_0^\infty dk D(k) e^{-\beta \epsilon(k)}, \quad D(k) = \frac{Vk^2}{2\pi^2}, \tag{6.103}$$

where D(k) is usually referred to as the density of states in k-space, i.e., D(k)dk is the number of states within the spherical shell between k and k + dk.

Finally, we can insert $\epsilon(k) = \hbar^2 k^2 / 2m$ and evaluate the integral in Eq. (6.103). To do this introduce x via $k = \sqrt{2m/\beta\hbar^2}x$, and get

$$Z_1^t = \frac{V}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \int_0^\infty dx \ x^2 e^{-x^2} = V \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2},\tag{6.104}$$

where we have used Gaussian integral¹

$$\int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}.$$
 (6.105)

Compare with Eq. (6.86). From Z_1^t we can calculate the average energy per molecule (please do this step yourself)

$$\frac{E^t}{N} = -\frac{\partial \ln Z_1^t}{\partial \beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T, \qquad (6.106)$$

same as Eq. (6.98) obtained from the classical approach.

The fact that we reproduce the classical results is not surprising as we have taken the continuous limit (converting the summations over k-modes into integrals). The discrete nature of the energy levels will show up only at temperature $T < \hbar^2/(k_B m V^{2/3}) \approx 10^{-14}$ K.

Remark 1:

The factor D(k) in Eq. (6.103) in the continuous-k limit plays the role of a 'degeneracy factor' $g(\epsilon_k)$ which we have seen e.g. in the discrete sum for Z_1 of Eq. (6.75).

Remark 2:

We want to emphasize that although the quantum mechanical single-particle partition function, Z_1 , obtained here is the same as classical result shown earlier, the formula for the total partition function

$$Z_N = \frac{1}{N!} Z_1^N \tag{6.107}$$

is a classical approximation. It ignores quantum effects of many-body systems.

[Refs.: (1) Mandl 7.1-7.3,; (2) Bowley and Sánchez 5.9,7.2.]

6.9 Example: The ideal spin-1/2 paramagnet

6.9.1 General results

Now we revisit the problem of the ideal spin-1/2 paramagnet at fixed temperature. We consider N spins in a magnetic field B. Each spin has only two states, either up with energy $\epsilon_{\uparrow} = -\mu B$, or down with energy $\epsilon_{\downarrow} = +\mu B$.

As seen above in Sec. 6.6.1, the partition function of the paramagnet is calculated as

$$Z_N = (Z_1)^N = [2\cosh(\beta\mu B)]^N, \quad \ln Z_N = N\ln(2\cosh(\beta\mu B)], \quad (6.108)$$

¹You can calculate this integral using the result of Q4 on example sheet 9. There you showed that $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$. Now differentiate with respect to a.



Figure 6.4: Energy of the spin-1 -2/ paramagnet, consisting of N non-interacting spins. The left-hand panel is shows the energy as a function of the inverse temperature β , the horizontal axis on the right-hand panel is T.

where $\beta = 1/k_BT$. We can now calculate the total average energy easily using Eq. (6.37):

$$E = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{N}{\cosh(\beta \mu B)} \cdot \sinh(\beta \mu B) \cdot (\mu B), \qquad (6.109)$$

hence

$$E = -N\mu B \tanh \frac{\mu B}{k_B T}.$$
(6.110)

The heat capacity at constant magnetic field is calculated as

$$C_B = \left(\frac{\partial E}{\partial T}\right)_B = -N\mu B \operatorname{sech}^2 \frac{\mu B}{k_B T} \cdot \left(-\frac{\mu B}{k_B T^2}\right) = N \frac{\mu^2 B^2}{k_B T^2} \operatorname{sech}^2 \frac{\mu B}{k_B T},$$
(6.111)

where we have used $\frac{d}{dx} \tanh x = \operatorname{sech}^2 x$. Recall, by the way, that $\operatorname{sech} x \equiv 1/\cosh x$.

6.9.2 Low-temperature and high-temperature limits of the energy

We can plot E as function of T using the fact that, as $x \to 0$, $\sinh x \approx x$ and $\cosh x \approx 1$; and as $x \to \infty$, $\sinh x \approx e^x/2$ and $\cosh x \approx e^x/2$. Hence, from Eq. (6.110)

$$E \to -N\mu B, \quad T \to 0.$$
 (6.112)

just as expected, since all spins will be in the low-energy up state. On the other hand, $tanh x \to x \text{ as } x \to 0$, hence

$$E \approx -\frac{N\mu^2 B^2}{k_B T} \to 0, \quad T \to \infty.$$
 (6.113)

As expected the energy at infinite temperatures is zero since the number of up spins and down spins become nearly equal. These behaviors are shown in Fig. 6.4.



Figure 6.5: Typical occupation patterns of the paramagnet at low and high temperatures respectively.

6.9.3 High-temperature and low-temperature limits of C_B

We can similarly investigate the heat capacity C_B . From Eq. (6.111), in the limit $T \to 0$ $(\beta \to \infty)$,

$$C_B \approx N k_B (\mu B \beta)^2 4 e^{-2\mu B \beta} = N k_B \left(\frac{2\mu B}{k_B}\right)^2 \frac{1}{T^2} e^{-2\mu B/k_B T}.$$
 (6.114)

Using the fact that the exponential decays to zero in the limit $T \to 0$ faster than $1/T^2$ tends to infinity,

$$C_B \to 0, \quad T \to 0.$$
 (6.115)

This behavior, which is quite general, is also easy to understand. At low T, thermal fluctuations that flip a spin are rare, so it is very difficult for the system to absorb heat. The quantization of energy levels means that there is always a minimum excitation energy for any system, and hence, if T is low enough, the system cannot easily absorb heat. In the opposite limit,

$$C_B \approx \frac{N\mu^2 B^2}{k_B} \frac{1}{T^2}, \quad T \to \infty.$$
(6.116)

The high-T behaviour arises as follows: at any temperature n_{\downarrow} is always smaller than n_{\uparrow} (you should understand why). As $T \to \infty$, n_{\downarrow} approaches n_{\uparrow} , they are essentially equal (again you should understand why), although we still have $n_{\downarrow} < n_{\uparrow}$. So if we are at high temperatures already, then raising T even higher makes little difference, i.e., the system has no further capacity to absorb heat. This is pictorially shown in Fig. 6.5. The resulting heat capacity is plotted in Fig. 6.6.

However, this behaviour is not universal, we here only look at the special case of two fixed energy levels. Most systems have an infinite number of energy levels of higher and higher energies. Hence in general there is no maximum energy and the heat capacity will not fall to zero in the high-T limit.

6.9.4 Entropy and magnetic moment

The Helmholtz free energy is calculated using Eq. (6.46). One finds

$$F = -k_B T \ln Z_N = -Nk_B T \ln \left(2 \cosh \frac{\mu B}{k_B T} \right).$$
(6.117)



Figure 6.6: Heat capacity of the paramagnet discussed in the text.

The entropy and magnetization then follow as

$$S = -\left(\frac{\partial F}{\partial T}\right)_{B,N}, \quad m = -\left(\frac{\partial F}{\partial B}\right)_{T,N}.$$
(6.118)

Hence, for the entropy

(ii) $T \to \infty$ (or

$$S = Nk_B \{ \ln[2\cosh(\beta\mu B)] - \beta\mu B \tanh(\beta\mu B) \}.$$
(6.119)

Consider the low-temperature and high-temperature limits:

(i)
$$T \to 0 \text{ (or } \beta \to \infty)$$

$$S \approx Nk_B \{ \ln[2 \times \frac{1}{2} e^{\beta \mu B}] - \beta \mu B \cdot 1 \} \to 0, \quad T \to 0$$
(6.120)

which is as expected, since as $T \to 0$ all spins are up, i.e. no disorder!

$$(\beta \to 0)$$

$$S \approx Nk_B \{\ln 2 - (\beta \mu B)^2\} \to Nk_B \ln 2$$
(6.121)

again, as expected, since as $T \to \infty$, the spins are equally likely to be up or down, entropy per spin is $k_B \ln 2$ as we have seen before.

The net magnetic moment is given by,

$$m = -\left(\frac{\partial F}{\partial B}\right)_{T,N} = N\mu \tanh(\beta\mu B) = -\frac{E}{B}$$

as expected, since E = -mB is the equation of state for the ideal paramagnet. Again look at the low-T and high-T limits:



Figure 6.7: Entropy and net magnetisation of the spin-1/2 paramagnet with non-interacting spins as a function of temperature.

(i) $T \to 0 \text{ (or } \beta \to \infty)$

$$m \to N\mu$$
 (6.122)

for all spins are up; and

(ii) $T \to \infty$ (or $\beta \to 0$)

$$m \approx \frac{N\mu^2 B}{k_B T}$$
, Curie's law
 $\rightarrow 0$

again, as expected, since we have nearly equal numbers of up and down spins.

We plot S and m versus T for several different external fields as shown in Fig. 6.7.

6.9.5 The third law of thermodynamics

As we have seen above, the entropy S tends to zero as $T \to 0$ as all spins align. This is generally true, namely, a system has no disorder in the limit of $T \to 0$. This is the

Third law of thermodynamics: The entropy of any system $S \to 0$ as $T \to 0$.

In the next section, we discuss a way to reach low temperature limit using paramagnets.

[Refs.: (1) Mandl 3; (2) Bowley and Sánchez 5.7.]

6.9.6 Adiabatic demagnetization and the third law of thermodynamics*

By magnetizing and demagnetizing a paramagnet sample, while controlling the heat flow, we can lower its temperature. To understand this refer to the curve of S vs. T for the ideal paramagnet, see Fig. 6.7. Similar curves are shown for two different magnetic field strengths in Fig. 6.8.

The procedure is as follows:



Figure 6.8: Illustration of the process of adiabatic demagnetisation.



Figure 6.9: Procedure of adiabatic demagnetisation: (a) Start, (b) Step 1, (c) Step 2.

- Step 0: Start with the sample in a magnetic field B_1 at an already fairly low temperature $\overline{T_1}$.
- Step 1, isothermal magnetization: Increase the field from B_1 to B_2 at constant T (i.e., in contact with heat bath). The entropy S hence decreases as spins align with the stronger field (i.e., the system becomes more ordered).
- <u>Step 2, adiabatic demagnetization</u>: Now isolate the system from the heat bath and demagnetize (i.e., reduce the magnetic field from B_2 to B_1). The system is isolated, so $\Delta Q = 0$, and if the process is quasistatic and reversible, $\Delta S = 0$. From Fig. 6.8 we see that the system's temperature reduces from T_1 to T_2 ; note that from Eq. (6.119) S is a function of B/T only, hence for constant S, if B is reduced, T must reduce by a same factor.
- Iterate steps 1 and 2.

Fig. 6.9 illustrates what happens to the spins. In step 1, we increase the level spacing, but keep T constant; the population of the upper level falls. In step 2 we reduce the level spacing again, but as the process is now adiabatic (spins isolated) there is no change in level occupations, the temperature is lowered.

This is actually a practical way to reach quite low temperatures, to small fractions of 1 K. If we start with a large sample we could repeat the process with a small sub-sample, with rest acting as a heat bath. However at each repeat of Steps 1 and 2 we would reduce the temperature by less and less, as the two curves come closer together as $T \rightarrow 0$, see Fig. 6.8. Thus it is impossible to reach T = 0 in a finite number of steps in this way. This is just one example of the third law of thermodynamics: namely, either

- (a) absolute zero is unattainable (in a finite number of steps) or, more precisely,
- (b) The entropy of any aspect of any system, $S \to 0$ as $T \to 0$.

<u>Note</u>: Statement (b) implies that the ground state is non-degenerate so that all particles fall into the same state as $T \to 0$.

[Ref.: (1) Mandl 5.6.]

6.10 Vibrational and rotational energy of diatomic molecules

In the previous sections we considered a classical ideal gas of N particles. If these particles are diatomic molecules, in addition to the translational motion for the center-of-mass of a molecule, there are also vibrational and rotational modes. We consider these three types of motions as independent of one another, hence write the partition function of N diatomic molecules as

$$Z_N = \frac{1}{N!} (Z_1)^N, \quad Z_1 = Z_1^t Z_1^v Z_1^r$$
(6.123)

where Z_1^t is the one-body partition function of translational motion, given by Eq. (6.86)), Z_1^v is that of the vibrational motion, and Z_1^r is that of the rotational motion.

We now compute Z_1^v and Z_1^r quantum mechanically.

6.10.1 Vibrational energy contribution

The energy levels of a simple quantum harmonic oscillator of angular frequency ω are

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots.$$
 (6.124)

Hence, the one-body partition function is the same as calculated in Eq. (6.89),

$$Z_1 = \sum_{n=0}^{\infty} e^{-(n+1/2)\hbar\omega\beta} = \frac{1}{2\sinh(\hbar\omega\beta/2)}.$$
 (6.125)

Hence, the vibrational energy per molecule at temperature T is

$$\frac{E^{v}}{N} = -\left(\frac{\partial \ln Z_{1}}{\partial \beta}\right) = \frac{1}{2\sinh(\hbar\omega\beta/2)} \cdot 2\cosh(\hbar\omega\beta/2) \cdot (\hbar\omega/2)$$
(6.126)

or

$$\frac{E^{\nu}}{N} = \frac{1}{2}\hbar\omega \coth(\hbar\omega\beta/2).$$
(6.127)

We now consider the low-temperature limit and the high-temperature limit:

(i)
$$T \to 0 \ (\beta \to \infty), \ \operatorname{coth}(\hbar\omega\beta/2) \to 1$$

$$\frac{E^v}{N} \to \frac{1}{2}\hbar\omega.$$
(6.128)

This is the quantum mechanical ground state energy.

(ii)
$$T \to \infty \ (\beta \to 0), \ \coth(\hbar \omega \beta/2) \approx \frac{2}{\hbar \omega \beta},$$

$$\frac{E^v}{N} \approx \frac{1}{\beta} = k_B T. \tag{6.129}$$

This is the result you would expect from a classical calculation (you should understand why).

Exercise:

Using the results of Sec. 6.6.2 compute the average energy per particle for system of N distinguishable independent simple classical harmonic oscillators.

<u>Remark:</u>

For most diatomic molecules, the high-T limit is effectively reached for $T \ge 1000$ K.

6.10.2 Rotational energy contribution

In classical mechanics the energy of a rigid rotor with moment of inertia I, rotating with angular velocity ω (or angular momentum $L = I\omega$) is $\epsilon = I\omega^2/2 = L^2/2I$ (you should remember this from your first-year courses on classical dynamics, if you don't then please revise your classical mechanics).

In quantum mechanics, the angular momentum is quantized as

$$L^2 \to \ell(\ell+1)\hbar^2, \quad \ell = 0, 1, 2, \cdots$$
 (6.130)

(again you should remember this from your quantum mechanics courses). Hence the energy levels are

$$\epsilon_{\ell} = \frac{\ell(\ell+1)\hbar^2}{2I}, \quad \ell = 0, 1, 2, \cdots.$$
 (6.131)

Also, for each eigenvalue l we have $g_{\ell} = (2\ell + 1)$ degenerate magnetic sublevels, specified by quantum number $m_{\ell} = -\ell, -\ell + 1, \dots, \ell - 1, \ell$, all with same energy ϵ_{ℓ} . Hence the one-body partition function is

$$Z_1^r = \sum_{\ell=0}^{\infty} (2\ell+1)e^{-\ell(\ell+1)\hbar^2\beta/2I}.$$
(6.132)

For general β , we can not simplify the above Z_1 further, as it is hard to compute the sum over ℓ explicitly (look at the sum, and you will understand why). However, we can look at the low-T and high-T limits as follows:

(a) $T \to 0 \ (\beta \to \infty)$: To obtain a good approximation we keep only the two most relevant terms (you should understand why these are the dominating terms in this limit, i.e. why are the $\ell = 0$ and $\ell = 1$ terms more important than say $\ell = 2$ and $\ell = 3$?),

$$Z_1 \approx 1 + 3e^{-\hbar^2 \beta/I}$$
. (6.133)

In this approximation the rotational energy per molecule is

$$\frac{E^r}{N} \approx 3\frac{\hbar^2}{I} e^{-\hbar^2\beta/I} \to 0, \quad \text{as } T \to 0.$$
(6.134)

(You should check this expression in detail yourself, I have omitted about 3-5 lines here. You should understand why this approaches zero!)

(b) $T \to \infty \ (\beta \to 0)$: In this limit $(k_B T \gg \hbar^2/2I)$ there are many thermally accessible energy levels, and the discrete series can be well approximated by a continuum, i.e.,

$$Z_1^r \approx \int_0^\infty dl (2l+1) e^{-l(l+1)\hbar^2 \beta/2I}.$$
 (6.135)

(You should understand why it is possible to replace the sum by an integral in this limit.) The above integral can be evaluated exactly by making the substitution x = l(l+1) and dx = (2l+1)dl. We obtain (you should do this in detail!)

$$Z_1^r \approx \frac{2I}{\hbar^2 \beta} = \frac{2Ik_B T}{\hbar^2}.$$
(6.136)

The rotational energy per molecule is then obtained from $\frac{E^r}{N} = -\frac{\partial}{\partial\beta} \ln Z_1^r$:

$$\frac{E^r}{N} \approx \frac{1}{\beta} = k_B T$$
, for large T. (6.137)

For further details, see Example Sheet 11.

Note: For typical diatomic molecules, $\hbar^2/2I \approx 10^{-3}$ eV, and so the high-T limit is reached well below room temperature.

6.10.3 Translational energy contribution

In Eq. (6.98) we have obtained the translational energy per molecule in an ideal gas as

$$\frac{E^t}{N} = \frac{3}{2}k_BT.$$
(6.138)

Remark:

We have now established that, in the high-temperature limit, the energy per particle is k_BT for vibrational degrees of freedom, k_BT for rotational degrees of freedom, and k_BT per translational degree of freedom. This is of course not an accident. These are examples of the so-called equipartition theorem, which we will discuss in Sec. 6.11.

[Refs.: (1) Bowley and Sánchez 5.11, 5.12.]

6.11 The equipartition theorem

The last three results (for vibrational, rotational and translational motion) provide examples of the equipartiton theorem.

We first state and prove the theorem in its general form for the canonical ensemble²:

Equipartition theorem:

Consider a classical physical system with Hamiltonian (energy function) $H = H(q_1, \ldots, q_M)$, where q_1, \ldots, q_M are generalised coordinates (degrees of freedom). Then the following holds

$$\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle = \delta_{k\ell} k_B T. \tag{6.139}$$

Remark 1:

The average $\langle f(q_1, \ldots, q_M) \rangle$ in the above theorem denotes the usual average in the canonical ensemble,

$$\langle f(q_1, \dots, q_M) \rangle = \frac{1}{Z} \int dq_1 \cdots dq_M e^{-\beta H(q_1, \dots, q_M)} f(q_1, \dots, q_M).$$
 (6.140)

Remark 2:

The generalised coordinates (degrees of freedom), q_1, \ldots, q_M represent the usual classical degrees of freedom. For example, for N particles of a mono-atomic ideal gas, we have 6N total degrees of freedom, three spatial coordinates per particle, and three components of the particle's momentum. In this case M = 6N. The first 3N variables q_1, \ldots, q_{3N} could represent the positions of the N particle, and the remaining q_{3N+1}, \ldots, q_{6N} coordinates their momenta.

<u>Remark 3:</u>

I have been very sloppy with factors of h^{3N} in the phase space measure. If Z is defined as $Z = \int \frac{d^{3N} r d^{3N} p}{h^{3N}} e^{-\beta H_N}$, then the corresponding definition of the phase-space average reads

$$\langle f \rangle = \frac{1}{Z} \int \frac{d^{3N} r d^{3N} p}{h^{3N}} e^{-\beta H_N} f(r_1, \dots, r_{3N}, p_1, \dots, p_{3N}).$$
(6.141)

Note that for averages it does not matter whether you include the factors of h or not, as long as you are consistent. If they are included they appear in the numerator and the denominator,

 $^{^{2}}$ The theorem can be shown to hold in the microcanonical ensemble as well.

so they drop out either way. IMPORTANT: When you calculate partition functions, it is crucial to include the factors of h, otherwise you get object such as Z, F etc wrong.

<u>Proof of the theorem:</u> The average $\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle$ can be written as

$$\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle = \frac{1}{Z} \int dq_1 \cdots dq_M \left(q_k \frac{\partial H}{\partial q_\ell} \right) e^{-\beta H}$$
$$= -\frac{1}{\beta} \frac{1}{Z} \int dq_1 \cdots dq_M q_k \left(\frac{\partial}{\partial q_\ell} e^{-\beta H} \right)$$
(6.142)

We now integrate by parts on the right-hand-side:

$$\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle = \frac{1}{\beta} \frac{1}{Z} \int dq_1 \cdots dq_M \ \frac{\partial q_k}{\partial q_\ell} e^{-\beta H},$$
 (6.143)

assuming that we can ignore the boundary term $q_k e^{-\beta H}$, i.e. that this term vanishes at the boundaries $q_k \to \pm \infty$ (this is not an unreasonable assumption). One now uses $\frac{\partial q_k}{\partial q_\ell} = \delta_{k\ell}$ (Kronecker delta) and arrives at

$$\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle = \delta_{k\ell} \frac{1}{\beta} \frac{1}{Z} \int dq_1 \cdots dq_M \ e^{-\beta H},$$
 (6.144)

Remembering that $Z = \int dq_1 \cdots dq_M e^{-\beta H}$ we are done, $\left\langle q_k \frac{\partial H}{\partial q_\ell} \right\rangle = \delta_{k\ell} k_B T$, q.e.d.

Many physical systems have quadratic degrees of freedom (i.e. degrees of freedom that enter quadratically into the energy function, H). For such systems the equipartition theorem can be formulated as follows:

Equipartition theorem for quadratic degrees of freedom:

For a physical system in which degrees of freedom contribute quadratically to the total energy function H the average energy is $k_B T/2$ per degree of freedom and its contribution to the heat capacity is $k_B/2$. This holds for classical systems. For quantum systems the statement applies at high enough temperatures.

Exercise (highly recommended!):

Derive this statement (average energy for quadratic degrees of freedom is $k_B T/2$ for classical systems) from the above general equipartition theorem. See also example sheet 11.

Examples:

Here are the examples we have discussed earlier:

• Vibrations:

$$E_{\rm vib} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 \tag{6.145}$$

Two quadratic degrees of freedom (d.o.f.): $\Rightarrow E \approx k_B T$.

• Rotations: Two perpendicular axes about which the molecule can rotate,

$$E_{\rm rot} = \frac{1}{2} I_1 \dot{\theta}_1^2 + \frac{1}{2} I_2 \dot{\theta}_2^2 \tag{6.146}$$

Two quadratic d.o.f., hence $E \approx k_B T$.



Figure 6.10: Illustration of the specific heat as a function of temperature for a diatomic gas.

• Translations:

$$E_{\rm tr} = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \tag{6.147}$$

Three quadratic d.o.f., hence $E \approx 3k_BT/2$.

The equipartition theorem is a classical theorem. From our present statistical mechanics treatment of quantum systems we see it breaks down when the separation between quantum energy levels is small compared with k_BT . If this happens the heat capacity of a particular d.o.f. will be reduced, dropping to zero at low temperatures. The corresponding d..o.f. is then said to be frozen out; e.g., this is typically the situation for the vibrational degrees of freedom at room temperature. More specifically, in quantum systems equipartition holds

- for vibrations, when $T \gg \hbar \omega / k_B \approx 10^3$ K;
- for rotations, when $T \gg \hbar^2 / I k_B \approx 10 100$ K;
- for translations, when $T \gg \hbar^2/(mV^{2/3}k_B) \approx 10^{-14}$ K.

Thus, at room temperature, only the rotational and translational degrees of freedom can be treated classically, giving $C_V = 3R/2$ for monatomic gases and $C_v = 5R/2$ for diatomic gases, for the molar heat capacity.

The diagram shown in Fig. 6.10 illustrates this for the example for a diatomic gas (e.g., H_2). We can predict the heat capacities of other substances using equipartition, simply by counting the quadratic degrees of freedom. An example is a solid, for which we expect the molar heat capacity to be 3R since each atom is free to to vibrate in 3 directions. This is the Dulong-Petit law, which works well for many solids at room temperature

[Refs.: (1) Mandl 7.9; (2) Bowley and Sánchez 5.14.]

6.12 The Maxwell-Boltzmann velocity distribution

In this section we derive the Maxwell-Boltzmann velocity distribution for an ideal classical gas you have learned in your year one module.

Consider a gas of N molecules in a volume V, in thermal equilibrium at a temperature T. From the Boltzmann distribution function the probability to find a particular particle in the one-particle state (\underline{r}, p) is

$$\rho(\underline{r},\underline{p}) = \frac{1}{Z_1} e^{-H_1(\underline{r},\underline{p})/(k_B T)}$$
(6.148)

where $H_1(\underline{r}, \underline{p})$ is the energy of the a single molecule in state $(\underline{r}, \underline{p})$. The average number of molecules inside a phase space volume $d^3r d^3p/h^3$ centred around (\underline{r}, p) is then given by

$$N\rho(\underline{r},\underline{p})\frac{d^3rd^3p}{h^3}.$$
(6.149)

You should at this point understand <u>exactly</u> why this is so. If you do not then please go back and study the sections on probability densities for continuous states (Sec. 5.3.3).

We now ask how many of the N particles will have velocity v on average? Note that $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. The corresponding probability distribution P(v) is the so-called Maxwell-Boltzmann distribution. If P(v) is the resulting probability distribution, i.e. P(v)dv is the probability to find a given particle to have a velocity between v and v + dv, then the expected total number of particles with a velocity in this interval is NP(v)dv.

For the ideal gas we have $H_1(\underline{r}, \underline{p}) = \frac{\underline{p}^2}{2m}$ with $\underline{p} = m\underline{v}$. We can therefore replace d^3p by m^3d^3v . Introducing the dummy variable \underline{v}' and writing $d^3v' = \sin \vartheta v'^2 dv' d\phi d\vartheta$ we have

$$P(v) = \frac{m^3}{Z_1} \int \frac{d^3 r d^3 v'}{h^3} \delta(v' - v) e^{-\beta H_1(\underline{r},\underline{p}=\underline{m}\underline{v}')}$$

$$= \frac{m^3}{Z_1} \int \frac{d^3 r dv' d\phi d\vartheta}{h^3} \sin \vartheta v'^2 \delta(v' - v) e^{-\beta H_1(\underline{r},\underline{p}=\underline{m}\underline{v}')}$$

$$= \frac{Vm^3}{Z_1h^3} v^2 e^{-\beta H_1(\underline{p}=\underline{m}\underline{v})} \times \int_0^{2\pi} d\phi \int_0^{\pi} d\vartheta \sin \vartheta$$

$$= \frac{4\pi Vm^3}{Z_1h^3} v^2 e^{-\beta H_1(\underline{p}=\underline{m}\underline{v})}$$

$$= \frac{4\pi Vm^3}{Z_1h^3} v^2 e^{-(mv^2)/(2k_BT))}.$$
(6.150)

Using our earlier result for the single-particle partition function for the ideal gas (see e.g. Eq. (6.86))

$$Z_1 = V \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2},\tag{6.151}$$

we have

$$P(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_B T)}.$$
(6.152)

Notice the normalization (which you should check!)

$$\int_0^\infty P(v)dv = 1. \tag{6.153}$$

This is the well-known Maxwell-Boltzmann velocity (speed) distribution. We plot distribution P(v) in Fig. 6.11.

A few physical quantities are calculated as follows.



Figure 6.11: Illustration of the Maxwell-Boltzmann distribution.

• Most probable speed: let v_p be the point of maximum P(v), i.e., dP/dv = 0, so

$$\frac{d}{dv}\left(v^2 e^{-mv^2\beta/2}\right) = 0 \quad \Rightarrow \quad (2v - v^2 m v\beta) = 0. \tag{6.154}$$

From this we have

$$v_p = \sqrt{\frac{2k_BT}{m}} \approx 1.41 \sqrt{\frac{k_BT}{m}}.$$
(6.155)

• Mean speed

$$\langle v \rangle = \int_0^\infty v \cdot P(v) dv = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2k_B T} dv$$

$$= \sqrt{\frac{8k_B T}{m}} \pi \approx 1.60 \sqrt{\frac{k_B T}{m}}.$$

$$(6.156)$$

• rms speed:

$$\langle v^2 \rangle \equiv v_{\rm rms}^2 = \int_0^\infty v^2 \cdot P(v) dv = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2k_B T} dv$$

= $3 \frac{k_B T}{m},$ (6.157)

or

$$v_{\rm rms} = \sqrt{\frac{3k_BT}{m}} \approx 1.73 \sqrt{\frac{k_BT}{m}}.$$
(6.158)

These three speeds are marked in Fig. 6.11. From Eq. (6.157) we have

$$E_1 = \frac{1}{2} \langle mv^2 \rangle = \frac{1}{2} mv_{\rm rms}^2 = \frac{m}{2} \cdot \frac{3k_B T}{m} = \frac{3}{2} k_B T, \qquad (6.159)$$

consistent with equipartition theorem.

Remark:

Planck's constant (h) appears in the phase-space volume and in the partition function, but it does not feature in the Maxwell-Boltzmann distribution. Otherwise one would not be able to deduce the Maxwell-Boltzmann distribution from classical arguments alone, e.g. from the kinetic theory of gases, as was done originally by Maxwell.

Remark:

In the above calculations, we have used the following general Gaussian integral

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}.$$
(6.160)

[Refs.: (1) Mandl 7.7; (2) Bowley and Sánchez 7.4.]
Chapter 7

What's next?*

"We can only see a short distance ahead, but we can see plenty there that needs to be done."

(Alan Turing)

Remark:

This chapter is not examinable!

7.1 Interacting systems

So far, we have completely ignored interactions between constituent particles in all of our examples, from the ideal spin-1/2 paramagnets to the classical ideal gas. All partition functions factorized, which made our calculations rather easy.

Clearly, the investigation of the effects due to, for example, interactions between molecules of a gas is the next main task. In fact, the most interesting physics emerges from such interactions. Examples are phase transitions from gases to liquids or solids as temperature is lowered, and even to superfluids or superconductors at extremely low temperatures where quantum physics dominates.

The material we have covered so far does – in principle – provide the formalism to tackle most of these problems, although some special techniques will be required.

We illustrated this using a gas of N identical classical molecules. We now explicitly acknowledge that these molecules interact with one another, let us assume the interaction is described by a pair-wise interaction potential, V(r), where r is the separation between the interacting pair. We draw a typical V(r) in Fig. 7.1. Qualitatively, we see the interaction potential consists of a hard-core potential at small distances (molecules repel each others strongly when they are very close) and an attractive tail which is responsible for condensation into liquids and formation of solids at low temperature.

In Sec. 2.5.3 we have qualitatively discussed the effects due to this interaction to the equation of state, the so-called van der Waals equation,

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - N\beta) = Nk_B T,\tag{7.1}$$



Figure 7.1: A schematic diagram for the interaction potential between two molecules.

where α and β are coefficients depending on the interaction potential. This empirical equation of van der Waals in fact provides a good description of a dense gas (recall that an ideal gas corresponds to dilute gas where interactions can be ignored) and it also predicts a phase transition from gas to liquid phase.

One of the tasks in statistical mechanics is to derive this van der Waals equation from, say, a canonical-ensemble approach. In canonical-ensemble approach, as discussed earlier, we first need to calculate the partition function of N molecules

$$Z_N = \sum_i e^{-\epsilon_i/k_B T},\tag{7.2}$$

As discussed before, the summation over microstate index i for N classical molecules corresponds to the integral in 6N-dimensional phase-space

$$\sum_{i} \dots \to \frac{1}{N!} \frac{1}{h^{3N}} \int d^3 r_1 d^3 p_1 \int d^3 r_2 d^3 p_2 \dots \int d^3 r_N d^3 p_N \dots$$
(7.3)

The factor 1/N! is due to the property of identical particles, as described earlier. The energy ϵ_i is then the classical Hamiltonian (total energy) of the N interacting molecules:

$$H = H(\underline{r}_1, \underline{r}_2; \underline{p}_1, \underline{p}_2, \ldots) = K + U;$$
(7.4)

$$K = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \dots + \frac{p_N^2}{2m} = \sum_{k=1}^N \frac{p_k^2}{2m},$$
(7.5)

$$U = V(|\underline{r}_1 - \underline{r}_2|) + V(|\underline{r}_1 - \underline{r}_3|) + \dots = \sum_{k < \ell} V(|\underline{r}_\ell - \underline{r}_k|),$$
(7.6)

where K is the total kinetic energy, U the total potential energy. Hence, the partition function of the gas is written as

$$Z_N = \frac{1}{N!} \frac{1}{h^{3N}} \int d^3 r_1 d^3 p_1 \int d^3 r_2 d^3 p_2 \cdots \int d^3 r_N d^3 p_N e^{-(K+U)/k_B T}.$$

We notice, contrast to the case of an ideal gas, the above multi-dimensional integral is <u>not separable</u> (you should understand what this means!) due the coupling terms in the potential U between molecular coordinates $\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N$. We note that the kinetic term K is still separable, hence the integrals over momenta $\underline{p}_1, \underline{p}_2, \ldots, \underline{p}_N$ can be factorized and computed one-by-one separately (you should understand what this means, and how this is done!).

The problem is the interaction part in the potential energy. Special techniques have been developed to evaluate this multi-dimensional integral. Broadly speaking, there are two sets of techniques:

- (i) Analytical methods, i.e. 'pen-and-pencil' calculations. For interacting systems, these can only be carried out in approximation, and ultimately, they result in equations which can only be dealt with numerically. One of such techniques is the so-called cluster-expansion for the factor e^{-U/k_BT} , or other series expansion techniques. Corrections to the ideal gas equation of state can then be evaluated.
- (ii) Monte Carlo simulations. We will discuss these in the next section.

7.2 Monte Carlo methods

Consider a system of N distinguishable spins (spin-1/2), s_i , i = 1, ..., N. Say these spins are arranged on a square lattice so that each spin has four nearest neighbours.

Each spin can be in one of two states, 'up', $s_i = 1$, or 'down', $s_i = -1$. In an external field B, and setting the magnetic moment of each spin to $\mu = 1$ for simplicity, the total energy of such a system is

$$H = -B\sum_{i} s_i \tag{7.7}$$

(you should understand why). We have here gone to a dimensionless representation, i.e. I ignore units.

Rea-world spin systems have interactions between the spins. The celebrated <u>Ising model</u> for example has the energy function

$$H(s_1, \dots, s_N) = -B \sum_{i} s_i - J \sum_{\langle i,j \rangle} s_i s_j,$$
(7.8)

where $\sum_{\langle i,j \rangle}$ indicates a sum of neares-neighbour pairs, (i, j). The quantity J > 0 is an interaction coefficient. The second term in this Hamiltonian makes neighbouring spins want to align, the energy contribution, $-Js_is_j$ of an aligned pair $(s_i \text{ and } s_j \text{ have the same sign, i.e.} s_is_j = 1)$ is lower than that of a pair which is not aligned $(s_i \text{ and } s_j \text{ have opposite signs, i.e.} s_is_j = -1)$.

This model describes ferromagnetic behaviour at low temperatures. It has a phase transition between a paramagnetic phase and a ferromagnetic phase, provided we are in at least two dimensions (i.e. square lattice, cubic lattice etc). There is no phase transition in the Ising model in one dimension (spins situated along a one-dimensional chain). The canonical partition function of this model is

The canonical partition function of this model is

$$Z(\beta) = \sum_{\{s_i\}} e^{-\beta H(s_1,\dots,s_N)},$$
(7.9)

keep in mind that this is a function of temperature (or equivalently of β). If the function $Z(\beta)$ is known explicitly all thermodynamic quantities can be derived (you should know how). The sum in Z is over all microstates. How many of these are there (you should know the answer)? Well, each spin can be in two states (up or down), and there are N spins, so there are 2^N terms in this sum.

Following issues:

• Due to the interaction we cannot do the sum analytically (pencil and paper).

• It is not feasible to compute this numerically either, there are just too many terms in the sum (keep in mind that N can be very large.

Monte-Carlo methods sample a representative subset of all 2^N configurations. This is known as <u>importance sampling</u>. A commonly used algorithm is the so-called <u>Metropolis algorithm</u>, which works roughly as follows:

- 1. Start from a random spin configuration, i.e. assign the $s_i = \pm 1$ randomly.
- 2. In each simulation step pick one specific spin at random, say spin number i is picked. Then compute the energy difference if this spin were to be flipped (i.e. if its sign is reversed), i.e.

$$\Delta E = H(s_1, \dots, s_{i-1}, -s_i, s_{i+1}, \dots, s_N) - H(s_1, \dots, s_{i-1}, s_i, s_{i+1}, \dots, s_N).$$
(7.10)

If $\Delta E < 0$ flip the spin, and go o 2, i.e. pick a new spin for potential flip, and repeat. If $\Delta E > 0$ flip the spin with probability

$$p = e^{-\beta \Delta E} \tag{7.11}$$

(and with probability 1 - p do not flip it). Then go o 2, i.e. pick a new spin and repeat.

This algorithm will produce a sequence of spin-configuations, and one can show that averaging over the spin configurations so obtained approximates the canonical average (over the 2^N terms in the partition function) very well. If the sequence of spin configurations is $\mathbf{s}(1), \mathbf{s}(2), \ldots, \mathbf{s}(t_{\text{final}})$, then for example

$$\langle E \rangle \approx \frac{1}{t_{\text{final}}} \sum_{t=1}^{t_{\text{final}}} H(\mathbf{s}).$$
 (7.12)

Good results are obtained without having to generate all 2^N possible configurations $\mathbf{s} = (s_1, \ldots, s_N)$. The 'importance sampling' of the algorithm makes sure that only the most relevant configurations are sampled.

There is a second-year Theory Computing Project which uses this technique to investigate the phase transition of the Ising model. Similar techniques are used in a variety of physics problems, including in particle physics, e.g. Monte-Carlo simulations of lattice gauge field theories (for example lattice QCD).

The Monte-Carlo method defines a stochastic process in the space of configurations. This involves stochastic dynamics (i.e. 'hopping' from one microstate to the next).

Some of these models with an actual <u>dynamics</u> are discussed in the fourth year module on Advanced Statistical Physics. See also the section on non-equilibrium systems below, Sec. 7.5.

7.3 Systems with variable particle numbers

So far, we have mostly looked at systems with a constant number of particles. In the microcanonical ensemble both energy and particle numbers are fixed. In the canonical ensemble energy can fluctuate (hence the Boltzmann factor, $e^{-\beta E}$), but particle numbers are fixed. The so-called grand canonical ensemble describes systems which can exchange of particles with the environment. A microstate *i* of the system is the characterised by its energy, E_i , and by the particle number, N_i in that microstate. The notion of the canonical partition function is extended to give the

Grand-canonical partition function:

$$\mathcal{Z}(\mu, T, V) = \sum_{i} e^{-\beta(E_i - \mu N_i)}, \qquad (7.13)$$

where μ is the chemical potential.

The corresponding statistics are given by the

Grand-canonical ensemble:

$$p_i = \frac{1}{\mathcal{Z}} e^{-\beta(E_i - \mu N_i)},\tag{7.14}$$

 p_i is the probability to find the system in microstate u, with energy E_i and particle number N_i .

The corresponding bridge equation is

$$\Phi_G = \langle E \rangle - TS - \mu \langle N \rangle = -\frac{1}{\beta} \ln \mathcal{Z}, \qquad (7.15)$$

where Φ_G is the so-called grand potential.

The grand canonical ensemble is crucial for the discussion of quantum gases. It will be covered in detail in the third-year module on Bose and Fermi gases.

7.4 Quantum systems

Most of the calculations in this course were classical calculations. Some of the few actual quantum calculations were carried out only in the large-temperature limit, where they effectively become classical. We have neglected the properties for example of Bosons occupying the same single-particle state (particularly the quantum ground m state) when we discussed the independent-particle approximation for identical particles. Such effects are important in the low temperature limit and inclusion of such quantum effects will result in the Bose-Einstein condensation. Electrons in conductors and other solid state systems are Fermions, and their statistical mechanics requires a full quantum approach.

The classical formalism we have covered is however somewhat analogous to the quantum case. For example, the classical Hamiltonian, $H(\underline{r}, \underline{p})$, is to be replaced by the quantum mechanical Hamilton operator, \widehat{H} , and the Gibbs entropy

$$S = -k_B \sum_{i} p_i \ln p_i, \tag{7.16}$$

is replaced by the von-Neumann entropy

$$S = -k_B \operatorname{tr}\left\{\hat{\rho} \ln \hat{\rho}\right\},\tag{7.17}$$

where $\hat{\rho}$ is the density operator describing the system at hand. This is formally an infinitedimensional matrix, tr describes its trace (sum of the diagonal elements). The quantum mechanical ensembles (microcanonical, canonical, grand canonical) can then be obtained by maximising the von Neumann entropy (7.17) subject to the appropriate constraints. This is again done using Lagrange multipliers.

These issues will be discussed in more detail in the third-year course on Bose and Fermi gases.

7.5 Non-equilibrium dynamics

All of what we have discussed is part of what is called <u>equilibrium statistical mechanics</u>. None of our calculations actually involve a <u>dynamics</u>. Instead what we do is to look at the distributions generated by energy functions (Hamiltonian), e.g. the canonical ensemble. Compare this to your first-year dynamics, where you study the trajectories of particles, i.e. their actual time behaviour, say x(t), derived from differential equations (Newton). These equations explicitly include time derivatives, which did not play any role in this course.

The starting point of all our calculations in the statistical physics part was the Hamiltonian $H_N(\underline{r}, \mathbf{p})$. But the mere existence of such an energy function is a severely limiting assumptions. For many systems in real life there is no energy function (or free energy), which is subject to some minimisation principle. Instead many real-world problems are defined <u>dynamically</u>, by a rule which characterises the time-behaviour of the system, say how to hop from one microstate to another. It is often not clear how to write down H from such rules, and more often than not, there is no Hamiltonian.

This is relevant in almost all transport problems where the system is driven, in many biological applications (life is mostly a non-equilibrium phenomenon).

The fourth year course on Advanced Statistical Physics focuses on non-equilibrium dynamics. It develops the mathematical formalism with which to characterise such off-equilibrium systems. As a taster I mention the so-called 'master equation'. Suppose the model is defined by rates (probabilities per unit time) to hop from one microstate to the next, $T_{i\to j}$. So $T_{i\to j}$ is the rate with which the system hops to state j if it is initially in state i.

The probability, $P_i(t)$ to find the system in state *i* at time *t* then obeys the following differential equation, the so-called master-equation

$$\partial_t P_i(t) = \underbrace{\sum_{j \neq i} T_{j \to i} P_j(t)}_{\text{inflow}} - \underbrace{\sum_{j \neq i} T_{i \to j} P_i(t)}_{\text{outflow}}.$$
(7.18)

Other techniques used to study such stochastic processes include stochastic differential equations, the Fokker-Planck equation (a Schrödinger equation in imaginary time), path integrals etc. Some of these will be discussed in the Advanced Statistical Physics module in 4th year.

7.6 Interdisciplinary applications of statistical physics: complex systems

The field of <u>statistical physics of complex systems</u> is a growing area of modern physics. It describes the application of tools from statistical physics to questions in adjacent disciplines, for example in biology, economics and the social sciences.

Many of the models in these disciplines effectively describe interacting individuals, subject to stochastic dynamical rules. The term individual can here refer to different things, depending on the specific application. In a model of traffic flow an individual may be an individual vehicle which moves forward along a road subject to certain rules. In a model of a stock market an invididual may be a trader, who in a most basic approach can be in one of two states (buy and sell). In biology an individual may represent an individual prey or predator in a model of population dynamics, or maybe a protein or a gene in evolutionary dynamics.

We study these topics in the Statististical Physics and Complex Systems group, see here for our web page:

http://theory.physics.manchester.ac.uk/~cssp/

Research questions we study include:

- The development of analytical techniques to study individual-based systems with stochastic interactions. We use tools and ideas from statistical physics to characterise such systems mathematically. This includes e.g. the theory of stochastic processes, stochastic differential equations, master equations, Fokker-Planck dynamics, path integrals and generating functionals, semi-classical WKB approaches, etc.
- The development of fast simulation algorithms for stochastic interacting agent models, e.g. kinetic Monte Carlo methods, the celebrated Gillespie algorithm, modified next-reaction schemes, Poissonian processes, etc.
- The application of these methods to specific problems, e.g.
 - evolutionary game theory
 - speciation dynamics in ecology
 - the spread of epidemics in populations
 - the dynamics of cancer initiation
 - models of opinion dynamics and voting
 - models of language evolution
 - chaotic dynamics in game learning and economics
 - pattern formation in stochastic systems
 - ...

Relevant third and fourth year modules include

1. PHYS 30471 (Introduction to nonlinear physics): mostly about the deterministic dynamics of complex systems.

- 2. PHYS 40571 (Advanced Statistical Physics, taught by myself from 2014): non-equilibrium statistical mechanics, stochastic dynamics of complex systems.
- 3. MPhys projects in this area in semester 7 and semester 8.

If you are interested in any of these topics, come to talk to us.