

6CCP3212 Statistical Mechanics

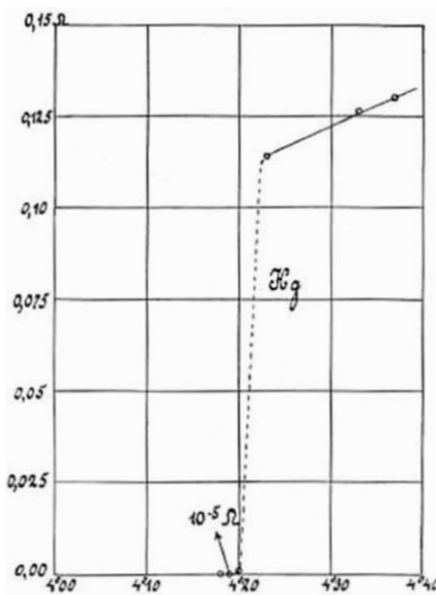
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Acknowledgments

As a statistical mechanical nincompoop, I have benefited from being able to learn from the many books and online lecture notes that exist, of which I have freely stolen and borrowed from for this set of lecture notes. In particular, I would like to thank David Tong for his excellent lecture notes that I have learned greatly from. Finally, I would like to thank Sophie for her patience and support.

Figure on the previous page shows the historic plot of the discovery of superconductivity, by Heike Kamerlingh Onnes in 1911. The figure shows the resistance (Ohms) vs temperature (K). At 4.2 K, there is a sudden drop in the resistance from 0.1 Ohms to 10^{-6} Ohms, a phase transition signaling the onset of superconductivity.

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What did we just sign you up for?

This is a 3rd year required course in statistical mechanics taught at the Department of Physics, King's College London. It is designed to be taught over a period of 10 weeks, for a total of 40 contact hours. I expect that we will not be able to cover the material presented in this lecture notes completely given the time – in this case I will assign some reading. Of course, if you can read ahead yourself, that's even better. This set of notes is not meant to be complete – I have provided some recommended textbooks to go along with it. Additional material will also appear on the class website from time to time.

Apart from the lectures themselves, and these notes, there will be 5 homework sets. Some of the homework problems will be alluded to in these lecture notes – you should absolutely do them as they will help you cover the gaps that inevitably exist. Like all physics courses, the key to mastery is to practice solving a lot of problems. So in addition to the homework sets, I will also provide some additional problems to help you along.

Finally, a confession: this is the first time I am teaching statistical mechanics. Actually, it's worse: I have never taken a statistical mechanics course in my life. So *caveat emptor*.

Recommended Books

* is highly recommended for this course.

Online resources will be posted on the class webpage.

- F. Reif, **Fundamentals of statistical and thermal physics.*, McGraw-Hill, 1965. This is a solid, rigorous book, and would make a good introductory standard text. It covers most of the basics very well, though due to its dated nature it falters when come to more advanced topics. Be careful when you use this though as it defines work as done *by* instead of *on* the system so there are a lot of minus sign differences when compared to these notes.
- F. Mandl, **Statistical Physics*, 2nd Ed., Wiley 1997. This is another intro level book which takes a more verbose approach to the basics, but does not go very deep. It is a good companion to Reif.
- D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press 1987. A good modern introduction, which covers most of the material of this lecture. It has a nice extended multi-chapter discussion on the basics of the Ising model without going too crazy with the math.
- L. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, 3rd Ed, Elsevier 1980. Ignore all the fear mongering about the “difficulty” of the Landau and Lifshitz 10-volume treatise of modern physics, this book is complete, clear and full of brilliant insight from one of the founders of modern statistical mechanics. It is aimed at a high level, but you will profit immeasurably even if you just dip into it.
- D. Goodstein, *States of Matter*, Dover 1985. This book is aimed at people who have already done a beginning statistical mechanics course, and would like to dig deeper into the more advanced topics. It is a very readable book for those who wanted to pursue some of the topics taught in this lecture further. Bonus : Goodstein is a good writer, albeit with a slightly warped sense of humour. (Solid-liquid transition is like pregnancy, really, David?)
- R. K. Pathria, *Statistical Mechanics*, Elsevier 1997. A PhD level book which covers the basics in detail with a very modern and excellent choice of advanced material. A good book to refer to if you want to investigate with further depth the topics taught in this module.
- D. Tong, **Lectures on Statistical Physics*, University of Cambridge Part II Mathematical Tripos [http : //www.damtp.cam.ac.uk/user/tong/statphys.html](http://www.damtp.cam.ac.uk/user/tong/statphys.html). Not a book, but might as well be. This is an excellent set of lecture notes (one of the many) by David Tong. It is aimed at 3rd year undergraduates, although at a slightly more mathematically inclined crowd.

Chapter 1

Introduction and Review of Classical Thermodynamics

..we must learn how to count the number of states it is possible for a system to have or, more precisely, how to avoid having to count that number.

D. Goodstein

1.1 The problem of counting

The universe is big. By that I don't mean in size (though it is quite large in size) – I mean it contains *a lot of things*. A small cup of tea contains about 5 moles of water, and that's 3×10^{24} molecules of water. The Earth has about 7.5×10^{18} grains of sand. Anfield stadium at Liverpool can hold 5.4×10^4 football fans. Our Milky Way galaxy contains about 3×10^{11} stars. This lecture room contains about 6×10^{27} molecules of air (O_2 , N_2 and CO_2). The permanent magnet that is on your refrigerator door contains 10^{18} little magnetic dipoles that arrange themselves to give you its collective magnetic property.

Each of these individual things obey some equation of motion – laws that tells them how to move or behave. Stars will move according to the Newton's law of motion, gas particles will move according to the laws of quantum mechanics, football fans will move depending on whether Liverpool is leading or losing, magnetic dipoles will flip depending on the presence of external magnetic fields governed by the Maxwell laws of electromagnetism etc. Of course, you have spent the last two years studying these laws (and perhaps a lifetime being a Liverpool football fan). We can perhaps solve the system when there are 2 or 3 things, but how on Earth are we suppose to solve a system of 10^{23} things?

We can try to use a computer. Scientists have tried to simulate the motion of the “entire universe”, in order to understand how the galaxies and stars come to be distributed around the cosmos the way they are today. These simulations employs a lot of CPUs, of the order 10^6 (another big number!). The record holder so far (2017) is the TianNu simulation, which simulated 3×10^9 particles with 3.3×10^6 CPUs for 52 hours. Not even close to getting the behaviour of your cup of tea correct.

Obviously, we do know a lot about how the universe actually works. We know that to make a good cup of tea, you need to boil water so that it is hot, and then dunk your favourite tea bag in. We know that we need to jiggle the tea bag, so that the flavour can diffuse into the water. Not only that, we can

calculate these processes – we know exactly how long the kettle takes to boil if we know how much heat we are adding to it. We can calculate how quickly the tea will diffuse into the water.

In words, we mostly understand how the **macroscopic** physics of the world works. We don't care about how each molecule in the cup of water behaves, all we need is its temperature. So instead of trying to solve the impossible 10^N particle system, we can write down *macroscopic* laws – the Laws of Thermodynamics is the canonical example of such a set of laws, for example, although not the only one.

Nevertheless, there are physical processes that defy our ability to attack it with macroscopic methods. Sometimes, the microphysics actually matter. For example, you are told to make sure your water is boiling before dunking your teabag in. How does water boil? *Why* does water boil? So, we are back to the problem of trying to count these things. This is where statistical mechanics come in.

Statistical mechanics is the branch of physics of which we try to explain the macrophysics of a system with many things from its fundamental microphysics, without actually trying to solve the entire system of equations describing all the particles. But more than that, it is a study of how, when we put *a lot* of things together, interesting physics that are not manifestly “fundamental” can appear. Famously, we can derive the Laws of Thermodynamics by considering 10^{23} particles, not by considering 3 particles¹. The history of the development of physics is rife with examples where deeper insight is gained when considering a phenomena from both its microphysics, its macrophysics *and* the interplay between them.

The goal of this course is to teach you the basic principles of statistical mechanics. We will then use this new knowledge to dip our toes into some more advanced topics, at least in an introductory and not-so-crazy-deep way, to give you a sense of the wide applications of statistical mechanical techniques. Hopefully this will provide you with a base to explore further.

1.2 The Laws of Thermodynamics

In the days of yore, when people do not quite understand the microscopic structure of matter, they did a bunch of experiments and came up with all sorts of definitions to figure out how matter behave. Furthermore, their experiments are blunt – they can only measure macroscopic quantities such as pressure P , volume V , work W etc. Despite these difficulties, remarkably they managed to come up with the correct laws that govern matter given these quantities, and these laws are known as the **Laws of Thermodynamics**.

To specify these laws, we first introduce the idea of the **thermodynamical state**. A state is simply a set of variables that completely describe the condition of the system. For example, the state of a particle can be described by its position x and momentum p . We cannot of course describe a system by specifying all the positions and momenta of all particles as we have discussed earlier, but we can still assign some macroscopic variables to it. The simplest way of describing a thermodynamical state is to specify its pressure P and volume V – these are known as **state variables**, and the space of all possible (P, V) is called the **state space**.

Of course, a thermodynamical system can have more than 2 state variables, for example the **temperature** T , **number of particles** N , its **entropy** S (of which we will have plenty to say later) etc. An important point, which is still not obvious, is that the state variables are *not* independent variables. Think of the state variables as coordinates and the state space as the space where these coordinates span. The number of independent variables define the **dimensions** of the state space. Like regular coordinates (x, y) , we can perform a change of coordinates to (x', y') in any way we like. As we will see below, P , V and T are not independent variables in general.

Furthermore, we also need a couple of definitions, which you might be familiar with. The first definition comes from the idea of that we can insulate a system from all external influences so that no

¹Sometimes, such “macro” from “micro” concepts are called by the sexy moniker **emergent**.

energy or particles are exchanged between the system and the rest of the universe. The special insulator that achieves this is called an **adiabatic wall**, and a system which is enclosed in adiabatic walls is called an **isolated system**. Two systems separated by adiabatic walls will not interact with each other. Conversely, if two systems are allowed to remain in **thermal contact** and hence exchange thermal energy but *not* exchange particles, they are said to be separated by **diathermal walls**. Systems which can exchange thermal energy and do work but not exchange particles with the environment are called **closed systems**. If they can exchange particles, then the systems are **opened**².

The second definition is that of **equilibrium** – *an isolated system left alone for some (usually long) time will relax to a state where there is no macroscopic changes*. This end state is called the **equilibrium state**. Unlike the first definition which are statements about the engineering of walls, this idea is actually a conjecture – why would a system want to evolve into its equilibrium state? Indeed, this is a puzzle of which the study of statistical mechanics sought to shed light on, so we will come back to this later. For now, we take this as a given (as you have been taught for many years).

Finally, before we continue, we can define the idea of **functions of state**, or **state functions**. Functions of state are any mathematical relations which relate the state variables of a system in thermodynamic equilibrium³.

Given these, we can state the laws.

1.2.1 Zeroth Law and the equation of state

The Zeroth Law states that if systems A and B are in equilibrium with system C, then they are also in equilibrium with each other.

Now you might have learned in your Thermal Physics course that this implies that the temperatures for A and B are equal with the temperature for C. While this is true, it seems like a tautology: isn't the being in equilibrium means that your temperatures are the same? Actually it is not: notice that we have specified the Zeroth law *without* specifying the notion of temperature – in fact it is the zeroth law that allows us to define a notion of temperature.

To see this, let's consider systems which can be described by their state variables pressure P and V . As we discussed earlier, in general a system can be described by more than 2 such state variables but let's keep things simple for now. Consider systems A and C in thermodynamic equilibrium. This means that their thermodynamic variables P_A , P_C , V_A , and V_C must be related in some way, so this means there must exist some function

$$F_{AC}(P_A, V_A; P_C, V_C) = 0. \quad (1.1)$$

Equation Eq. (1.1) is a **functions of state**. Note that it is a *constraints* – it tells us that only three of the four possible thermodynamic quantities are free. Why are we allowed to write down such a function? We use the notion of equilibrium we described above, i.e. the state does not change with time, so $dF_{AC}/dt = 0$, and hence $F_{AC} = \text{const}$, and we can set the constant to zero WLOG. We further assume that we can solve Eq. (1.1) to obtain V_C as a function of P_A , V_A and P_C , i.e.

$$V_C = f_{AC}(P_A, V_A; P_C). \quad (1.2)$$

Similarly since systems B and C are also in equilibrium, we can find a similar relation

$$V_C = f_{BC}(P_B, V_B; P_C), \quad (1.3)$$

²Note that sometimes people say “closed” when they really mean “isolated” – and this include an older version of these notes! To get ahead of ourselves, entropy of a closed system *can* decrease but that of isolated systems cannot.

³At the risk of getting ahead of ourselves, as a well known example, you recall that an ideal gas in equilibrium can be described by the **equation of state** $PV = Nk_bT$, where k_b is the Boltzmann constant. This is a function of state.

which implies that

$$f_{AC}(P_A, V_A; P_C) - f_{BC}(P_B, V_B; P_C) = 0. \quad (1.4)$$

But now, invoking the zeroth law, A and B is also in equilibrium, so there must exist an equivalent function of state

$$F_{AB}(P_A, V_A; P_B, V_B) = 0. \quad (1.5)$$

Since Eq. (1.4) must be the same as Eq. (1.5), it means that P_C in the former must appear in such a way that it cancels. In other words there must exist some quantity which is *common* to both system A and B such that $f_{AC} \leftrightarrow T_A$ and $f_{BC} \leftrightarrow T_B$, i.e.

$$f_{AC}(P_A, V_A) - f_{BC}(P_B, V_B) = 0 \Rightarrow T_A(P_A, V_A) = T_B(P_B, V_B). \quad (1.6)$$

This quantity T , as you all must have guessed, is the temperature, and the equation which relates the thermodynamic quantities P and V (and possibly other quantities) to temperature $T = T(P, V)$ is called an **equation of state**. As an example, you have met the equation of state of an ideal gas

$$T = \frac{PV}{Nk_b} \quad (1.7)$$

where N is the number of particles and $k_b = 1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ is the Boltzmann constant. Note that since the equation of state relate the temperature T to the state variables P , V , N and possibly others, we can use it to replace a state one of the state variable with T . In other words, for an ideal gas P , V , T and N are not independent variables but is related by the equation of state Eq. (1.7) as we discussed earlier.

Having said all that, we will come back when we discuss statistical mechanics proper and show you a much more remarkable definition of temperature.

1.2.2 1st Law of Thermodynamics

The first law of thermodynamics is nothing but a statement on the principle of conservation of energy. Consider an *isolated* system A , then if we do **work** W on it, then its **internal energy** (or simply just the energy) E will change by

$$\Delta E = W. \quad (1.8)$$

Notice that the change in internal energy E is independent of what kind of work done to the system (you can stir it, compress it with a piston etc). Similarly, how the system “accommodate” this additional energy is not specified – it could be that the particles move faster, or they vibrate more vigorously if they are di-atomic etc. In any case, the state of the system will change. Hence, one can imagine the existence of a function of state for energy, $E(P, V)$.

Suppose now that the system is not isolated, this means that not all the work done affects the internal energy, but “leaks” in or out, then we can write

$$\Delta E = W + Q \quad (1.9)$$

where Q is called **heat**. When $Q = 0$, the process is **adiabatic**. Note that despite the temptation, it is *incorrect* to write

$$E = W + Q \text{ Wrong!} \quad (1.10)$$

This is wrong because while $E(P, V)$ is a function of state (i.e. E depends on the state of the system), neither W nor Q are functions of state, i.e. you can’t write them as $W(P, V)$ nor $Q(P, V)$. The reason is obvious when you think a bit more about it : W is work done on the system, and Q is the energy that

got transferred in or out of the system via its diathermal walls, neither which has anything to do with the actual state of the system.

At this point, we should now kill a pernicious misconception that is taught in high school that seems to pervade into college: heat is *not* a form of energy, but *a form of energy transfer*. Indeed, both work and heat are different forms of energy transfer. Work usually refers to energy transfer through observable macroscopic degrees of freedom – piston moving, stirring with a spoon, magnetic work done by turning on an external magnetic field etc. Heat, on the other hand, refers to energy transfer through microscopic degrees of freedom (the kinetic energy or vibrational individual particles). This is the “word” version of why equations like $E = W + Q$ is wrong – we cannot subdivide up the internal energy E into “heat” energy and “work” energy.

However, since heat and work are energy transfers, it makes sense to think of them as *infinitesimal* changes to the internal energy. We can then rewrite Eq. (1.9) in differential form known as the **1st Law of Thermodynamics**,

$$\boxed{dE = \delta Q + \delta W} \quad (1.11)$$

where we have written the differentials δQ and δW instead of dQ and dW to emphasise the fact that Q and W are not functions of state, and hence not expressible as $Q(P, V)$ or $W(P, V)$. Such differentials are called **inexact differentials**.

Exact vs Inexact Differentials

Consider a differential dF ,

$$dF = A(x, y, z)dx + B(x, y, z)dy + C(x, y, z)dz. \quad (1.12)$$

If furthermore, there exists some scalar $F(x, y, z)$ such that

$$A(x, y, z) = \left(\frac{\partial F}{\partial x}\right)_{y,z}, \quad B(x, y, z) = \left(\frac{\partial F}{\partial y}\right)_{x,z}, \quad C(x, y, z) = \left(\frac{\partial F}{\partial z}\right)_{x,y}, \quad (1.13)$$

then we say that dF is an **exact differential**. The implication is that the differential dF can be integrated to obtain a value $\int_{\mathbf{x}_1}^{\mathbf{x}_0} dF = F(x_0, y_0, z_0) - F(x_1, y_1, z_1)$. In other words, the integral *only depends on the beginning and end point of the boundaries* and do not depend on *paths*. For example, consider the exact differential $dF = xdy + ydx$, then $\int_{x_1, y_1}^{x_0, y_0} dF = x_0y_0 - x_1y_1$ where $F(x, y) = xy$. It then simply follows that the loop integral of an exact differential is always identically zero

$$\oint dF = 0. \quad (1.14)$$

On the other hand, if there exists no scalar function $F(x, y, z)$, then the differential Eq. (1.12) is called **inexact**. Inexact integrals depend on the *paths* of the integration. In the context of classical thermodynamics, if dF is exact then F is a function of state, otherwise F is not.

Since dE is an exact differential, we can express it as

$$dE = \left(\frac{\partial E}{\partial P}\right)_V dP + \left(\frac{\partial E}{\partial V}\right)_P dV, \quad (1.15)$$

which is a trivial consequence of the fact that $E(P, V)$ is a function of state. Integrating this equation between two states (P_1, V_1) and (P_0, V_0) gives us the total internal energy change $E(P_1, V_1) - E(P_0, V_0)$, which is independent of paths.

Let's now consider the inexact differential dW , where you have learned from your thermal physics course can be given by

$$dW = -PdV \quad (1.16)$$

where P is the pressure and dV is the infinitesimal volume change⁴. Since P, V are our state variables, it's clear that we cannot find a scalar function $W(P, V)$ such that $dW = -PdV$ (you can try). There is a negative sign because we have defined dW to be work done *on* the system, so if a positive change in V means that system has expanded and done work on the environment. We can still integrate this of course, but the integral will now depends on the path of the process (Fig. 1.1).

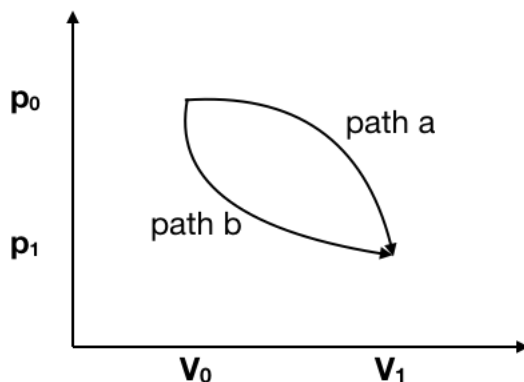


Figure 1.1: The work done ΔW between two states (P_0, V_0) and (P_1, V_1) is dependent on the path.

Indeed, if we make a loop, say flip the direction of the arrows of path a or b in Fig. 1.1, then the *loop integral*

$$\oint dW = - \oint PdV \neq 0, \quad (1.17)$$

a calculation of which you have done many times in your thermal physics course, e.g. if the loop is clockwise, then the system converts heat to work and is an **engine**.

1.2.3 2nd Law of Thermodynamics

Since the 1st Law is just a statement on the conservation of energy, it does not tell us *how* a state will evolve. A system in equilibrium will remain so if we leave it alone, but it will not remain in equilibrium if we do something to do it – we can do work on it, apply heat to it, remove adiabatic walls etc. If we are gentle and careful however, we can change the state of the system slowly, making sure that while the state is changing (e.g. its P and V is changing with time), it remains in equilibrium. Hence the state travels around its state space, remaining in equilibrium at every point – such a process is called **reversible**. As its name implies, it means that we can happily (and gently) reverse the process, going back to its original state.

On the other hand, in general, changing the state of a system will move it far away from equilibrium. Once this occurs, we cannot undo this process – such processes are called **irreversible**. Of course, such a definition seems like tautology: “irreversible processes are those that are not reversible” doesn't really explain any physics. To truly understand this, we would need to understand how states evolve from non-equilibrium towards equilibrium – we will discuss this when we have the tools of statistical mechanics.

For now, let's consider a hand-wavy argument. Consider a thermally isolated system, with two compartments V_1 and V_2 separated by a physical adiabatic partition in the middle which can be opened

⁴Be warned that the sign convention we have used is not universal! Some references uses $dW = PdV$, so W defines work is done *by* the system.

or closed (see Fig. 1.2). Compartment V_1 is initially filled with an ideal gas at temperature T and pressure P , while compartment V_2 is empty. Now we play a game : without explicitly tracking the motion of each particle, we are asked to guess which compartment all the particles are, and we get a point for each correct answer. Of course, initially, we will ace the game: all the particles are in container V_1 and we get full marks. However, if we then open up the adiabatic partition between the two compartments, the gas will now expand and fill up both compartments. The gas then fills up the entire container and hence is changing, but as we noted earlier, it will evolve towards equilibrium after some time. Playing the same game again, it is clear the game is now harder, since for each particle, we have roughly a 50% chance of getting the answer correct. In other words, our *knowledge of where the individual particles have decreased*. This decrease in our knowledge, or equivalently, the *increase in the disorder*, means that we cannot reconstruct *for free* the original state since we have “forgotten” some information. Such a process is hence irreversible. Of course, this does not mean that we can no longer go back to the original state, to do that we have to painstakingly hunt down each particle and move them physically back to V_1 – i.e. doing work⁵.

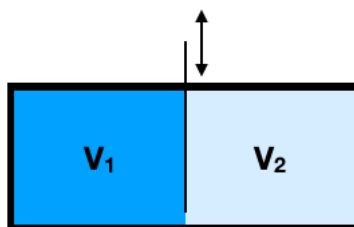


Figure 1.2: A thermally isolated container with two compartments, separated by an adiabatic wall which can be opened or closed.

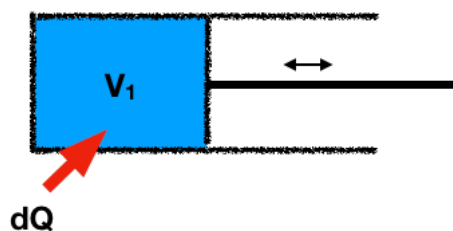


Figure 1.3: A gas inside a piston is allowed to expand as we add heat dQ to it such that it is reversible.

We can quantify this loss of knowledge, or increase in the disorder, with a quantity S , called **entropy**. In an isolated system as shown in Fig. 1.2, this implies that

$$\boxed{\Delta S \geq 0 \text{ for thermally isolated systems.}} \quad (1.18)$$

On the other hand, consider a system which is *not isolated* and undergoes a reversible infinitesimal process which it absorbs some quantity of heat dQ . For example, a gas inside a piston expands by dV via the transfer of an infinitesimal quantity of heat dQ (see Fig. 1.3), keeping the temperature T fixed. We then *define* the infinitesimal change in entropy

$$\boxed{dS = \frac{dQ}{T} \text{ for reversible processes.}} \quad (1.19)$$

⁵You might ask: how do we regain knowledge by doing work? As it turns out, there is a very deep connection between *information* and *work* – it can be shown that possession of a bit of information can be converted into work via the **Szilard’s Engine**. We won’t discuss this, but it is well worth checking it out yourself.

Combined, the pair of equations Eq. (1.18) and Eq. (1.19) is the **2nd Law of Thermodynamics**. Notice that in Eq. (1.19), we have written dS instead of δS – in other words, $dS = \delta Q/T$ is an exact differential. This means that the entropy S is a function of state – a much more useful thing. But wait! How do you prove that this is true? As it turns out, in “pure” classical thermodynamics, there is no satisfactory answer. However, in statistical mechanics, there is a very clear answer – we will learn that we have gotten the whole definition the wrong way round as Eq. (1.19) is not a definition of S but instead can be thought of as a definition of T in a reversible system. Entropy S is *defined* to be

$$S \equiv k_b \ln \Omega(E, V, N, \dots) \quad (1.20)$$

where Ω is called the **statistical weight** of the system and is a function of all the independent state variables of the system, and hence S is a function of state. Anyhow, we have gotten ahead of ourselves, and this will be clear when we tackle statistical mechanics proper in the next chapter.

Since S is a function of state and hence its integral only depends on the boundaries, then its loop integral vanishes identically viz.

$$\oint dS = \oint \frac{\delta Q}{T} = 0 \text{ for reversible processes.} \quad (1.21)$$

Eq. (1.21) is known as the **Clausius Equality**. As you will be asked to show in a Homework problem, the Carnot cycle which you have studied in great detail in your Thermal Physics course obeys this equality as it is a reversible cycle.

What is the relationship between δQ and dS in the case of *irreversible* processes? Consider a non-isolated system undergoing some process where we inject some quantity of heat δQ at some temperature T , evolving in time t . If the process is reversible, then the following holds according to Eq. (1.19)

$$\frac{\delta Q}{dt} = T \frac{dS}{dt}. \quad (1.22)$$

However, if the process is irreversible, then according to Eq. (1.18), its entropy can only increase regardless of whether we inject any heat or not, and hence for a general process

$$\frac{\delta Q}{dt} < T \frac{dS}{dt}, \quad (1.23)$$

Combining this result with Eq. (1.21), leads to the **Clausius Inequality**, which states that cyclic processes (both reversible and irreversible) obey the following

$$\oint \frac{\delta Q}{T} \leq 0, \quad (1.24)$$

or, using the 1st Law Eq. (1.11)

$$\frac{dE}{dt} + P \frac{dV}{dt} \leq T \frac{dS}{dt} \quad (1.25)$$

where the equality holds only for reversible processes.

1.3 Thermodynamic potentials

1.3.1 Free energies and thermodynamic potentials

Since dS is an exact differential, we can combine the 2nd law with the 1st law to get the so called **fundamental equation of thermodynamics** for systems with fixed number of particles

$$\boxed{dE = TdS - PdV}. \quad (1.26)$$

Fancy name aside, Eq. (1.26) tells us that since dE is a total differential as are dS and dV , this means that the function of state for internal energy E can be expressed with the state variables S and V , i.e. $E(S, V)$. Taking the differential, we get

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV, \quad (1.27)$$

where

$$\left(\frac{\partial E}{\partial S}\right)_V \equiv T \quad (1.28)$$

and

$$\left(\frac{\partial E}{\partial V}\right)_S \equiv -P. \quad (1.29)$$

Harking back to Section 1.2.2 and Eq. (1.15), we have written that $E(P, V)$, i.e. the state variables are P and V . This is a common theme in thermodynamics: we can express functions of states in equivalent sets of state variables. Combining this with the temperature T , we then have a set of four variables which seems to come in pairs (T, S) and (P, V) . Of these four, S and V depends directly on the size of the system and are said to be **extensive** variables while T and P are independent of system size, and called **intensive** variables. Such pairs of variables are called **conjugate variables**. We will discuss these variables in detail in the coming section 1.5, but let's carry on for now.

In general, we have the freedom to choose which pair of variables as our state variables to describe our energy, or any other functions of state. If the choice allows us to fully determine all the other variables, then they are called a **proper independent** pair. For example, if we choose $E(S, V)$ then, we can compute $T(S, V)$ and $P(S, V)$ from Eq. (1.28) and Eq. (1.29) respectively, and if we want S we can invert $T(V, S)$. We emphasise that proper independence depends on the functions of state we are using.

Hence, if we want to know all the thermodynamics properties of a system, all we need to do is to find the functional form of $E(S, V)$ for any system. However, this is a problem: while we can easily measure quantities like T , P and V , the quantities E and S are much harder or even impossible to measure. Thus, it would be convenient if we can find some other forms of “energies” measure whose proper independent variables can be easily measured. As it turns out, there are actually quite a few of them.

- The first is the **Helmholtz Free Energy**, F , defined as

$$\boxed{F \equiv E - TS}. \quad (1.30)$$

Taking the differential, we have

$$dF = dE - TdS - SdT = -SdT - PdV \quad (1.31)$$

where we have used Eq. (1.26), which implies that $F(T, V)$, and⁶

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \quad (1.32)$$

The Helmholtz Free Energy has the nice property that at fixed temperature, $\Delta F_T = -P\Delta V_T$, i.e. changes to it is just the work done. In other words, the Helmholtz free energy measures the capacity for the system to do work at fixed temperature – the “free” should be read as “available”. It is also directly related to a very fundamental statistical mechanical property called the partition function, of which we will meet in due time.

⁶Mathematically, $F(T, V)$ is a Legendre Transform of $E(S, V)$.

- Next, we have the **Gibbs Free Energy**, Φ , defined as

$$\boxed{\Phi \equiv E - TS + PV}. \quad (1.33)$$

Again, taking differentials and combining with Eq. (1.26), we get

$$d\Phi = -SdT + VdP \quad (1.34)$$

which implies that $\Phi(T, P)$ and

$$S = - \left(\frac{\partial \Phi}{\partial T} \right)_P, \quad V = \left(\frac{\partial \Phi}{\partial P} \right)_T \quad (1.35)$$

Since Φ is a function of just the intensive variables T and P , it is most useful when the size of the system is not important.

- Finally, we have the **enthalpy**, defined as

$$\boxed{H \equiv E + PV}. \quad (1.36)$$

As usual, taking differentials and combining with Eq. (1.26) we get

$$dH = TdS + VdP \quad (1.37)$$

which implies $H(S, P)$ and

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S. \quad (1.38)$$

The main utility of H occurs in processes under constant pressure, in which

$$\Delta H_P = T\Delta S = \Delta Q \quad (1.39)$$

i.e. the change in the enthalpy is exactly equal to the heat transfer. The enthalpy H measures roughly the total internal energy plus the work required to make space for it. It is an extremely useful quantity for engineers.

Finally, we should emphasise that these potentials (including E) describe the potentials of all the particles of the system *minus* any “bulk” kinetic energy resulting from “bulk” motion, plus the interaction energies between the particles. Thus, for example, the E of two identical boxes of gas, with one of them on a moving train, and the other sitting in a room, is equal.

Free energy and equilibrium

Sometimes the above energy functions of state are known as **thermodynamic potentials** – they measure in some ways the capacity of the system to change – be it do work, absorb heat etc. For any isolated system, the ultimate arbiter of whether the system can change is the 2nd law of thermodynamics – a system that is not in equilibrium will try to move towards equilibrium (as we asserted). Conversely, an isolated system already in equilibrium will no longer undergo any change⁷. Let’s see what this means to the free energies.

Using the 2nd law expressed by Eq. (1.23), $dQ/dt < TdS/dt$ and the 1st law $dE = dQ - PdV$, we find

$$\frac{dE}{dt} + P \frac{dV}{dt} < T \frac{dS}{dt}. \quad (1.40)$$

⁷Unless you wait for a really, really, really long time – see section 2.2.5.

Now consider a system at constant temperature and constant volume – for example a gas in a box with diathermal walls kept at fixed temperature and fixed volume, then $dT = 0$ and after a bit of algebra we can write this as

$$\frac{d(E - TS)}{dt} = \frac{dF}{dt} < 0. \quad (1.41)$$

In other words, left to its own, *just as the system wants to evolve towards a state of higher entropy, it also wants to evolve towards a state of lower F* . Eventually, once the state reaches equilibrium, S is maximum, and

$$\boxed{F = \text{minimum at equilibrium}}. \quad (1.42)$$

You will show in a homework set that, for processes at constant pressure and constant temperature, the Gibbs free energy evolves as

$$\frac{d\Phi}{dt} < 0, \quad (1.43)$$

so at equilibrium $\Phi = \text{minimum}$.

1.3.2 The Maxwell Relations

Given these energy functions of state, we can derive a set of identities between partial derivatives of the state variables with each other as follows;

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T} \left(-\left(\frac{\partial F}{\partial V}\right)_T\right)_V = \frac{\partial}{\partial V} \left(-\left(\frac{\partial F}{\partial T}\right)_V\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \quad (1.44)$$

where in the first and third equalities we have used Eq. (1.32), while the second equality is a consequence that partials commute.

The other 3 energy functions of state also give you a similar relationship. Using the differential for the internal energy dE , Eq. (1.28) and Eq. (1.29), we have

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial}{\partial V} \left(\left(\frac{\partial E}{\partial S}\right)_V\right)_S = \frac{\partial}{\partial S} \left(\left(\frac{\partial E}{\partial V}\right)_S\right)_V = -\left(\frac{\partial P}{\partial S}\right)_V, \quad (1.45)$$

while from Eq. (1.35) we get

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(-\left(\frac{\partial \Phi}{\partial T}\right)_P\right)_T = \frac{\partial}{\partial T} \left(-\left(\frac{\partial \Phi}{\partial P}\right)_T\right)_P = -\left(\frac{\partial V}{\partial T}\right)_P \quad (1.46)$$

and from Eq. (1.38) we get

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial}{\partial S} \left(\left(\frac{\partial H}{\partial P}\right)_S\right)_P = \frac{\partial}{\partial P} \left(\left(\frac{\partial H}{\partial S}\right)_P\right)_S = \left(\frac{\partial T}{\partial P}\right)_S. \quad (1.47)$$

These relations Eq. (1.44), Eq. (1.45), Eq. (1.46), Eq. (1.47) are called **Maxwell Relations**, and *they hold for all systems* as they are mathematical identities. They are very useful as they allow us to interchange things that we find hard to measure (e.g. entropy) with things we can easily measured like pressure or temperature. You should memorize them, although they are not that hard to memorize – if you multiply the top right term with the bottom left term and vice versa, you will get TS and PV , so the only thing you need to remember are the signs.

1.3.3 Heat capacity and specific heat

In your thermal physics course, you were taught that when you transfer a quantity of heat dQ into or out of a system, the change in its temperature T , while keeping all the other variables such as P or V fixed, is controlled by its **heat capacity** C . For example, the heat capacity at fixed volume is

$$C_V \equiv \left(\frac{dQ}{dT}\right)_V \quad (1.48)$$

of which you can define the more common “specific heat per mass m ”

$$c_V = \frac{1}{m} C_V. \quad (1.49)$$

Now since we have fixed V , from the first law $dE = dQ$, and Eq. (1.48) becomes

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \quad (1.50)$$

Notice that we can change the total to partial derivatives $(dE/dT)_V \rightarrow (\partial E/\partial T)_V$ because we have fixed V so the only free variable is T . Now $E(S, V) = E(S(T, V), V)$, i.e. we execute a “coordinate transform” from $E(S, V)$ to $E(T, V)$, Eq. (1.50) then becomes

$$\left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\partial E}{\partial S} \right)_V \left(\frac{\partial S}{\partial T} \right)_V \quad (1.51)$$

or

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (1.52)$$

using Eq. (1.28). This is a remarkable result: the heat capacity is really the measure of the change in the entropy of the system as temperature changes, for a fixed volume. Indeed, this result can be generalized: the heat capacity for *fixed pressure* is

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P. \quad (1.53)$$

You will show in a Homework problem that this is equivalent to

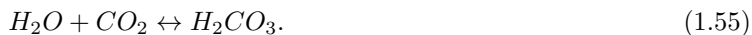
$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (1.54)$$

where H is the enthalpy.

As you will have learned from doing many problems in your thermal physics class, the heat capacity is a very useful quantity – it is easily measured with experiments. To measure C_V , simply heat up a system under fixed volume, and measure the temperature increase (and similarly for C_P). Furthermore, it allows us a direct measure into the entropy via Eq. (1.52) and Eq. (1.53) – and as we will see, this is a much more interesting and powerful quantity than dQ (other than the fact that S is a function of state, and dQ is not).

1.4 The chemical potential

In our discussion so far, we have assumed that the system has fixed number of identical particles, so N is constant. In general, the number and the species of particles are free to vary – for example a jar of carbonic acid will contain three species of particles H_2O , CO_2 and H_2CO_3 in equilibrium



Each of the species of molecules possess their own kinetic energies, and the own internal degrees of vibrational energies contribution to the internal energy. Furthermore, the interactions between these particles also contribute to the internal energy. Let i labels the species of particle, and N_i be the number of particles of species i . We also define the **chemical potential** μ_i to be the change in the internal energy to create (or destroy) a single particle of species i at fixed S and V , i.e.

$$\mu_i \equiv \left(\frac{\partial E}{\partial N_i} \right)_{S,V}. \quad (1.56)$$

The key subtle point here is *at fixed S*. If μ is positive, then adding a particle will increase E according to the first law. However, increasing E means that the *system as a whole will have more possibilities* and hence the entropy in general will also increase. So counter-intuitively, μ is often negative unless there are restrictions on how the additional energy is shared among other particles.

Given this additional pair of conjugate variables (μ, N) , the first law of thermodynamics is modified to become (remember that the first law is just an expression of conservation of energy)

$$dE = \delta Q + \delta W + \sum_i \mu_i dN_i . \quad (1.57)$$

This modification to the internal energy E means that the fundamental law of thermodynamics Eq. (1.26) becomes

$$\boxed{dE = TdS - PdV + \sum_i \mu_i dN_i} . \quad (1.58)$$

As should be clear, N_i are state variables, so the internal energy $E = E(S, V, N_i)$ now depends on a larger state space, whose dimensionality is now $2 + k$ where k is the number of new particle species. We can then go through the same derivation for energy functions of state in section 1.3.1 to obtain the following new definitions

$$dF = -SdT - PdV + \sum_i \mu_i dN_i \quad (1.59)$$

for the Helmholtz free energy and

$$d\Phi = -SdT + VdP + \sum_i \mu_i dN_i \quad (1.60)$$

for the Gibbs free energy and

$$dH = TdS + VdP + \sum_i \mu_i dN_i \quad (1.61)$$

for the enthalpy. This means that μ_i can be computed from

$$\mu_i = \left(\frac{\partial F}{\partial N_i} \right)_{T, V, N_{j \neq i}} = \left(\frac{\partial \Phi}{\partial N_i} \right)_{T, P, N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i} \right)_{S, P, N_{j \neq i}} . \quad (1.62)$$

Since μ_i does not depend on the size of the system, it is an intensive variable, but clearly N_i is extensive. They are conjugate to each other.

Finally, since we have a new set of conjugate variables μ_i and N_i , we can define a new energy function of state,

$$\boxed{\Psi \equiv F - \sum_i \mu_i N_i} \quad (1.63)$$

such that

$$d\Psi = -SdT - PdV - \sum_i N_i d\mu_i . \quad (1.64)$$

This new energy function of state Ψ is called the **grand canonical potential** or **Landau potential**. Why such a “grand” name will be discussed when we discuss statistical mechanics proper.

1.5 Intensive/extensive variables and conjugacy

In section 1.3.1, we mentioned that (T, S) , (P, V) and (μ, N) are conjugate pairs of variables, with the first of each pair an **intensive** variable and the second an **extensive** variable. It is worthwhile to dig a bit deeper into the concept.

You might have noticed from the fundamental equation of thermodynamic, Eq. (1.58),

$$dE = TdS - PdV + \mu dN , \quad (1.65)$$

that the conjugate variables appear in pairs. The RHS has the structure, for a conjugate pair (X, Y)

$$\underbrace{X}_{\text{intensive action}} \times \underbrace{dY}_{\text{extensive change}} . \quad (1.66)$$

So pressure P drives a change in the volume V , temperature T drives a change in the entropy S and the chemical potential μ drives a change in the particle number N . In this vein, one can think of μ as a “generalized” force, causing a change in the extensive quantity N . They are *conjugate* to each other because they are intimately tied to each other as “cause” and “effect”. This is why we often see the conjugate variables appearing in pairs.

How does the system change extensively? If we double the system (think of it as taking two copies of the system and putting them together side by side), then the volume $V + V = 2V$. Likewise, N is also an extensive quantity and clearly $N + N = 2N$. The less obvious one is entropy, we will show later in section 2.2 that it is also an additive quantity $S + S = 2S$. On other hand, doubling a system would not change T , P and μ . Hence if we rescale

$$V \rightarrow aV , N \rightarrow aN , S \rightarrow aS , \quad (1.67)$$

where $a > 0$ is some real number and plugging this into Eq. (1.65), we see that $E \rightarrow aE$. In other words, *energy scales linearly with size*, and hence is also an extensive quantity – consistent with our assertion about the extensiveness of entropy. From Eq. (1.65), we see that E is an exact differential of the extensive variables $E(S, V, N)$ so we can express the above argument as

$$E(aS, aV, aN) = aE(S, V, N) . \quad (1.68)$$

Using Eq. (1.58) and taking the total derivatives of the LHS, we get

$$\begin{aligned} dE(aS, aV, aN) &= Td(aS) - Pd(aV) + \mu d(aN) \\ &= a(TdS - PdV + \mu dN) + (TS - PV + \mu N)da \end{aligned} \quad (1.69)$$

while taking the RHS is simply

$$d(aE) = adE + E da . \quad (1.70)$$

Comparing the two equations, we obtain the “energy potential”

$$\boxed{E = TS - PV + \mu N} . \quad (1.71)$$

We can also use this kind of scaling to figure out the scaling properties of other thermodynamic quantities. For example, the Helmholtz free energy is clearly an extensive quantity

$$F = E - TS \rightarrow aF = aE - aTS, \quad (1.72)$$

since E and S are extensive and T is intensive. From Eq. (1.31), we see that F can be written as a function of $F(E, S, T)$ or $F(T, V)$. Eq. (1.72) tells us then, for the former

$$F(aE, aS, T) = aF(E, S, T) . \quad (1.73)$$

In general, we can write any extensive function as

$$g(A_1, A_2, \dots, A_i; aB_1, aB_2, \dots, aB_j) = ag(A_1, A_2, \dots, A_i; B_1, B_2, \dots, B_j) \quad (1.74)$$

where A_i and B_j are intensive and extensive variables respectively. A function which scales like Eq. (1.74) is called a **homogenous function**⁸. It is easy to show that such a function obey the following **Euler's homogenous function theorem**,

$$g(A_1, A_2, \dots, A_i; B_1, B_2, \dots, B_j) = \sum_j B_j \left(\frac{\partial g}{\partial B_j} \right)_{\text{all except } B_j} . \quad (1.75)$$

You can check that for $F = E - TS$, using Eq. (1.75) we get

$$F = E \left(\frac{\partial F}{\partial E} \right)_{S,T} + S \left(\frac{\partial F}{\partial S} \right)_{E,T} = E - TS , \quad (1.76)$$

recovering the original equation.

But the theorem sometimes buys you new shiny things. Consider the Landau potential Eq. (1.63),

$$\Psi = E - TS - \mu N . \quad (1.77)$$

Now, since E , S , and N are extensive, while T and μ are intensive, it's clear that Ψ is also an extensive variable. From Eq. (1.64), we see that the Landau potential is a function of $\Psi(T, V, \mu)$, and hence rescales as

$$\Psi(T, aV, \mu) = a\Psi(T, V, \mu) . \quad (1.78)$$

Invoking Euler's theorem Eq. (1.75), it is

$$\Psi(T, V, \mu) = V \left(\frac{\partial \Psi}{\partial V} \right)_{T,\mu} . \quad (1.79)$$

Using Eq. (1.63) and Eq. (1.32), we obtain the very useful relationship

$$\boxed{\Psi(T, V, \mu) = -P(T, \mu)V} . \quad (1.80)$$

Combining Eq. (1.80) with the Gibbs free energy Eq. (1.33), we get

$$\Phi = E - TS + PV = E - TS - \Psi = \mu N , \quad (1.81)$$

which tells us that the Gibbs free energy is the total chemical potential of the particles in the system.

We will later use Eq. (1.80) to derive the ideal gas law in section 3.5.

⁸To be precise, a homogenous function of degree one.

Chapter 2

Statistical Ensembles

It is a fairly widespread delusion among physicists that statistical physics is the least well-founded branch of theoretical physics.

Landau and Lifshitz, in the less enlightened time of 1937

2.1 Phase space of microstates

Consider a single point particle with mass m . At any moment in time, it is described by its position \mathbf{x} and its momentum \mathbf{p} . This particle moves under the influence of some potential $V(\mathbf{x})$, and hence obeys Newton's 2nd law of motion $-\nabla V(\mathbf{x}) = d\mathbf{p}/dt$. Solving this equation, given some initial conditions, we can then compute its trajectory $(\mathbf{x}(t), \mathbf{p}(t))$. A useful way to plot this trajectory is on a 6 dimensional plot with \mathbf{p} and \mathbf{x} as its axes, called its **phase space**, see Fig. 2.1. Depending on differential initial

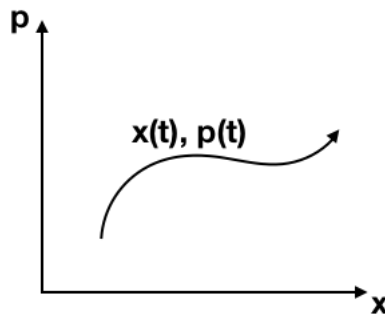


Figure 2.1: The trajectory of a particle in its phase space, which is 6-dimensional – here we have represented the three dimensions of \mathbf{p} and its conjugate \mathbf{x} with a single axis.

conditions, the particle can trace out completely different trajectories, filling out the entire phase space. So, if we are completely ignorant about the initial conditions of this particle, there is no particular reason to guess that the particle is at any **phase point** or another.

On the other hand, suppose we know a bit more about the particle, say that we know that the total energy of this particle is a constant and is $E(t) = E_0$, thus this means that we have an idea about where the particle might be. Since total energy of the particle is the sum of its kinetic and potential energy,

$E = (1/2m)|\mathbf{p}|^2 + V(\mathbf{x})$, and with $E(t) = E_0$ we have

$$E_0 = \frac{1}{2m}|\mathbf{p}|^2 + V(\mathbf{x}). \quad (2.1)$$

This is a **constraint** equation – once \mathbf{x} is known, the amplitude $|\mathbf{p}|^2$ is totally determined by Eq. (2.1). This means the dimensionality of the phase space where this particle can exist given $E = E_0$, is 5-dimensional instead of 6 – a large reduction in possibilities. This smaller space is called the **accessible phase space** given energy E_0 .

Now, instead of one particle, let's consider N particles, and for simplicity let's make them non-interacting. One way to make them non-interacting is to space them far apart – i.e. number densities are low. If they actually collide, we make the collisions elastic so there is no energy loss to friction. Each particle will have its own $(\mathbf{x}_i(t), \mathbf{p}_i(t))$. The phase space of this set of N particles is then $6N$ dimensional – a very large phase space indeed. Each point in this phase space describes a possible configuration of $(\mathbf{x}_1(t), \mathbf{x}_2(t), \dots, \mathbf{p}_1(t), \mathbf{p}_2(t), \dots)$, i.e. each phase point describes a single configuration of these N particles. Each such configuration (i.e. each phase point) is called a **microstate**.

Without any constraints, the space of all possible microstates is simply the phase space of the system. However, like the case of the single particle, if we know something about the system, say its total energy

$$E_0 = \sum_i \left[\frac{1}{2m}|\mathbf{p}_i|^2 + V(\mathbf{x}_i) \right], \quad (2.2)$$

then the accessible phase space will be reduced, although it will still be very large. Such a reduced space is called an **ensemble** (or **statistical ensemble**). In other words, the ensemble described above is the space of all possible microstates consistent with an energy of E_0 . More generally:

An ensemble is the space of all possible microstates consistent with some constraints. Different constraints will lead to different ensembles.

For example, a gas of N particles is put in a box of volume V , and their kinetic action has pressure P (Fig. 2.2). N is in general very large – $N \sim 10^{23}$, prohibitively large for us to try to calculate the motion of individual particles. But since we know something about the system, i.e. its P and V , the accessible phase space for this gas is constrained and hence is smaller than the entire phase space of the system, and defines an ensemble. We will now describe some important ensembles in the following sections.

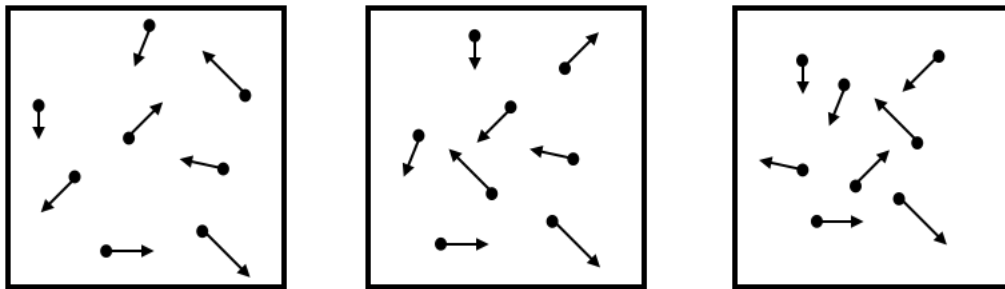


Figure 2.2: A box of N particles with fixed macroscopic properties such as P , V can have many different microstates.

2.2 The microcanonical ensemble

Consider an isolated gas of fixed number of particles N and in a fixed container of volume V . As described earlier, isolated means that the gas is thermally insulated so cannot exchange heat with the

surroundings, and furthermore fixing V means that we cannot do work, so the total energy of the system remains constant throughout.

Of course, the particles of the gas themselves can still move around – and indeed they can collide with one another (or the walls of the container), exchange energy with each other – doing what normal particles do. Furthermore, we let the system evolve for a while, until it reaches equilibrium and nothing else changes – this is a conjecture for now, but as we will soon see below, this is inevitable.

At equilibrium, there exists many different microstates in which the constraint with some constant E is obeyed. This fixed E ensemble is called the **microcanonical ensemble**. Note that the condition for equilibrium is important – the ensemble for *non-equilibrium* configurations is much larger than the microcanonical ensemble.

Let's now define

$$\Omega(E) = \text{Total Number of Microstates with energy } E. \quad (2.3)$$

As we discussed earlier, for a mole of gas with 10^{23} particles, $\Omega(E)$ is a mind-blowingly large number, even with all the constraints and conditions. Each member of this ensemble represents a possible microstate. As time evolves, microscopically speaking the particles are constantly moving and evolving, and hence the system do not stay in one microstate for long (even in equilibrium) but evolves from microstate to microstate. If we are only interested in the macroscopic properties of the system, it is not important (and not interesting) to know exactly which microstate the system is in at any particular moment.

On the other hand, one can perhaps imagine that some microstate is more “popular” than others. Ask another way – what is the probability for each of the microstate to be the “true” microstate at any time t ? This is in general an extremely difficult question, and indeed has definite no fool-proof mathematical answer. However, we can invoke the so-called **postulate of equal *a priori* probability** and assert that

All microstates are equally probable.

Why are we allowed to make this postulate? Roughly speaking, the idea is that the particles will move around in whatever way they want (given the constraints), and given sufficient long time, they will “explore” the entire possible space of possibilities – this is called the **ergodic hypothesis** (it's a hypothesis because very special counterexamples exist in classical mechanics). Combined with the **Liouville Theorem** – which states that *if the density of microstates in phase space is uniform it will remain uniform at all time* – then this leads to the postulate.

Given this postulate, the probability for us finding the system in any particular microstate at any time t is then simply

$$\text{Probability} = \frac{1}{\Omega(E)}. \quad (2.4)$$

In other words, $\Omega(E)$ is the *weight* of each state, and hence Ω is called the **statistical weight** of the ensemble. In the microcanonical ensemble we have impose the constraints that all microstates have energy E . As we have studied earlier in Chapter 1, E is a function of thermodynamic variables P, V, N and possible others, so we can also write $\Omega(P, V, N, \dots)$. The statistical weight is not just a definition for the microcanonical ensemble, but it is general for any ensemble as we will see later.

In general, for any given N number of particles, the total number of accessible states *increase* with E . This is not surprising – the greater E , the more ways we can partition the energies into N particles. We can express this fact by a power law

$$\Omega(E) \sim E^\alpha \quad (2.5)$$

where α is some large positive number which depends on the exact microphysics of the system. What exactly α is not very important – when α is large enough, then whether it is 50 or 500 actually does not matter so much.

Hence, for a given E (the macroscopic variable), there is a huge but equally probable ensemble of microstates – effectively quantifying our lack of knowledge – **entropy** – of the true configuration of the system itself. The bigger the Ω the less we know, so it is natural then to define the entropy $S(E)$ as

$$\boxed{S(E) \equiv k_b \ln \Omega(E)} \quad (2.6)$$

where k_b is the Boltzmann constant¹. Why not just $S \stackrel{?}{=} k_b \Omega$? There are the usual ease of use reasons – firstly Ω is a ginormous number, so taking the log makes the numbers less ridiculous. Also, it makes the entropy an *additive* quantity. Consider the entropy of two non-interacting separate boxes of particles, each with internal energy E_1 and E_2 , each with statistical weight $\Omega(E_1)$ and $\Omega(E_2)$. Since they are non-interacting, their *joint* statistical weight is simply $\Omega(E_1, E_2) = \Omega(E_1)\Omega(E_2)$, but their joint entropy is

$$S(E_1, E_2) = k_b \ln \Omega(E_1, E_2) = k_b \ln \Omega(E_1) + k_b \ln \Omega(E_2) = S(E_1) + S(E_2). \quad (2.7)$$

But most importantly, this definition means that Eq. (2.6) is *the* entropy function of state S that we have encountered earlier when discussing classical thermodynamics in Chapter 1, as we will now show in sections that follows.

2.2.1 Statistical equilibrium and the 2nd Law

Defining entropy as disorder's not complete, cause disorder as a definition doesn't cover heat, so my first definition I would now like to withdraw, and offer one that fits thermodynamics second law.

MC Hawking, *Entropy*

Consider two systems, A and B , whose internal energies are in E_A and E_B initially, with fixed volumes V_A, V_B and fixed number of particles N_A and N_B . They placed next to each other, separated by a diathermal (see section 1.2) partition which allows heat to be exchanged between the two systems, but not particles, as shown in Fig. 2.3. Note that we have not assumed that they are in equilibrium – indeed we want to *show* that they will evolve into equilibrium.

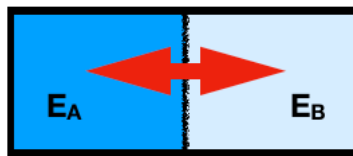


Figure 2.3: Two systems initially with energies E_A and E_B allowed to exchange heat, and nothing else, with one another through a diathermal partition. They will eventually reached thermal equilibrium. Their *total* energy $E_0 = E_A + E_B$ remains constant throughout, through the conservation of energy.

Since heat is exchanged, the two systems' individual energies E_A and E_B will change with time t but the total energy of this combined system

$$E_0 = E_A + E_B \quad (2.8)$$

remains constant throughout since it is a conserved quantity (recall the systems are not allowed to exchange heat with their surroundings).

¹This definition Eq. (2.6) is sometimes known as the **Boltzmann entropy**, as it was Ludwig Boltzmann who proposed it – leading to a revolution in our understanding of statistical mechanics and thermodynamics. It was engraved on his gravestone.

Writing $E_A(t) = E_0 - E_B(t)$ with their respective entropies $S_A(E_A)$ and $S_B(E_B) = S(E_0 - E_A)$, and using the additivity property of entropy Eq. (2.7) that the combined entropy of the system is $S = S_A + S_B$, we have

$$\begin{aligned} \left(\frac{\partial S}{\partial E_A} \right)_{E_0} &= \left(\frac{\partial S_A}{\partial E_A} \right)_{E_0} + \left(\frac{\partial S_B}{\partial E_A} \right)_{E_0} \\ &= \left(\frac{\partial S_A}{\partial E_A} \right)_{E_0} + \frac{\partial E_B}{\partial E_A} \left(\frac{\partial S_B}{\partial E_B} \right)_{E_0} \end{aligned} \quad (2.9)$$

and from Eq. (2.8),

$$\frac{\partial E_B}{\partial E_A} = -1$$

so

$$\left(\frac{\partial S}{\partial E_A} \right)_{E_0} = \left(\frac{\partial S_A}{\partial E_A} \right)_{E_0} - \left(\frac{\partial S_B}{\partial E_B} \right)_{E_0}. \quad (2.10)$$

Note that Eq. (2.8) allow us to express the total entropy of the combined system S as a function of E_A , and from Eq. (2.6), the statistical weight of the *combined* system, $\Omega_0(E_A)$.

So far this is all mathematics. Let's now ask the question: what will the systems evolve to? Since we have expressed the combined entropy $S(E_A)$ as a function of the energy of system A , this is equivalent to asking what the energy of $E_A(t)$ will evolve to. To answer this question, we investigate what kind of function the total entropy $S(E_A)$ can be. As it turns out, it is more physically intuitive to go back to the statistical weight

$$\Omega_0(E_A) = \Omega_A(E_A)\Omega_B(E_B), \quad (2.11)$$

where $S(E_A) = k_b \ln \Omega_0(E_A)$. As we seen earlier Eq. (2.5), $\Omega(E) \sim E^\alpha$ is a rapidly increasing function of E in general. For each systems A and B , we then have $\Omega_A(E_A) \sim E_A^{\alpha_A}$ and $\Omega_B(E_B) = \Omega_B(E_0 - E_A) \sim (E_0 - E_A)^{\alpha_B}$, which when substituted back into Eq. (2.11)

$$\Omega_0(E_A) \sim E_A^{\alpha_A} \times (E_0 - E_A)^{\alpha_B}. \quad (2.12)$$

Since $E_A^{\alpha_A}$ is a rapidly *increasing* function of E_A , then it is clear that $(E_0 - E_A)^{\alpha_B}$ must be a rapidly *decreasing* function of E_A , $\Omega_0(E_A)$ must look like a sharply peaked function of E_A as shown in Fig. 2.4 at some $E_A = E_*$. So the picture is now as follows. Beginning with some $E_A(t)$ (and hence $E_B(t)$ for fixed

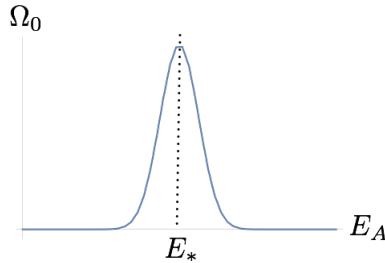


Figure 2.4: The statistical weight Ω as a function of energy E_A of the combined system is sharply peaked at some E_* .

E_0), we allow the systems to exchange heat. System A 's energy $E_A(t)$ will evolve according to whatever microphysics that governs the interactions. According to the ergodic hypothesis, the *combined* system will then evolve through the enlarged phase space, exploring every microstate described by $\Omega_0(E_A)$.

Now, after some time for the particles to interact, we ask: what is the most likely *energy* of a microstate of the combined system? Given that the statistical weight $\Omega_0(E_A)$ is sharply peaked at E_* , if you are asked to bet your life on it, you would be wise to choose the microstate described by $E_A = E_*$. There are of course other microstates described by $E_A \neq E_*$, but invoking our postulate of equal probability,

since the number of microstates with $E_A = E_*$ far outweighs the other microstates, microstates with $E_A = E_*$ are the *most likely microstates*. We define the ensemble of microstates described by E_* as the **equilibrium**, and we say that the combined system is in **statistical equilibrium**. Since $\Omega_0(E_*)$ is maximum, this means that S is also maximum at equilibrium, and hence we have shown that:

At statistical equilibrium, the entropy is maximum.

So if any system initially is not in its state of maximum entropy, then statistically it will tend to evolve towards this point, and hence the time evolution of the entropy is semi-positive definite

$$\frac{dS}{dt} \geq 0. \quad (2.13)$$

This is simply the first part of **the 2nd Law of Thermodynamics!** Making contact with our classical thermodynamics definition in section 1.2.3 – we see that our combined system is an isolated system, and so is consistent with Eq. (1.18), which asserts that $\Delta S \geq 0$ in an isolated system. But now we see the statistical mechanical explanation of *why* this is so – when we let two systems that were not initially in equilibrium (i.e. $E_A(t_{initial}) \neq E_*$) interact, the combined system will be dominated by microstates around $E_A = E_*$. So, statistically speaking, after interactions have occurred, the most likely microstates the system will be in are the ones accessible when $E_A = E_*$. Notice that we have not specified the initial values of $E_A(t)$ and $E_B(t)$ at all – but our postulates have told us the, whatever those are, the most likely microstate is that the ones that are accessible at E_* . This is a remarkable result: the likely final state does not depend on initial conditions – all initial states tend to flow towards statistical equilibrium.

2.2.2 Temperature

Since $\Omega_0(E_A)$, and thus $S(E_A)$ is a maximum at $E_A = E_*$, this means that we want to find E_A when Eq. (2.10) vanishes, i.e.

$$\left(\frac{\partial S(E_*)}{\partial E_A} \right)_{E_0} = \left(\frac{\partial S_A(E_*)}{\partial E_A} \right)_{E_0} - \left(\frac{\partial S_B(E_*)}{\partial E_B} \right)_{E_0} = 0 \quad (2.14)$$

or

$$\left(\frac{\partial S_A(E_*)}{\partial E_A} \right)_{E_0} = \left(\frac{\partial S_B(E_*)}{\partial E_B} \right)_{E_0}. \quad (2.15)$$

To make contact with classical thermodynamics, we want to assign a property to the systems in equilibrium. Furthermore, we want this property to be *equal* for both systems A and B , a property which we will call, *ta-da!* – the **temperature** T following the zeroth law. By inspecting Eq. (2.15), we make the wonderfully remarkable definition for the temperature T_i

$$\boxed{\frac{1}{T_i} \equiv \frac{\partial S_i}{\partial E_i}} \quad (2.16)$$

where S_i, E_i are the entropy and energy of system i respectively². This definition immediately implies that, at equilibrium $T_A = T_B$ as required. Why $1/T$, and not T ? As it turns out, this is simply to make contact with “already established” classical thermodynamics. Indeed, if history has been a bit different and we have discovered statistical mechanics before classical thermodynamics, we would have defined

$$\frac{\partial S}{\partial E} \equiv k_b \beta \quad (2.17)$$

or

$$\boxed{\beta \equiv \frac{1}{k_b T}} \quad (2.18)$$

²Note that $\partial S/\partial E_A$ is *not* the definition of temperature for the combined system! Indeed if it is, it would be infinite at equilibrium. The reason is that E_A is not the internal energy for S , but E_0 .

and call β the temperature. Sadly, β (which in many ways is the more natural parameter) is relegated to be known as the **coldness**, though we would just call it “beta” in this course – you won’t catch a proper theoretical physicist calling β coldness. The nice thing about β is that it is continuous through $\beta = 0$ hence can take both negative and positive values while at $T = 0$, $\partial S/\partial E$ blows up to infinity. This means that the definition Eq. (2.17) allows for the phenomenon of **negative temperatures**. What does it mean to have negative temperatures? Eq. (2.16) tells us that if $T > 0$, then as we add heat into the system, S increases and become more disordered, which most everyday material obeys. However, there exists some material where if you add more heat into the system, its entropy S decreases and it becomes *more ordered*. We will consider such systems in a homework problem.

There is one more thing we can learn from this definition of entropy, which is the direction of heat flow. Taking the time derivative of S , we get

$$\begin{aligned} \frac{dS}{dt} &= \frac{\partial S}{\partial E_A} \frac{dE_A}{dt} \\ &= \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{E_0} - \left(\frac{\partial S_B}{\partial E_B} \right)_{E_0} \right] \frac{dE_A}{dt} \\ &= \left[\frac{1}{T_A} - \frac{1}{T_B} \right] \frac{dE_A}{dt} \geq 0 . \end{aligned} \tag{2.19}$$

The last inequality means that if $dE_A/dt > 0$, i.e. heat flows from B to A , then $T_B > T_A$ and *vice versa*, which is to say, heat flows from a warmer body to a colder body as asserted by Lavoisier in his (now defunct) theory of calorific heat as you have studied in high skool.

2.2.3 An example : Schottky Defects

Let’s consider a very system as an illustration of our ideas discussed so far. Consider a lattice of N atoms arranged in a crystal lattice, where n number of those atoms have migrated to the surface, resulting in n holes in the lattice as shown in Fig. 2.5.

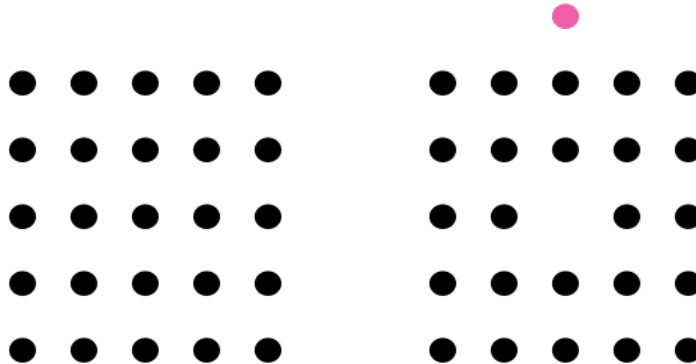


Figure 2.5: On the left is a lattice of atoms, while on the right is a lattice of atoms with a “hole” where one of its atom (purple) has migrated to the surface. Such a hole is called a Schottky defect. In general, a lattice of N atoms can possess $n \ll N$ number of such defects. We have illustrated it with a grid lattice, though the exact configuration is not important as long as there is some symmetry.

Schottky defects occur when we transfer energy into the lattice – the atoms will vibrate in their places, and once in a while there is a chance that an atom will shake itself loose and migrate to the surface. Let ϵ be the energy required to move an atom from its slot to the surface, so for n defects, the total energy required to move all of them to the surface is then

$$E(n) = n\epsilon . \tag{2.20}$$

For a given n , there exist ${}^N C_n$ ways of arranging the n holes in a lattice of N points, so then the statistical weight is

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \quad (2.21)$$

In other words, for a given n , the energy of the system is given by $E = n\epsilon$ and there are $\Omega(n)$ microstates which are consistent with this energy. The entropy as a function of n and hence as a function of E is then

$$S(n) = k_b \ln \Omega(n). \quad (2.22)$$

Using Stirling's formula (see Appendix A)

$$\ln n! \approx n \ln n - n \quad \text{for } n \gg 1 \quad (2.23)$$

Eq. (2.22) becomes

$$S(n) = k_b [N \ln N - n \ln n - (N-n) \ln(N-n)]. \quad (2.24)$$

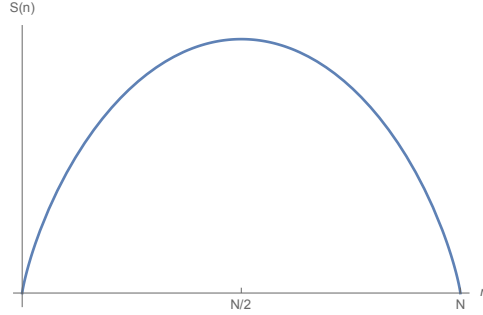


Figure 2.6: The entropy $S(n)$ as a function of n for a lattice of N atoms and n holes. The maximum occurs at $n = N/2$.

We plot $S(n)$ in Fig. 2.6, for $0 \leq n \leq N$. Notice that there is a maximum at $n = N/2$ – of course, it makes no sense for the Schottky anomalies since $n \ll N$. Nevertheless, this model is completely equivalent to that of paramagnetism where n can range from 0 to N , which we will come back to in section 2.3.4.

We can then calculate the temperature of the lattice via Eq. (2.16),

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ &= \frac{1}{\epsilon} \frac{\partial S}{\partial n} \\ &= \frac{k_b}{\epsilon} \ln \frac{N-n}{n}. \end{aligned} \quad (2.25)$$

When there are not defects $n = 0$, then $T = 0$ – the lattice is at its minimal energy, or **ground state**. Rewriting Eq. (2.25) by taking the exponent, we get

$$\frac{n}{N} = \frac{1}{\exp(\epsilon/k_b T) + 1} \quad (2.26)$$

which in the limit of $n \ll N$ so from Eq. (2.25) means that $\epsilon \gg k_b T$, we obtain the formula for the number of defects as a function of temperature

$$n = N e^{-\epsilon/k_b T} = N e^{-\beta \epsilon}. \quad (2.27)$$

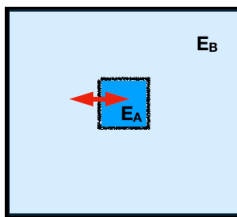


Figure 2.7: An isolated combined system, where system A is diathermally partitioned from system B , and system B is much larger than system A and hence acts as a heat bath or heat reservoir.

2.2.4 Heat bath

Consider the combined system A and B where B is a much larger system than A , as shown in Fig. 2.7. Suppose $T_A \neq T_B$ initially, then there will be transfer of heat ΔQ between the two systems (in either direction).

We can Taylor expand the entropy B as follows

$$\begin{aligned} S_B(E_B + \Delta Q) &= S_B(E_B) + \frac{\partial S_B}{\partial E_B} \Delta Q + \frac{1}{2} \frac{\partial^2 S_B}{\partial E_B^2} \Delta Q^2 + \dots \\ &= S_B(E_B) + \frac{1}{T_B} \Delta Q + \frac{1}{2} \frac{\partial}{\partial E_B} \left(\frac{1}{T_B} \right) \Delta Q^2 + \dots \end{aligned} \quad (2.28)$$

where we have used Eq. (2.16) to define the temperature in the 2nd term. Meanwhile, the 3rd term is

$$\begin{aligned} \frac{\partial}{\partial E_B} \left(\frac{1}{T_B} \right) &= -\frac{\partial T_B}{\partial E_B} \frac{1}{T_B^2} \\ &= -\frac{1}{C_V T_B^2} \end{aligned} \quad (2.29)$$

where we have used the definition for the heat capacity (for equal volume) Eq. (1.50), recall that we since $T(E)$, i.e. T is a function of E and nothing else, we can invert $E(T)$, and thus also invert the partial derivatives $(\partial E / \partial T)^{-1} = \partial T / \partial E$.

Rearranging Eq. (2.28) after dropping the higher order terms, we have

$$\Delta S_B = S_B(E_B + \Delta Q) - S_B(E_B) = \frac{1}{T_B} \Delta Q \left(1 - \frac{\Delta Q}{2C_V T_B} \right). \quad (2.30)$$

Now we use the fact that B is a heat bath, so $C_V T_B$ is roughly the heat needed to bring the temperature of the bath from zero to T_B , which is much larger than any heat that it can absorb ΔQ from A so $\Delta Q \ll 2C_V T_B$. Dropping this term, we get

$$\Delta S_B = \frac{\Delta Q}{T_B}. \quad (2.31)$$

This is the change in the entropy of the heat bath given a small (in comparison to its total energy) injection of heat ΔQ .

But wait! Notice we have not specified anything about A other than “ A is smaller than B ”. Indeed, we are free to make A as small as possible, and B being “normal sized” compared to A . In other words, Eq. (2.31) is valid as long as the heat injected ΔQ is infinitesimally small, $\Delta Q \rightarrow dQ$. So we can express this equation as a differential (dropping B since it is a general equation)

$$\boxed{dS = \frac{dQ}{T}} \quad (2.32)$$

which is the definition for the heat dQ (Eq. (1.19)) we have seen when we discuss the classical thermodynamics definition of the 2nd law in section 1.2.3. There we have stated that Eq. (2.32) is valid for

reversible processes in non-isolated systems. Mathematically, reversibility is imposed by the fact that we have assumed that we can Taylor expand the entropy in Eq. (2.28) – meaning that we can move back from $S_B(E_B + \Delta Q)$ to $S_B(E_B)$ by rejecting an amount of heat ΔQ . This is of course not true in general.

Since we have defined $S = k_b \ln \Omega$, and $1/T = \partial S / \partial E$, we can use Eq. (2.32) as the definition for heat dQ , which is what we said we will do way back in section 1.2.3.

2.2.5 *Recurrence time

We have shown that statistically, a system is driven towards statistical equilibrium simply because that there are simply so many more accessible microstates at that point. However, there is no microphysical reason that, statistically, the system cannot evolve into a microstate that is very far away from the equilibrium point, just by random chance. Indeed, this is *guaranteed* to happen by Liouville’s theorem and ergodicity – if the orbits of the trajectory in phase space is bounded (which it usually is), then given infinite time to evolve, the trajectory will intersect every phase point an infinite amount of times, including those very rare phase points that are far away from equilibrium. In other words, if we wait long enough, we will come back to the same configuration of particles. This is known as the **Poincaré Recurrence** time, and roughly it is

$$t_p \sim e^{e^S} \tag{2.33}$$

where S is the maximum entropy (at equilibrium), which is a very long time indeed, If we consider the entire observable universe as our combined system, then we can compute the recurrence time as

$$t_{rec} \sim 10^{10^{10^{10^2}}} \text{ years.} \tag{2.34}$$



Figure 2.8: T-Rex contemplating Poincaré recurrence, though Utahraptor insightfully points out that the recurrence requires the universe to be ergodic, which is not necessarily true. Credit : www.qwantz.com.

This has been suggested as a solution to the problem of cosmological origins as follows. The universe is eternal, and spends most of its time in thermal equilibrium and hence is at the state of maximum entropy – the so-called “heat death”. However, once in a Poincaré time (i.e. a really long while), the

universe randomly fluctuates to a state of lower entropy. It will then statistically evolve towards the state of maximum entropy following the 2nd law, and we are simply living in this very special moment where the universe is still evolving to its equilibrium. In this universe, there is infinite time, so everything and anything can happen an infinite number of times. There are many issues with this model, and one of them is helpfully pointed out by Utahraptor in Fig. 2.8.

2.3 The canonical ensemble

While the microcanonical ensemble is an extremely useful idea for us to construct many ideas in statistical mechanics and connect it to classical thermodynamics, it is in practice not a very useful ensemble since it is really hard to experimentally set up a system where the energy remains constant³ – imagine trying to keep the energy of a glass of water constant! On the other hand, it is much easier to keep a glass of water at constant *temperature* – simply stick the glass of water into a refrigerator kept at fixed temperature. This leads us to the **canonical ensemble**:

The canonical ensemble is the set of microstates at constant volume V , particle number N and temperature T .

To set up such an ensemble, we immerse the system inside a heat bath as we described previously in section 2.2.4, so at equilibrium the system will take on the temperature of the heat bath. Let's call the system S and the heat bath B , as in Fig. 2.9.

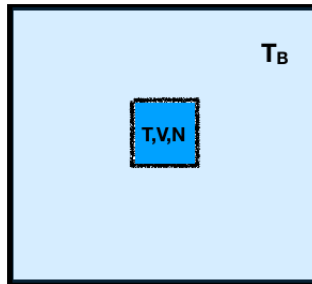


Figure 2.9: A system with fixed V and N immersed in a bath of temperature T_B is called the canonical ensemble.

The total energy of the combined system is $E_0 = E_B + E_S$, but now since the heat bath is so much more larger than the system, its energy remains roughly constant in the presence of random fluctuations. However, these small fluctuations in the bath $\Delta E_B/E_B \ll 1$ will have *large* effects on the total energy of the much smaller system $\Delta E_S/E_S \gg 1$. This means that while we can assume that the energy of the bath remains constant, we *can no longer assume that the energy of the system remains constant*. This means that instead of a fixed energy E_S , the system can possess a set of microstates that are consistent with different energies that are consistent with the temperature of the bath being T_B . Labeling each individual microstates by r , each which can possess an energy⁴ of E_r . *We emphasise that for each energy level E_r , there can be a large degeneracy of microstates with the same energy* – hence the canonical ensemble is roughly a set of microcanonical ensembles, as the latter's name imply.

We now ask: what is the probability of finding a microstate with energy E_r , P_r ? Suppose Ω_T is the *total* statistical weight for the combined bath and system, then it must be

$$\Omega_T = \sum_r \Omega_B(E_0 - E_r) \quad (2.35)$$

³Such systems exist of course, we have seen the Schottky defects system for example.

⁴Think E_r as “energy of microstate r ” instead of “energy level r ”.

where the sum is *over all the microstates* and not just the energy levels r and $\Omega_B(E_0 - E_r)$ is the statistical weight of the *bath* assuming that the system has the definite energy E_r . Hence, the probability of finding microstate labeled r must then simply be $P_r = \Omega_B(E_0 - E_r)/\Omega_T$, or

$$P_r = \text{const} \times \Omega_B(E_0 - E_r), \quad (2.36)$$

This seems counter-intuitive – why is P_r independent of the statistical weight of the system itself? The statistical weight of the system is in principle hidden inside the “const”, so in principle this constant should be a function of E_r , but since heat bath is so much larger than the system, and hence contains way more degrees of freedom, the primary contribution to P_r is through $\Omega_B(E_0 - E_r)$.

Since the system must be in some definite microstate r , this means that

$$\sum_r P_r = 1 \quad (2.37)$$

which, again, we emphasise that we are summing over all possible microstates r (some which may have the same energy E_r). Writing P_r out in full, Eq. (2.36) is then

$$P_r \equiv \frac{\Omega_B(E_0 - E_r)}{\sum_r \Omega_B(E_0 - E_r)}. \quad (2.38)$$

Eq. (2.38) is the probability of finding a microstate with energy E_r .

Focusing on $\Omega_B(E_0 - E_r)$, its associated entropy is given by Eq. (2.6), and as in section 2.2.4 we can expand the entropy around E_r (recall that $E_0 \gg E_r$ for any conceivable fluctuation since the heat bath is so much larger)

$$S_B(E_0 - E_r) = S_B(E_0) - \frac{\partial S_B(E_0)}{\partial E_0} E_r + \frac{1}{2} \frac{\partial^2 S_B}{\partial E_0^2} E_r^2 + \dots \quad (2.39)$$

The 2nd term is

$$\frac{\partial S_B(E_0)}{\partial E_0} E_r = \frac{E_r}{T_B} \quad (2.40)$$

using the definition for temperature Eq. (2.16). The 3rd term is again negligible following the arguments we discussed in section 2.2.4, giving us (dropping the subscript B from T_B since it is clear there is only one temperature)

$$\Omega_B(E_0 - E_r) = e^{S(E_0)/k_b} e^{-E_r/k_b T}. \quad (2.41)$$

Plugging this back into Eq. (2.38) we finally get the canonical ensemble

$$P_r = \frac{e^{-E_r/k_b T}}{Z}, \quad (2.42)$$

where the normalization factor, known as the **partition function**

$$Z \equiv \sum_r e^{-E_r/k_b T}, \quad (2.43)$$

where, for the umpteenth time, we remind you that the sum is over all microstates r and not just the energy levels E_r . Don't let the innocuous partition function fool you – despite its prosaic function as a normalization factor here, it is actually one of the most important quantity in statistical physics, and merits its own section later (section 2.3.2).

2.3.1 The Boltzmann Distribution

Nevertheless, Eq. (2.42) is not a very useful equation – who in the right mind wants to know the probability of finding a particular microstate? Indeed, a more useful equation would be one that tells us the *probability of finding a microstate with energy E* (dropping the subscript r now since we are referring to the energy levels themselves). As we emphasised many times, for each E there usually exists a degeneracy of microstates, $f(E)$. So hence we can write the probability of finding a microstate with E as

$$P(E) = \frac{f(E)e^{-E/k_bT}}{\sum_{E'} f(E')e^{-E'/k_bT}} , \quad (2.44)$$

where we have rewritten the partition function Eq. (2.43) as a sum over energies

$$Z = \sum_{E'} f(E')e^{-E'/k_bT} . \quad (2.45)$$

Thus, instead of the probability of finding an individual microstate, we have an equation that tells us the *density* of microstates at energy E_r . Such an equation is called a **distribution**, and Eq. (2.44) is also known by its more famous name of the **Boltzmann distribution**, which you have already encountered in your thermal physics module. Boltzmann first derived this distribution in 1868.

What is the form of $f(E)$ then? A good guess for $f(E)$ would be the microcanonical ensemble of an isolated system with energy E , $f(E) \stackrel{?}{=} \Omega(E)$, that we studied in section 2.2. As it turns out, this is not quite right (since it is not an isolated system in reality), but it is close when the number of microstates are very large. More to the point, it contains the important property that $f(E)$ is a rapidly increasing function of E as in Eq. (2.5), so

$$f(E) \sim E^\alpha . \quad (2.46)$$

This is a rapidly increasing function of E , but on the other hand the factor $\exp(-E/k_bT)$ is a rapidly *decreasing* function of E . This means that the function $f(E)\exp(-E/k_bT)$ will be a sharply peaked function at some mean energy \bar{E} .

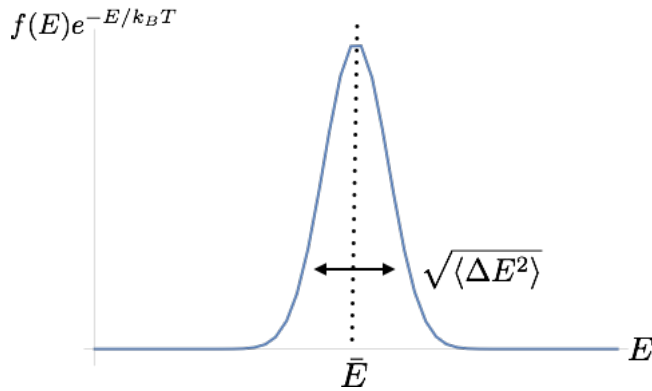


Figure 2.10: The function $f(E)\exp(-E/k_bT)$ is a sharply peaked function at some mean \bar{E} .

To find the mean \bar{E} , we defined the following **ensemble average** of any property of the microstate X_r

$$\langle X \rangle \equiv \sum_r P_r X_r = \frac{1}{Z} \sum_r X_r e^{-E_r/k_bT} , \quad (2.47)$$

i.e. it is the weighted (by P_r) sum over the property X_r . Then the mean $\bar{E} = \langle E_r \rangle$ is

$$\bar{E} = \sum_r P_r E_r . \quad (2.48)$$

The width of the distribution, written clumsily for now as $\sqrt{\langle \Delta E^2 \rangle}$ is called its **dispersion** or **fluctuations**. It measures the fact that even though the system is in thermal equilibrium with the heat bath, there is random motion and interactions between the system and the heat bath, and there is a possibility of the system gaining and losing a bit of energy in the process. So the probability of finding a microstate with energy $E_r \sim \bar{E} \pm \sqrt{\langle \Delta E^2 \rangle}$ is non-zero, albeit small.

In fact, as the number of particles N increases, the dispersion in general decreases as follows⁵

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\bar{E}} \sim \frac{1}{\sqrt{N}}. \quad (2.49)$$

In the limit $N \rightarrow \infty$, the dispersion $\sqrt{\langle \Delta E^2 \rangle} \rightarrow 0$, and for all intents and purposes, the distribution is peaked at some fixed energy $\bar{E} = E$ with no fluctuations, i.e. it becomes a *microcanonical ensemble*. This system we have studied in great detail in the previous section 2.2. This $N \rightarrow \infty$ limit is called **thermodynamic limit**⁶ – since the energy E has no fluctuation and hence is equivalent to the thermodynamic internal energy.

This limit gives us a general prescription of connecting (probabilistic) statistical mechanical variables to the “exact” values of classical thermodynamics – since we are usually dealing with very large N systems, at a pinch one can take the ensemble average of any quantity to represent its thermodynamic counterpart.

2.3.2 The partition function

We alluded to the fact that the partition function Eq. (2.43) is one of the most important object in statistical mechanics. Indeed, it can be argued it is the *most* important – you will be spending a lot of time with it. Rewriting it using $\beta = 1/k_b T$ instead of T as the parameter, it is

$$Z = \sum_r e^{-\beta E_r} = \sum_E f(E) e^{-\beta E}. \quad (2.50)$$

The partition function⁷ is a sum over all the states in the ensemble – in other words, it contains *all the information about the entire system*. The only question is: what kind of useful information can we extract from it? The answer is: a lot. Let’s do some simple ones first.

- **Mean energy \bar{E} and dispersion $\langle \Delta E^2 \rangle$.** The mean energy of a canonical ensemble is previously given by Eq. (2.48)

$$\bar{E} = \sum_r P_r E_r. \quad (2.51)$$

But since

$$\frac{\partial Z}{\partial \beta} = - \sum_r E_r e^{-\beta E_r} \quad (2.52)$$

and hence

$$\begin{aligned} -\frac{1}{Z} \frac{\partial Z}{\partial \beta} &= \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \\ &= \sum_r P_r E_r \end{aligned} \quad (2.53)$$

or

$$\boxed{\bar{E} = - \frac{\partial \ln Z}{\partial \beta}}. \quad (2.54)$$

⁵You will do a more precise derivation of this in a homework problem, but this result intuitively follows from any distribution of events whose individual probability is independent of time.

⁶To be more specific, we have to keep the number density N/V constant as we take this limit.

⁷Its symbol, Z , comes from its German name, *Zustandsumme*, or “sum over states”.

Eq. (2.54) provides to us a direct relationship between the macroscopic thermodynamic potential \bar{E} and the partition function.

We can further compute the dispersion or the variance of the distribution is the ensemble average of the square of the difference of the energies of the microstates with the mean, i.e.

$$\langle \Delta E^2 \rangle \equiv \langle (E - \bar{E})^2 \rangle . \quad (2.55)$$

This is given by

$$\langle \Delta E^2 \rangle = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (2.56)$$

as you will show in a homework problem. The dispersion $\langle \Delta E^2 \rangle$ describes the “width” of the sharp peak in Fig. 2.10. In other words, the dispersion tells us how broadly or narrowly the microstates of the system is “spreaded” around the mean energy \bar{E} .

Now, for our next trick, recall that the heat capacity for the canonical ensemble is given by Eq. (1.50), $C_V = \partial E / \partial T$. In the canonical ensemble, we replace $E \rightarrow \bar{E}$ instead, so

$$\begin{aligned} C_V &= \frac{\partial \bar{E}}{\partial T} \\ &= \frac{\partial \bar{E}}{\partial \beta} \frac{\partial \beta}{\partial T} \\ &= \frac{\langle \Delta E^2 \rangle}{k_b T^2} . \end{aligned} \quad (2.57)$$

This is an amazing result. C_V measures how much energy a system needs to absorb before raising its temperature, which is a *systematic* response, while $\langle \Delta E^2 \rangle$ measures the *random* fluctuations of the energy around the mean. How on earth are these two quantities related? But if we think deeper, we see that this is entirely plausible.

Consider Fig. 2.10 again. The greater the dispersion, the broader the area under the mean value \bar{E} – this means that the system is more capable of “absorbing” energy from the environment (in our case, the heat bath) without moving the mean energy which roughly corresponds to its absolute temperature, and hence a bigger C_V . This subtle and powerful connection is actually very general in statistical mechanics – the dispersion, or *random* fluctuation of a system is deeply related to the *systematic* response of the system to absorption, or dissipation of energy. This result is an example of a general theorem called **the fluctuation-dissipation theorem**. In our example, we have considered systems in thermal equilibrium, but this theorem goes beyond equilibrium and hence is a powerful connection to non-equilibrium physics. Unfortunately, this is the subject of a more advanced module. A wonderful description of this theorem is given by R. Kubo (<https://www.mrc-lmb.cam.ac.uk/genomes/madanm/balaji/kubo.pdf>).

- **External Work and Pressure.** Suppose we do some work dW on the system, changing the system by some parameter which we call x for now. The energies of the microstates can then be parameterized by x , so $E_r \rightarrow E_r(x)$, given us the *change in the energy per microstate*

$$\delta E_r = \frac{\partial E_r}{\partial x} \delta x . \quad (2.58)$$

You might rightfully ask – why doesn’t work change the probability P_r instead of the energy E_r ? As we will soon see in the next section 2.3.3, the change in P_r is related to heat input dQ . For now,

let's plow on. The total work done dW on the system is the ensemble average of δE_r ,

$$\begin{aligned}
dW &\equiv \langle \delta E_r \rangle \\
&= \sum_r P_r \delta E_r \\
&= \sum_r P_r \frac{\partial E_r}{\partial x} \delta x \\
&= -\frac{1}{Z} \frac{1}{\beta} \frac{\partial}{\partial x} \left(\sum_r e^{-\beta E_r(x)} \delta x \right) \\
&= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial x} \delta x,
\end{aligned} \tag{2.59}$$

which gives us the total work done on the system by changing one of the parameters x . x in principle can be any kind of external parameter. In section 2.3.4 when we discuss paramagnets, we see that it is the external magnetic field H . For now, let's choose x to be the *volume* V , then Eq. (2.59) becomes

$$dW = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \delta V \tag{2.60}$$

or, using our old thermodynamic formula for mechanical work

$$dW = -PdV, \tag{2.61}$$

we see that we can then *define* the pressure as

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}. \tag{2.62}$$

- **Combined systems.** One of the nice things about the partition function is that if we put two systems with partition functions Z_A and Z_B together *and* they don't interact, then the partition functions of the combined system is simply $Z = Z_A Z_B$. We can see this as follows. Let the microstates of systems A and B be labeled r_A and r_B respectively. The combined system's microstates can then be labeled by the pair of numbers (r_A, r_B) , and the energy of these microstates is simply the sum of the two individual energies⁸

$$E_{r_A, r_B} = E_{r_A} + E_{r_B} \tag{2.63}$$

and its partition function Eq. (2.43) is

$$\begin{aligned}
Z &= \sum_{r_A, r_B} e^{-\beta E_{r_A, r_B}} \\
&= \sum_{r_A, r_B} e^{-\beta E_{r_A} - \beta E_{r_B}} \\
&= \left(\sum_{r_A} e^{-\beta E_{r_A}} \right) \left(\sum_{r_B} e^{-\beta E_{r_B}} \right) \\
&= Z_A Z_B.
\end{aligned} \tag{2.64}$$

The mean energy Eq. (2.54) simply follows

$$\bar{E} = \bar{E}_A + \bar{E}_B. \tag{2.65}$$

⁸If the particles interact, the total energy per pair is $E_{r_A, r_B} = E_{r_A} + E_{r_B} + V(r_A, r_B)$ where V is the interaction energy.

2.3.3 Entropy of canonical ensembles

From the last section, we see that the partition function is in general a function of β and some external parameter x which regulates the energy per microstate $E_r(x)$. Suppose now the system described by $Z(\beta, x)$ undergoes a quasi-static (reversible) process, we want to consider its differential (of its log)

$$d \ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta . \quad (2.66)$$

Using the relations for the mean energy and work Eq. (2.54) and Eq. (2.59), we can write it as

$$\begin{aligned} d \ln Z &= -\beta d\bar{W} - \bar{E} d\beta \\ &= -\beta d\bar{W} + \beta d\bar{E} - d(\bar{E}\beta) \end{aligned} \quad (2.67)$$

where we have used $d(\bar{E}\beta) = \beta d\bar{E} + \bar{E} d\beta$ in the 2nd line. Rearranging, we get

$$d(\ln Z + \beta\bar{E}) = \beta(-d\bar{W} + d\bar{E}). \quad (2.68)$$

Now using the 1st law of thermodynamics Eq. (1.11), which is simply imposing energy conservation, we reexpress the RHS as heat transfer $-d\bar{W} + d\bar{E} = d\bar{Q}$,

$$d(\ln Z + \beta\bar{E}) = \beta d\bar{Q}. \quad (2.69)$$

Comparing Eq. (2.69) with Eq. (1.19) $TdS = dQ$ (for reversible processes), we can identify

$$\boxed{S \equiv k_b(\ln Z + \beta\bar{E})} . \quad (2.70)$$

This is the entropy of the canonical ensemble, and since $\bar{E} = -\partial \ln Z / \partial \beta$, it can be expressed entirely in terms of the partition function

$$S = k_b \left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right) , \quad (2.71)$$

and hence using $k_b T = \beta^{-1}$ again (homework)

$$S = k_b \frac{\partial}{\partial T} (T \ln Z). \quad (2.72)$$

This relationship is analog to the entropy of the microcanonical ensemble Eq. (2.6) as we have previously seen in section 2.2 – we will discuss this further below.

Now using $k_b T = \beta^{-1}$, we can rewrite Eq. (2.70) as

$$\bar{E} - TS = -k_b T \ln Z \quad (2.73)$$

the LHS of which is just our definition for the **Helmholtz free energy** Eq. (1.30)

$$\boxed{F \equiv -k_b T \ln Z} . \quad (2.74)$$

Combined with the relationship between the energy Eq. (2.54), $\bar{E} = -\partial \ln Z / \partial \beta$, these provide to us a direct connection of the thermodynamic potentials and the partition function. You can further show (homework) that we can use Eq. (1.32) to derive Eq. (2.62).

Let's discuss the relationship of the entropy of the canonical ensemble with its microcanonical counterpart Eq. (2.6), $S = k_b \ln \Omega(E)$. As we have discussed in at the end of section 2.3.1, the canonical ensemble becomes the microcanonical ensemble in the limit of the number of particles $N \rightarrow \infty$. In this limit, the dispersion $\langle \Delta E^2 \rangle \rightarrow 0$, so almost all the microstates will be at (or very close to) the mean energy $E = \bar{E}$. This means that sum over energies of the partition function Z will be dominated by the \bar{E} ,

$$Z = \sum_r e^{-\beta E_r} = \Omega(\bar{E}) e^{-\beta \bar{E}} \quad (2.75)$$

where $\Omega(\bar{E})$ is the number of microstates in \bar{E} , which is in this limit, (almost) all the microstates. Plugging this into Eq. (2.71), we obtain

$$S = k_b \ln \Omega(\bar{E}) \quad (2.76)$$

which is the entropy for the microcanonical ensemble as asserted.

Finally, let's rewrite the entropy in terms of the probabilities P_r as defined in Eq. (2.42). From Eq. (2.70), and using the definition of the mean energy Eq. (2.48), we have

$$\begin{aligned} S &= k_b \left(\ln Z + \beta \sum_r P_r E_r \right) \\ &= k_b \left(\ln Z - \sum_r P_r \ln(Z P_r) \right) \\ &= k_b \left(\ln Z - \ln Z \sum_r P_r - \sum_r P_r \ln P_r \right) \end{aligned} \quad (2.77)$$

and using $\sum_r P_r = 1$ since probabilities are conserved, we get

$$\boxed{S \equiv -k_b \sum_r P_r \ln P_r} . \quad (2.78)$$

which is often used as the starting point for discussion of the canonical ensemble.

Indeed, all instances of energies E_r have been cancelled from Eq. (2.78). The beauty of the entropy expressed purely as a function of the probabilities P_r is that we have abstracted away the physical system – as long as we have the *information* about the probabilities regardless of the underlying physics, we can compute the entropy. This is sometimes called the **Shannon Entropy**, named after the great mathematician Claude Shannon who founded the discipline of Information Theory⁹.

2.3.4 An example : Paramagnetism

Let's consider the **paramagnet**. Paramagnets are systems where, when an external magnetic field is applied on it, it induces internal magnetic fields due to the presence of non-zero magnetic moments μ of the particles. Physically, in materials where *unpaired electrons* (i.e. electrons in the orbits of atoms which occupy the orbital singly) are present are paramagnets, due to the non-zero magnetic moments μ (don't confuse this μ for the chemical potential μ) of the electrons (in paired electrons, the moment cancel).

We can model such a system as a grid of spin-1/2 particles. Each particle are held in place (think of them as electrons on a fixed crystal lattice), but are allowed to be in a spin-up \uparrow or spin-down \downarrow state. If we apply a magnetic field $H > 0$ which is parallel to the spin of the electron and pointing in the \uparrow direction, then each electron can possess either of the following energies depending on whether it is parallel or anti-parallel to the direction of the magnetic field

$$E_{\uparrow} = -\mu H , E_{\downarrow} = \mu H. \quad (2.79)$$

Let's consider the case of a *single* electron surrounded by a “heat bath” of a lattice of electrons (see left figure of Fig. 2.11). The partition function Z is a sum of all possible states – there are only two possible microstates in this case, \uparrow or \downarrow ,

$$\begin{aligned} Z &= e^{-\beta E_{\downarrow}} + e^{-\beta E_{\uparrow}} \\ &= e^{-\beta \mu H} + e^{\beta \mu H} \\ &= 2 \cosh(\beta \mu H) . \end{aligned} \quad (2.80)$$

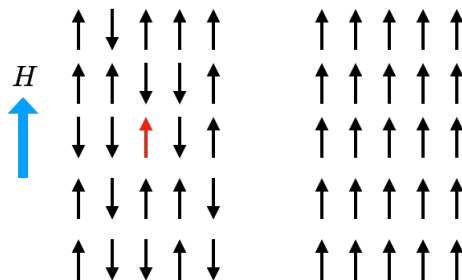


Figure 2.11: The left figure is the system of a single electron (red) dipole in a “heat bath” of a crystal lattice of electron dipoles. The right figure is the configuration of a system of electrons when the external magnetic field H is large.

The probabilities of finding the states are given by Eq. (2.44),

$$P_{\uparrow} = \frac{1}{Z} e^{\beta\mu H}, \quad P_{\downarrow} = \frac{1}{Z} e^{-\beta\mu H}. \quad (2.81)$$

For very weak field $\beta\mu H \ll 1$, or $H \ll k_b T/\mu$, $P_{\uparrow} = P_{\downarrow} = 0.5$ – the electron has an equal chance of being in either state unsurprisingly. Now as we dial up the amplitude of H , the probability for P_{\uparrow} increases rapidly while that of P_{\downarrow} decreases, until when $H \gg k_b T/\mu$, $P_{\uparrow} = 1$ and $P_{\downarrow} = 0$. At this point, the electron wants to align with the magnetic field, which is exactly as we expected.

We can compute the mean energy of the system, using Eq. (2.48),

$$\bar{E} = \frac{\mu H}{Z} (e^{-\beta\mu H} - e^{\beta\mu H}) = -\mu H \tanh \beta\mu H. \quad (2.82)$$

This can also be computed using Eq. (2.54).

Notice that in this case, the magnetic field H is an external parameter, we can compute the work done on the system when we dial up the magnetic field using the “generalized work” formula (Eq. (2.59))

$$dW = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial x} \delta x \quad (2.83)$$

with the external parameter $x \equiv H$ to write

$$\begin{aligned} dW &= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial H} dH \\ &= -\mu \tanh(\beta\mu H) dH \\ &\equiv -\bar{\mu} dH, \end{aligned} \quad (2.84)$$

where we have defined

$$\bar{\mu} \equiv \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} = \mu \tanh(\beta\mu H) \quad (2.85)$$

as the **mean magnetic moment** of the system.

Here, it is worth noting that in page 37 we have used the same generalized work equation Eq. (2.59), with $x \equiv V$ to define the pressure

$$P \equiv \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \quad (2.86)$$

i.e. the change in the external parameter is the change in volume. Our use of the same equation to define the mean magnetic moment means that there is an equivalence between the pressure and the mean magnetic moment

$$P \leftrightarrow \bar{\mu}, \quad dV \leftrightarrow dH. \quad (2.87)$$

⁹For example, consider the sentence word “ABACADABBA”. There are 10 characters in the word, with 5 A’s, 3 B’s, 1 C and 1 D. So if we pick a character randomly from the word, there is a 50% chance of A, 30% of B, and 10% of C and D. One can then compute the *information entropy* as $S = -\sum_r P_r \ln P_r$ where $P_A = 0.5$, $P_B = 0.3$, $P_C = P_D = 0.1$.

We will see the importance of this in Chapter 5.

Generalizing the single electron dipole to N number of electron dipoles is completely straightforward, as long as we assume that the interactions between the electrons are very weak. In this case, as we have seen earlier in section 2.3.2, the total partition function is just the product of N partition functions of single electrons, hence

$$Z_N \equiv \prod_N Z = 2^N \cosh^N(\beta\mu H) \quad (2.88)$$

The other results follow straightforwardly. The mean energy is

$$\bar{E}_N = -\frac{\partial \ln Z_N}{\partial \beta} = -N\mu H \tanh(\beta\mu H) \quad (2.89)$$

which is the additive sum over all mean energies of individual electrons as expected $\bar{E}_N = \sum_N \bar{E}$. The total magnetic moment $\bar{\mu}_N$ is also an additive sum (which you can show yourself using Eq. (2.59))

$$\bar{\mu}_N = N\bar{\mu} = N\mu \tanh(\beta\mu H). \quad (2.90)$$

The **magnetization** M is defined to be the magnetic moment per volume

$$M = \frac{\bar{\mu}_N}{V} = \frac{N}{V} \mu \tanh \frac{\mu H}{k_b T}, \quad (2.91)$$

where we have restored $k_b T = \beta^{-1}$. In the limit of weak magnetic field, $\mu H \ll k_b T$, $\tanh \mu H/k_b T \sim \mu H/k_b T$ becomes linear, and the magnetization is

$$M \sim \frac{N\mu^2 H}{k_b V T}, \text{ for weak field } \mu H \ll k_b T. \quad (2.92)$$

The **magnetic susceptibility** measures how paramagnetic a material can be (zero for non-paramagnetic material), and is defined as

$$\chi = \frac{\mu_0 M}{H} \quad (2.93)$$

where μ_0 is the vacuum permeability of the material. In the weak field limit, this is

$$\chi = \frac{N\mu^2 \mu_0}{k_b V T}. \quad (2.94)$$

Notice that the susceptibility is $\chi \propto 1/T$, which is known as **Curie's Law**¹⁰. This is the familiar result that tells you that a magnet loses its properties when you heat it up in an oven (don't use a microwave though), as you were taught in pre-skool.

As we increase the magnitude of H , χ loses its linearity, but since $\lim_{x \rightarrow \infty} \tanh x \rightarrow 1$, the magnetization asymptotes to

$$M = \frac{\mu N}{V}, \text{ for strong field } \mu H \gg k_b T. \quad (2.95)$$

This is not surprising – once all the electron dipoles are aligned in one direction as in the right figure of Fig. 2.11, increasing H will not change its configuration. The behavior of M as a function of field strength H is plotted in Fig. 2.12.

Finally, it is instructive to compute the entropy of the system given by Eq. (2.70), which is

$$\begin{aligned} S &= k_b (\ln Z + \beta \bar{E}) \\ &= k_b N [\ln 2 + \ln \cosh(\beta\mu H) - \beta\mu H \tanh(\beta\mu H)]. \end{aligned} \quad (2.96)$$

Consider when the field is very weak $\beta\mu H \ll 1$, the last two terms of Eq. (2.96) becomes very small, and the entropy is then

$$S = k_b \ln 2^N. \quad (2.97)$$

¹⁰Named after Pierre Curie. Pop quiz: how many Nobel Prizes did the Curie family earn in total?

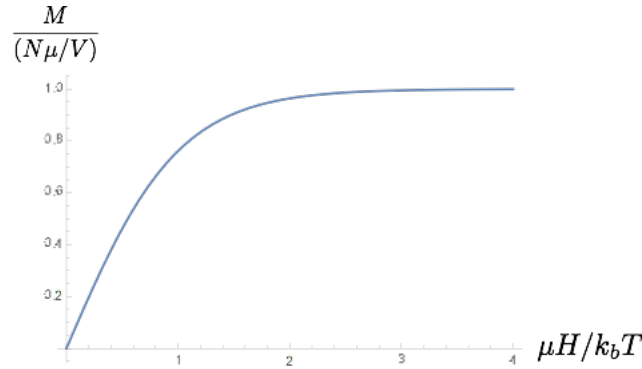


Figure 2.12: The magnetization M as a function of field strength H . When H is weak, $\mu H \ll k_b T$ is linearly a function of H . At very strong fields $\mu H \gg k_b T$, the magnetization is a constant.

In this limit, physically since the field is very small, the energy per electron $\mu H \sim 0$, which means that all the microstates will have roughly the same energy. In other words, the microstate resembles that of a microcanonical ensemble with $E \sim 0$. Every electron has an equal chance of being spin \uparrow or spin \downarrow , so the total number of possible microstates must be 2^N , completely consistent with Eq. (2.97) which is the microcanonical ensemble entropy with statistical weight $\Omega = 2^N$.

In the limit of very strong field however, $\beta\mu H \equiv x \gg 1$, we have

$$\lim_{x \rightarrow \infty} \tanh x \rightarrow 1, \quad \lim_{x \rightarrow \infty} \cosh x \rightarrow \frac{1}{2} e^x, \quad (2.98)$$

we have

$$S = kN \left[\ln 2 + \ln \frac{e^x}{2} - x \right] = 0. \quad (2.99)$$

The entropy vanishes, and the statistical weight is 1 – there is only one possible configuration (microstate) which is that of all the electron dipoles possessing spin \uparrow .

2.4 The grand canonical ensemble

So far we have discussed mostly system where the number of particles N is a constant. We now relax this condition, and allow the number of particles to vary. As you might expect, this will greatly increase the size of any ensemble. In general, there can be particles of different species, but for simplicity we will restrict our attention to just one species – the generalization is straight forward and you will be asked to do that in a homework problem.

As we have studied in section 1.4, the chemical potential of a particle μ , is the change in the mean energy¹¹ to create (or destroy) a single particle at fixed S and V

$$\mu \equiv \left(\frac{\partial \bar{E}}{\partial N} \right)_{S,V}. \quad (2.100)$$

In the canonical ensemble, we placed the system in a heat bath of fixed temperature T – the walls are diathermal. We now allow the particles to flow through in and out of the system. The heat bath in this case is fixed at constant T and constant μ . Thus the system can exchange both energy and particles with the environment.

Such an ensemble is called the **grand canonical ensemble** (“grand” since it is usually bigger than the canonical ensemble), which is

¹¹Recall that in statistical mechanics, the energy fluctuates, so we use the mean energy.

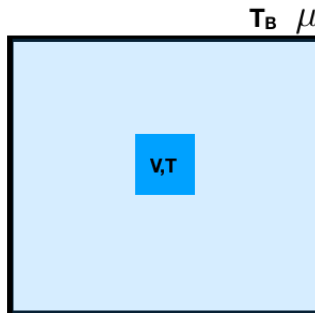


Figure 2.13: The grand canonical ensemble describes a system bathed in an environment with fixed temperature T and chemical potential μ , with system allowed to exchange energy and particles with the environment.

The grand canonical ensemble is the set of microstates at constant volume V , temperature T and chemical potential μ .

The probability of finding microstate r must now depend on its energy E_r and also its particle number N_r . We will now assert that it is as follows

$$P_r \equiv \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}, \quad (2.101)$$

where the **grand canonical partition function** \mathcal{Z} is given by

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}, \quad (2.102)$$

Comparing these equations to the canonical ensemble versions Eq. (2.42) and Eq. (2.43), we see that we have replaced $E_r \rightarrow E_r - \mu N_r$. To see that this is the case, we run through the arguments that we have discussed for the canonical ensemble in section 2.3. In addition to the conservation of energy $E_0 = E_B + E_r$, we have the conservation of particle number $N_0 = N_B + N_r$, so the probability must be

$$P_r = \text{const} \times \Omega_B(E_0 - E_r, N_0 - N_r), \quad (2.103)$$

where $\Omega_B(E_0 - E_r, N_0 - N_r)$ is the statistical weight of the environment. Expanding the entropy around E_0 and N_0 , we have

$$S_B(E_0 - E_r, N_0 - N_r) = S_B(E_0, N_0) - \left(\frac{\partial S_B}{\partial E_0} \right)_{E_0, N_0} E_r - \left(\frac{\partial S_B}{\partial N_0} \right)_{E_0, N_0} N_r + \dots \quad (2.104)$$

where

$$\left(\frac{\partial S_B}{\partial E_0} \right)_{E_0, N_0} = \frac{1}{T_B}, \quad (2.105)$$

as usual. Meanwhile, we define the partial derivative with respect to particle number

$$\left(\frac{\partial S_B}{\partial N_0} \right)_{E_0, N_0} \equiv -\frac{\mu}{T_B}. \quad (2.106)$$

We will see soon that Eq. (2.106) is indeed equivalent to Eq. (2.100). Using the definition of entropy $S = k_b \ln \Omega_B$ (i.e. the microcanonical definition, not the canonical definition, since the bath is a heat sink so doesn't suffer from energy fluctuations) immediately leads to Eq. (2.101).

We can then roll out the formulas quickly. The mean total energy $\langle E \rangle - \mu \langle N \rangle$

$$\langle E \rangle - \mu \langle N \rangle = \sum_r P_r (E_r - \mu N_r) = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}, \quad (2.107)$$

while the **mean particle number** is

$$\langle N \rangle \equiv \sum_r P_r N_r = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}. \quad (2.108)$$

To derive the entropy, we run through the arguments of section 2.3.3, with the additional variable μ . Viz

$$\begin{aligned} d \ln \mathcal{Z} &= \frac{\partial \ln \mathcal{Z}}{\partial x} dx + \frac{\partial \ln \mathcal{Z}}{\partial \beta} d\beta + \frac{\partial \ln \mathcal{Z}}{\partial \mu} d\mu \\ &= -\beta dW - (\langle E \rangle - \mu \langle N \rangle) d\beta + \beta \langle N \rangle d\mu \\ &= -\beta dW - d(\beta \langle E \rangle) + \beta d\langle E \rangle + d(\mu \beta \langle N \rangle) - \beta \mu d\langle N \rangle \end{aligned} \quad (2.109)$$

where we have integrated by parts as usual via $Y dX = d(XY) - X dY$ etc. Rearranging, we get

$$d(\ln \mathcal{Z} + \beta \langle E \rangle - \mu \beta \langle N \rangle) = \beta(-dW + d\langle E \rangle - \mu d\langle N \rangle). \quad (2.110)$$

Now, using the first law with the chemical potential defined in Eq. (1.57), the right hand side becomes βdQ , which means that using the relation $T dS = dQ$, we can identify the entropy for the grand canonical ensemble as

$$\boxed{S = k_b (\ln \mathcal{Z} + \beta \langle E \rangle - \beta \mu \langle N \rangle)}. \quad (2.111)$$

Again, you can show that (homework) this can be neatly written in analogy to Eq. (2.72),

$$S = k_b \frac{\partial}{\partial T} (T \ln \mathcal{Z}). \quad (2.112)$$

Finally, just as in the canonical ensemble, we can express the Landau potential Eq. (1.63) or grand canonical potential (explaining the name as we promised back in page 19) as

$$\langle E \rangle - TS - \mu \langle N \rangle = -k_b T \ln \mathcal{Z} \quad (2.113)$$

so we get

$$\boxed{\Psi = -k_b T \ln \mathcal{Z}}. \quad (2.114)$$

As with the energy, the particle number of the system fluctuates as it can exchange particles with its environment. The mean fluctuations can be similarly defined as

$$\langle \Delta N^2 \rangle \equiv \langle (N - \langle N \rangle)^2 \rangle \quad (2.115)$$

which you can show in a homework problem that this is given by

$$\langle \Delta N^2 \rangle = \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu}. \quad (2.116)$$

And just like energy, in the limit of very large N , this fluctuation is very small and scales like a Poisson distribution

$$\frac{\sqrt{\langle \Delta N^2 \rangle}}{\langle N \rangle} \sim \frac{1}{\sqrt{N}}. \quad (2.117)$$

2.5 Some final remarks

2.5.1 Ensemble Averages of energy and particle number

The fact that the dispersion for the energy $\langle \Delta E^2 \rangle$ and particle number is so small $\langle \Delta N^2 \rangle$ means that the system often spend most of its time in its ensemble averages $\langle E \rangle$ and $\langle N \rangle$. So sometimes when we talk about the (grand) canonical ensembles, we often drop the mean brackets $\langle E \rangle$ or $\langle N \rangle$ and simply refer to them as E and N . We will restore the brackets when there is a chance of misunderstanding. You should get familiar with the context (i.e. don't just blindly plug formulas in because they "look alike").

2.5.2 Discrete to continuous distributions

So far we have expressed the partition function as a sum over discrete microstates. To be specific, the microstates of the canonical ensemble are labeled by its energy Eq. (2.43)

$$Z = \sum_r e^{-\beta E_r} . \quad (2.118)$$

What about continuous distributions? For example, classically, the canonical ensemble of a single particle, whose energy of a microstate is given by its kinetic energy

$$E_r = \frac{|\mathbf{p}|^2}{2m} \quad (2.119)$$

where \mathbf{p} is its momentum and m is its mass. Since \mathbf{p} is continuous, we replace the sum with an integral

$$\sum_{E_r} \rightarrow \mathcal{N} \int d^3x \int d^3p , \quad (2.120)$$

where the first integral is over the volume to account for all the possible locations the particle can be, and the second over all possible momenta – recall that the state of a particle is given by both its momentum and position.

What is the normalization constant \mathcal{N} ? Notice that the sum counts microstates, so is *dimensionless*, but the integral $\int d^3x \int d^3p$ has dimensions of $[L^6][M^3S^{-3}]$. So \mathcal{N} has to be some *dimensionful* constant which has dimensions of $[L^{-6}][M^{-3}S^3]$ to cancel this. This gives us a clue – the Planck's constant h , has dimensions of $[L^2MS^{-1}]$, so perhaps we can choose

$$\mathcal{N} = \frac{1}{h^3} = \frac{1}{(2\pi\hbar)^3} , \quad (2.121)$$

to cancel out the dimensions and give us a final dimensionless number?

As it turns out, our guess is exactly right, although we will never get this through classical physics considerations – the Planck constant h tells us that the reason must be due to the fact that we live in a quantum mechanical world. We will discuss this in greater detail when we consider quantum gasses in Chapter 4, but let's do a quick derivation here to convince you.

For simplicity, consider just the case of a 1 dimensional box with length a with *periodic boundary conditions*¹². The time-independent Schrodinger's equation with potential $U(x) = 0$ is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = E_n\psi_n , \quad (2.122)$$

where ψ_n the eigenfunction with energy E_n . Expressing the wavevector

$$k_n = \sqrt{\frac{2mE_n}{\hbar^2}} , \quad (2.123)$$

as usual, the solution to the eigenfunction equation Eq. (2.122) is

$$\psi_n(x) = \mathcal{A}e^{ik_nx} , \quad (2.124)$$

where \mathcal{A} is some normalization factor. Imposing periodic boundary conditions $\psi(x) = \psi(x+a)$ gives us the quantization condition

$$k_n = \frac{2\pi}{a}n , \quad n = 0, \pm 1, \pm 2, \dots \quad (2.125)$$

¹²The physics does not change if we impose other conditions, for example we can instead consider an infinite square well potential with size a .

as usual. The momentum p is given by

$$p = \hbar k = \frac{2\hbar\pi n}{a}, \quad n = 0, \pm 1, \pm 2, \dots \quad (2.126)$$

so the energy eigenstates are given by

$$E_n = \frac{p^2}{2m} = \frac{4\hbar^2\pi^2 n^2}{2ma^2}. \quad (2.127)$$

Meanwhile, the number of states between the momentum p and $p + \Delta p$ is given by Eq. (2.126), i.e.

$$\Delta p = \frac{2\hbar\pi}{a} \Delta n, \quad (2.128)$$

which we can do if we take n to be a very large number so that the density of states are dense. The number of states is then

$$\Delta n = \frac{a}{2\hbar\pi} \Delta p. \quad (2.129)$$

Meanwhile, taking the integral over the states Eq. (2.120) in the limit of all L but only within p and $p + \Delta p$, we have

$$\Delta n = \mathcal{N} \int_a dx \int_{\Delta p} dp = \mathcal{N} a \Delta p. \quad (2.130)$$

Comparing Eq. (2.129) with Eq. (2.130), we see that the normalization constant is

$$\mathcal{N} = \frac{1}{2\pi\hbar}, \quad (2.131)$$

in a 1 dimensional system. Using symmetry, we can deduce that for a 3D box, the normalization constant must be $1/(2\pi\hbar)^3$, as we guessed earlier.

One intuitive way to understand this is to recall Heisenberg's uncertainty principle

$$\Delta p \Delta x \sim 2\pi\hbar \quad (2.132)$$

which tell us that a particle's position and momentum cannot be determined arbitrarily accurately – we can only “pack” a particle into a phase space region with volume $(2\pi\hbar)^3$. This means that for any phase space volume $V = \Pi_i \int d^3\mathbf{x}_i d^3\mathbf{p}_i$, the number of grid points is $\mathcal{N} \sim V/(2\pi\hbar)^3$, which is a humongous number, but importantly, a *discrete* one.

Putting everything together, the partition function for a single particle labeled i is then

$$Z_i = \frac{1}{(2\pi\hbar)^3} \int d^3x_i \int d^3p_i e^{-\beta E_i(\mathbf{p}_i, \mathbf{x}_i)}. \quad (2.133)$$

For N number of particles, this become

$$Z = \prod_{i=1}^{i=N} Z_i = \frac{1}{(2\pi\hbar)^{3N}} \int d^3x_1 \dots d^3x_N \int d^3p_1 \dots d^3p_N e^{-\beta \sum_{i=1}^{i=N} E_i}. \quad (2.134)$$

Eq. (2.134) can be quite intimidating, and it should be as it contains a lot of information.

Chapter 3

Classical Gas

In this section, we will use our statistical methods to investigate the “classical gas”. What we mean by “classical” is that individual particles obey classical equations of motion, such as Newton’s equations, Maxwell equations or the Wave equation.

3.1 Ideal gas

An **ideal gas**, as you have learned in high-school, is a collection of particles which do not interact with one another – they do not exert long distance force on nor collide with each other. They *do* interact with the surroundings (e.g. the box they are placed in), and interact with external forces, so they can exchange heat with their surroundings and we can do work on them. Despite these simplifications, the ideal gas is a very good model for many gasses in common conditions. Examples of gasses that are approximately ideal includes the air in this room, the hydrogen atmosphere of the sun, the sparse gas between galaxies etc. In your thermal physics class, you are taught that the equation of state for the ideal gas is given by Eq. (1.7)

$$T = \frac{PV}{Nk_b}. \quad (3.1)$$

We will now roll out the machinery we studied in Chapter 2 and derive this equation.

Consider a single particle of mass m . For now, let’s consider a “point” particle, so it cannot vibrate or rotate. Hence the only **degree of freedom** for this particle is then translational – it can move in the three axial directions (x, y, z) . The energy of the particle is given by its translational kinetic energy

$$E_1 = \frac{\mathbf{p}^2}{2m}. \quad (3.2)$$

Let’s put this particle in a box. The box is surrounded by a heat bath of temperature T . The particle bounces around the box, and as we mentioned above, is allowed to exchange energy with the box and hence the heat bath. What are the possible microstates for this particle? In other words, we want to derive the partition function of this *canonical ensemble*.

The partition function Eq. (2.50) is

$$Z_1 = \sum_{\text{all microstates}} e^{-\beta E_1} = \sum_{\text{all microstates}} e^{-\beta \mathbf{p}^2/2m}. \quad (3.3)$$

The number of microstates of this single particle is the span of all possible momenta at all possible positions of its restricted *phase space* that we have discussed in section 2.1. Following section 2.5.2, the sum Eq. (3.3) becomes an integral since \mathbf{p} and \mathbf{x} are continuous

$$Z_1 \rightarrow \frac{1}{(2\pi\hbar)^3} \int d^3\mathbf{x} d^3\mathbf{p} e^{-\beta \mathbf{p}^2/2m}. \quad (3.4)$$

As explained, we have added an extra factor $(2\pi\hbar)^3$ into the partition function. The phase space is divided into cells of size $\Delta\mathbf{p}\Delta\mathbf{x} \sim (2\pi\hbar)^3$, so the total number of grid points is then divided by $(2\pi\hbar)^3$.

Since the integrand is independent of position \mathbf{x} , the volume integral is trivial

$$\int d^3\mathbf{x} \rightarrow V \quad (3.5)$$

where V is the volume of the box. Meanwhile, the momentum integrand is

$$\begin{aligned} \int d^3\mathbf{p} e^{-\beta\mathbf{p}^2/2m} &= \int_{-\infty}^{\infty} dp_x dp_y dp_z e^{-\beta(p_x^2+p_y^2+p_z^2)/2m} \\ &= \left(\frac{2m\pi}{\beta}\right)^{3/2}, \end{aligned} \quad (3.6)$$

where we have used the gaussian integral (see Appendix A)

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad (3.7)$$

in the 2nd line. Putting everything together, and rewriting $k_bT = \beta^{-1}$, the partition function for a single massive particle is then

$$Z_1 = V \left(\frac{mk_bT}{2\pi\hbar^2}\right)^{3/2}. \quad (3.8)$$

For N non-interacting particles, as we have already seen in Eq. (2.64), the partition functions simply multiply¹ so the total partition function for N particles is

$$Z = \prod_N Z_1 = V^N \left(\frac{mk_bT}{2\pi\hbar^2}\right)^{3N/2}. \quad (3.9)$$

The partition function Eq. (3.9) contains almost all the thermodynamical information we need. To derive the equation of state Eq. (3.1), we need to know the Helmholtz free energy Eq. (2.74)

$$F = -k_bT \ln Z. \quad (3.10)$$

The pressure is then given by Eq. (1.32), $P = -(\partial F/\partial V)_T$, or

$$\begin{aligned} P &= k_bT \left(\frac{\partial \ln Z}{\partial V}\right)_T \\ &= \frac{Nk_bT}{V} \end{aligned} \quad (3.11)$$

which is exactly the equation of state for the ideal gas. Notice that, the complicated factor,

$$\lambda \equiv \sqrt{\frac{2\pi\hbar^2}{mk_bT}}, \quad (3.12)$$

such that $Z = V^N/\lambda^{3N}$ has dropped out. λ has the dimension of length, and is called **the thermal de Broglie wavelength**. We will see why this is related to the quantum mechanical de Broglie wavelength you have learned in quantum mechanics

$$\lambda_{dB} = \frac{2\pi\hbar}{|\mathbf{p}|}, \quad (3.13)$$

in the following section.

¹Actually, this is not quite right, but we postpone the discussion till later.

3.1.1 Equipartition Theorem

Let's compute the mean energy of the system using Eq. (2.54)

$$\begin{aligned}\bar{E} &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{3}{2}Nk_bT.\end{aligned}\tag{3.14}$$

Using Eq. (1.50), the heat capacity of the monoatomic ideal gas is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk_b\tag{3.15}$$

as you might have learned in your thermal physics class.

Now, you might have learned that the energy per degree of freedom of each particle is

$$E_{\text{dof}} = \frac{1}{2}k_bT.\tag{3.16}$$

In our system, each particle can travel in 3 spatial directions, hence there are 3 translational degrees of freedom, so we get $\bar{E} = (3/2)k_bT$. If these particles can rotate, then there are 3 axes of rotations, adding 3 more degrees of freedom into the system so the mean energy becomes $\bar{E} = 3Nk_bT$. If the particles can vibrate, they will get more degrees of freedom and so forth. This is usually called the **Equipartition Theorem**, and it is an incredibly powerful theorem in *classical mechanics* that is very general².

The proof is not very hard, but requires a bit of knowledge of classical mechanics, and some tricky calculus which you have enough knowledge to do. Consider a single particle of mass m . The energy of a particle (or any system in general) is given by its **Hamiltonian** $H(p_i, q_i)$ where p_i and q_i are its generalized momentum and generalized position respectively, with $i = 1, 2, 3$ labeling the number of dimensions. For example, for the particle we considered earlier with 3 translational degrees of freedom the Hamiltonian is

$$H(p_i, q_i) = \sum_i \frac{p_i^2}{2m}.\tag{3.17}$$

The Hamiltonian is the energy of the particle, so the probability of the particle at phase point (p_i, q_i) is given by Eq. (2.42)

$$P(p_i, q_i) = \frac{1}{Z}e^{-\beta H(p_i, q_i)}, \quad Z = \mathcal{N} \int \left(\prod_{i,j} dp_i dq_j \right) e^{-\beta H(p_i, q_i)},\tag{3.18}$$

where \mathcal{N} is a normalization constant which is some power of $(2\pi\hbar)$ which depends on the dimensions of the system. Now, as it turns out, whether it is p_i or q_i is also not that important, and we can collect them into a single variable $x_i \in (p_i, q_i)$. For example, we can write $x_1 = p_x, x_2 = p_y, x_3 = p_z, x_4 = q_x, x_5 = q_y, x_6 = q_z$. The probability becomes

$$P(x_i) = \frac{1}{Z}e^{-\beta H(x_i)}, \quad Z = \mathcal{N} \int \left(\prod_i dx_i \right) e^{-\beta H(x_i)}.\tag{3.19}$$

Conservation of probability means that the sum over the probabilities must be 1, or

$$\mathcal{N} \int \left(\prod_i dx_i \right) P(x_i) = 1,\tag{3.20}$$

²Eq. (3.16) is actually not always true – in the sense that not all d.o.f. possesses $k_bT/2$ energy, although it is a good rule of thumb.

and hence

$$\begin{aligned} \mathcal{N} \int P(x_i) \prod_i dx_i &= \frac{\mathcal{N}}{Z} \int e^{-\beta H(x_i)} \prod_i dx_i \\ &= \frac{\mathcal{N}}{Z} \left[\int d \left(e^{-\beta H(x_i)} x_k \right) \prod_{i,i \neq k} dx_k + \int e^{-\beta H(x_i)} \beta \frac{\partial H}{\partial x_k} x_k \prod_i dx_i \right]. \end{aligned} \quad (3.21)$$

Here, we have integrated by parts for some choice of x_k . For example, for a two variable function $f(x, y)$, you can show that integrating by parts the x variable gives you

$$\int f(x, y) dx dy = \int d(f(x, y)x) dy - \int x \frac{\partial f}{\partial x} dx dy. \quad (3.22)$$

The first term of Eq. (3.21) is the boundary term, so we evaluate it at the boundaries, say at $x_k(\text{max})$ and $x_k(\text{min})$. Mathematically, the boundary is not necessarily zero, but *physically*, the boundaries values are where $H(x_k) \rightarrow \infty$ – i.e. very large energies. For example, if x_k is the momentum, then the boundaries are where the momenta are very big – which means that the probability of finding them $P_r \propto e^{-\beta H}$ is very small since $H = p^2/m \rightarrow \infty$. This simply means that, for a given distribution of particles, ultra relativistic particles at very high energy are extremely rare (not surprisingly). Thus in general, we can set this boundary term to zero. This leaves us with

$$\mathcal{N} \int P(x_i) \prod_i dx_i = \frac{\mathcal{N}}{Z} \int e^{-\beta H(x_i)} \beta \frac{\partial H}{\partial x_k} x_k \prod_i dx_i = \beta \left[\int P(x_i) \frac{\partial H}{\partial x_k} x_k \prod_k dx_k \right] = 1. \quad (3.23)$$

But comparing this equation to Eq. (2.47), we see that the expression in the square brackets of the last term is just the ensemble average of the property $x_k(\partial H/\partial x_k)$, hence

$$\left\langle x_k \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{\beta} = k_b T. \quad (3.24)$$

Eq. (3.24) is the formal statement of the equipartition theorem, it states the ensemble average of the quantity $x_k(\partial H/\partial x_k)$ is equal to $k_b T$. Notice that *we have not done a single integration* (except for the integration by parts), and we have not specified H at all. This is a very general theorem.

Now we can use Eq. (3.24) to prove the theorem. The ensemble average of each translational degree of freedom is, say for the x direction is,

$$\begin{aligned} \langle H(p_x) \rangle &= \frac{1}{2m} \langle p_x^2 \rangle \\ &= \frac{1}{2m} \left\langle m p_x \frac{\partial H}{\partial p_x} \right\rangle \\ &= \frac{1}{2} k_b T. \end{aligned} \quad (3.25)$$

So for 3 translational axes, we have $\bar{E} = 3/2 k_b T$ as we asserted.

Finally, we hark back to the question of why we call λ the thermal de Broglie wavelength. Since the mean energy per particle is $(1/2)k_b T$, this gives us $p^2/2m = (1/2)k_b T$, or $p^2 = m k_b T$. Plugging this into the quantum mechanical de Broglie relation Eq. (3.13), we obtained the thermal de Broglie wavelength as we discussed earlier, up to a factor of $\sqrt{2\pi}$. Thus the thermal de Broglie wavelength is the *mean* de Broglie wavelength.

3.1.2 An example : diatomic gasses

For **diatomic** gasses, we can model each diatomic particle as consisting of two atoms 1 and 2 connected together by a spring, with spring constant k (see Fig. 3.1). We can also model the diatom as a semi-rigid

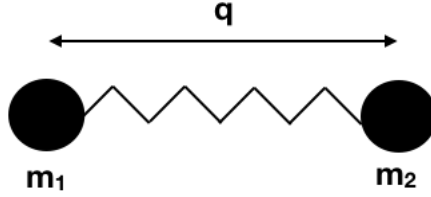


Figure 3.1: A model of a diatomic particle, with two atoms of mass m_1 and m_2 , connected by a spring with constant k . The 2 atoms have the usual 3 translational degrees of freedom each, while they can also mutually vibrate, adding an extra degree of freedom for a total of 7. Using the equipartition theorem, the mean energy per particle is then $(7/2)k_bT$. There is an alternate model of the diatom, where the entire diatom is considered a rigid “dumbbell” – you will solve that model in your homework set.

“dumbbell” which can vibrate along its axis (this is actually a better model quantum mechanically as we will see in chapter 4) – you will do this the problem set. Coming back to the model in Fig. 3.1, the energy of each particle is then given by the Hamiltonian

$$H(\mathbf{p}_1, \mathbf{p}_2, q) = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + \frac{1}{2}kq^2 \quad (3.26)$$

where q is now the relative distance between the two atoms $q = |\mathbf{x}_1 - \mathbf{x}_2|$. Each atom, as usual, contributes a mean energy of $(3/2)k_bT$ for the 3 translational degrees of freedom. Meanwhile, for the **vibrational** degree of freedom between the atoms, the energy is a function of the distance q , hence

$$\begin{aligned} \langle H(q) \rangle &= \frac{1}{2} \langle kq^2 \rangle \\ &= \frac{1}{2} \left\langle q \frac{\partial H}{\partial q} \right\rangle \\ &= \frac{1}{2} k_b T, \end{aligned} \quad (3.27)$$

which is as we have asserted earlier. Thus the mean energy for a diatomic ideal gas is $\bar{E} = (7/2)Nk_bT$, which you may have learned in high-skool.

So how does this stack up against experiment? As it turns out, this is an easy experiment to do. We heat up a gas, and measures the energy needed as a function of temperature. Our *classical* theory predicts that the heat capacity is

$$C_V = \frac{7}{2}k_bN \quad (3.28)$$

which is a independent of temperature. When we measure the heat capacity, and plot it as a function of temperature T , we obtain the result shown in Fig. 3.2.

The answer for this weirdness is *quantum mechanics* – our classical treatment will not capture it. As we will see when we discuss quantum gasses in section 4.2.3 at low temperatures, some degrees of freedom “freeze” out so the heat capacity is lower. In the case of the diatomic gas, at low temperature $T < T_{\text{rot}}$, only the *rigid* translational degrees of freedom (i.e. both atoms of the diatom travel in the same direction) are active. At $T_{\text{rot}} < T < T_{\text{vib}}$, rigid rotation and translational degrees of freedom are active while above $T > T_{\text{vib}}$ all degrees of freedom become active. Not only that, the “activation” is sudden – there is no active rotation degrees of freedom until T_{rot} is hit and then *all* the particles began to rotate. We will come back to discuss this in section 4.2.3 after we have build up some quantum mechanical muscle in the next chapter.

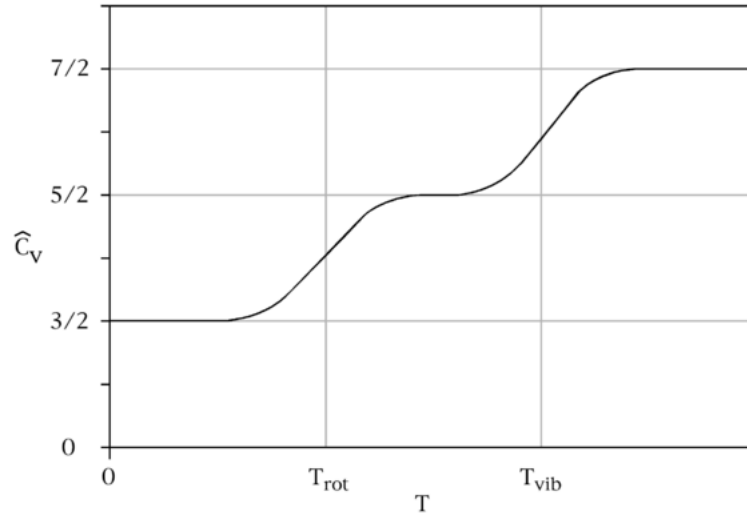


Figure 3.2: The heat capacity C_V of a diatomic gas as a function of temperature. Instead of the classically predicted $C_V = (7/2)k_b$, C_V stays constant at $(3/2)k_b$ at low temperatures, until some fixed temperature T_{rot} where it jumps to $(5/2)k_b$. It stay at that value until T_{vib} is reached, where it then jumps to the predicted value of $(7/2)k_b$. (Figure stolen from Wikipedia.)

3.2 Maxwell-Boltzmann distribution

Before we continue on with new things, let's take a moment to rederive an old friend, the **Maxwell-Boltzmann distribution** of molecular speeds of a gas at temperature T . Assuming that the gas is held at fixed temperature in a diathermal box (i.e. no particles are exchanged), so we are dealing with a canonical ensemble. As we have learned from section 2.3.1, the probability of finding a microstate of energy E is given by the Boltzmann distribution Eq. (2.44).

Now instead of considering a gas, we consider the canonical ensemble of *single* particle of mass m . The kinetic energy for this particle is $E = mv^2/2$ with $v \equiv |\mathbf{v}|$ being the *absolute* velocity of this particle as usual. The probability of finding a particle at absolute velocity v is then given by (following Eq. (2.44))

$$P(v) = \frac{f(v)e^{-mv^2/2k_bT}}{Z} \quad (3.29)$$

with the partition function being the sum over all possible states as usual. So the probability of finding the particle between the velocities v and $v + dv$ is the integral

$$P(v)dv = \frac{1}{Z}f(v)e^{-mv^2/2k_bT} dv . \quad (3.30)$$

Our goal is now to compute $f(v)$. To do this, we again deploy the omnipotent partition function (in integral form)

$$\begin{aligned} Z &= \frac{1}{(2\pi\hbar)^3} \int d^3x \int d^3p e^{-E/k_bT} \\ &= \frac{V}{(2\pi\hbar)^3} \int d^3p e^{-mv^2/2k_bT} , \end{aligned} \quad (3.31)$$

where we have done the volume integral as usual. We now need to convert the 3-momentum integral d^3p into an integral over the absolute velocity – for every value of v , there exist many possible combinations

of $\mathbf{v} = (v_x, v_y, v_z)$ such that $v = |\mathbf{v}|$, e.g. $\mathbf{v} = (v, 0, 0)$, $\mathbf{v} = (0, v, 0)$, $\mathbf{v} = (0, v/\sqrt{2}, v/\sqrt{2})$ etc. This traces out a locus of a 2-sphere with radius v , and thus

$$d^3p = m^3 d^3v = m^3 v^2 dv d\Omega .$$

The solid angle integral $\int d\Omega = \int \int \sin \theta d\theta d\phi = 4\pi$ as usual, so Eq. (3.31) becomes

$$Z = \frac{4m^3\pi V}{(2\pi\hbar)^3} \int dv v^2 e^{-mv^2/2k_bT} . \quad (3.32)$$

This means that the Maxwell-Boltzmann distribution must be $f(v) \propto v^2$, or

$$f(v)e^{-mv^2/2k_bT} dv = Av^2 e^{-mv^2/2k_bT} dv , \quad (3.33)$$

The normalization constant A can be computed by insisting that the total probability

$$\int_0^\infty Av^2 e^{-mv^2/2k_bT} dv = 1 , \quad (3.34)$$

which gets us

$$A = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} . \quad (3.35)$$

Putting everything together, we get the famous Maxwell-Boltzmann distribution as promised

$$\boxed{f(v)e^{-mv^2/2k_bT} = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} v^2 e^{-mv^2/2k_bT}} . \quad (3.36)$$

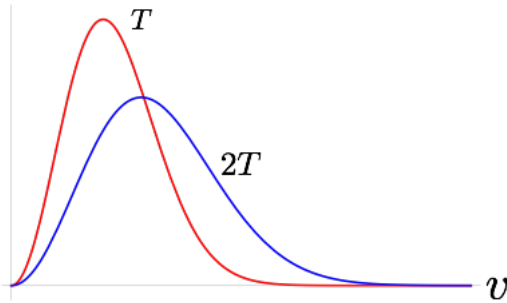


Figure 3.3: The Maxwell-Boltzmann distribution.

Notice this is the velocity distribution for a *single* particle. However, if we assume that the particles are non-interacting, so that the partition function simply multiplies $\prod Z$, it's easy to show that the entire calculation follows through, and Eq. (3.36) remains the same. In other words, the distribution *do not depend on density*. Of course, real gasses' particles interact with one another, and as we will see later in section 3.5, the partition function no longer multiplies and distribution will be dependent on the density. Nevertheless, the Maxwell-Boltzmann distribution is an excellent model for low density systems.

Let's take a moment to reacquaint ourselves with this distribution (Fig. 3.3). For a given fixed m and T , the distribution of the velocities at small v is dominated by the v^2 term since the exponent $\lim_{v \rightarrow 0} e^{-v^2} \rightarrow 1$ so it rises until some maximum v_{\max} which can be found by setting

$$\frac{d}{dv} \left[f(v)e^{-mv^2/2k_bT} \right] \Big|_{v_{\max}} = 0 , \quad (3.37)$$

which you can show in a homework problem to be $v_{\max} = \sqrt{2k_bT/m}$.

Notice that there the probability drops to zero at $v = 0$ – the probability of finding a particle that is standing still is effectively zero. At high v on the other hand, the exponential starts to dominate, and we experience an exponential tail off. This tail off has a “half-life” that scales as T . So the higher that temperature, the slower the tail-off, i.e. the particles are more likely to be at higher velocities comparatively which is exactly as one intuitively would have guessed.

Like all distribution functions, we can use it to compute averages of quantities that are functions of v . For example, the mean velocity of the particle is given by

$$\begin{aligned}\langle v \rangle &= \int_0^\infty dv v f(v) e^{-mv^2/2k_bT} \\ &= \sqrt{\frac{8k_bT}{\pi m}}.\end{aligned}\tag{3.38}$$

We can also calculate the mean kinetic energy of the system of particles using Gauss’ integrals (see Appendix A.2)

$$\begin{aligned}\langle E \rangle &= \frac{1}{2}m\langle v^2 \rangle \\ &= \frac{1}{2}m \int_0^\infty dv v^2 f(v) e^{-mv^2/2k_bT} \\ &= \frac{3k_bT}{2},\end{aligned}\tag{3.39}$$

which is exactly the same answer we have gotten from equipartition arguments in section 3.1.1 for particles with 3 translational degrees of freedom – not surprising because we are using the same distribution.

The Maxwell-Boltzmann distribution is historically the first statistical law of physics – it was derived by Maxwell in 1859 from the principles of the **Kinetic Theory of Gas** which postulates that gas can be described as a large number of particles in random motion. This theory, which you have studied in your Thermal Physics course, is the progenitor of statistical mechanics, and is still widely applicable in the description from the universe from the evolution of the universe to describing fluids in your bath tub.

3.3 Distinguishable vs indistinguishable particles

We now have a confession to make. The partition function for the ideal gas we have derived in section 3.1, Eq. (3.9),

$$Z = V^N \left(\frac{mk_bT}{2\pi\hbar^2} \right)^{3N/2},\tag{3.40}$$

is actually *incorrect*. The reason is that we are overcounting the microstates in the following way. When we derived Eq. (3.9), we have simply multiplied the partition function of N different single particle partition functions. This procedure makes the extremely important (and incorrect) assumption that these N particles are **distinguishable**, i.e. there are labels on them numbering them from 1 to N . But in reality, at the quantum mechanical level, the particles of a real gas is **indistinguishable** – e.g. every hydrogen molecule is exactly the same as every other hydrogen molecule. This point is illustrated in Fig. 3.4. In general, for N indistinguishable particles, we will overcount the number of microstates $N!$ times, so the partition function should be modified to

$$\tilde{Z} \rightarrow \frac{Z}{N!} = \frac{V^N}{N!} \left(\frac{mk_bT}{2\pi\hbar^2} \right)^{3N/2}.\tag{3.41}$$

We emphasise that particles that can be labeled in some way – say same-colored billiard balls – are not indistinguishable. Indistinguishable particles cannot be labeled at all. For example, in Fig. 3.4, the right hand set is not “6 identical sets”, but they are *exactly the same set*.

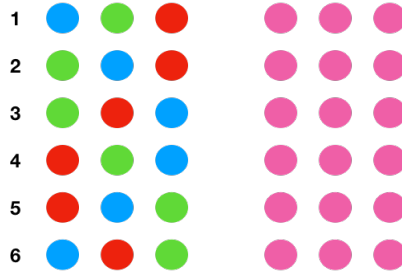


Figure 3.4: Indistinguishable vs distinguishable particles: if 3 particles are distinguishable then we can label them (left plot, blue, green and red), we can arrange it in $3! = 6$ different configurations or microstates. However, if they are indistinguishable we cannot label them (right plot, all pink), there is only one configuration or microstate.

Fortunately, many of the results that we have computed such as that of the Maxwell-Boltzmann distribution in section 3.2 does not change because the factorial factor only changes the normalization. On the other hand, any quantity that directly requires the actual number of microstates may require modification. The most important of this is of course, the entropy, Eq. (2.70)

$$S = k_b(\ln \tilde{Z} + \beta \bar{E}) . \quad (3.42)$$

Now the mean energy does not change

$$\begin{aligned} \bar{E} &= -\frac{\partial \ln \tilde{Z}}{\partial \beta} \\ &= -\frac{\partial(-\ln N! + \ln Z)}{\partial \beta} \\ &= -\frac{\partial \ln Z}{\partial \beta} , \end{aligned} \quad (3.43)$$

since the log makes the $N!$ factor additive and the partial then gets rid of it. This is a mnemonic to remember when figuring out which equations are affected.

On the other hand, the first $\ln \tilde{Z}$ term now gets this extra term

$$\begin{aligned} S &= k_b(\ln \tilde{Z} + \beta \bar{E}) \\ &= k_b(\ln Z - \ln N! + \beta \bar{E}) . \end{aligned} \quad (3.44)$$

Hence the entropy is *smaller* of $\ln N!$ – this is not surprising since in reality there are less possible configurations.

Finally, you might wonder about the case of the paramagnet we studied in section 2.3.4 – aren't electrons also indistinguishable particles? You would be right, but in that case, the electrons are held in place in a lattice – hence we can label them with the lattice coordinates, rendering them distinguishable.

3.4 Ideal gas as a grand canonical ensemble

In the section on the ideal gas section 3.1, we have considered the canonical ensemble, which means the particle number N is constant. In general, this can change – for example, in the atmosphere of the sun, the number density of the hydrogen atoms changes as nuclear processes fuse them into helium.

As usual, we begin with the grand canonical partition function Eq. (2.102),

$$\begin{aligned}
\mathcal{Z}(\mu, T, V) &= \sum_r e^{-\beta(E_r - \mu N_r)} \\
&= \sum_{E_r, N_r} e^{-\beta(E_r - \mu N_r)} \\
&= \sum_{N_r} \tilde{Z}(N_r, T, V) e^{\beta \mu N_r} ,
\end{aligned} \tag{3.45}$$

where \tilde{Z} is the canonical partition function of the ideal gas (taking into account indistinguishable particles), Eq. (3.41), so we can just copy down the answer

$$\mathcal{Z}(\mu, T, V) = \sum_{N_r} \frac{V^{N_r}}{N_r! \lambda^{3N_r}} e^{\beta \mu N_r} , \tag{3.46}$$

where we have used the thermal de Broglie wavelength Eq. (3.12). This terrible looking sum can actually be easily computed in the limit of very large N , using the series

$$e^x = \sum_{n=0}^{n=\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \dots \tag{3.47}$$

so it sums to our final expression for grand partition function of the ideal gas,

$$\mathcal{Z}(\mu, T, V) = \exp\left(\frac{V e^{\beta \mu}}{\lambda^3}\right) . \tag{3.48}$$

With Eq. (3.48), we can then roll out all the thermodynamical quantities as we have seen in section 2.4. The mean particle number is

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{V e^{\beta \mu}}{\lambda^3} , \tag{3.49}$$

so the chemical potential of the ideal gas is given by

$$\mu = \frac{1}{\beta} \ln\left(\frac{\langle N \rangle \lambda^3}{V}\right) . \tag{3.50}$$

Now recall that λ^3 is roughly the de Broglie wavelength, so is the length scale when quantum effects are important. Meanwhile, V/N is the “available” volume for each particle, so to trust our classical calculation of the ideal gas, $\lambda^3 \ll V/N$ – this means $N\lambda^3/v \ll 1$ – i.e. $\mu < 0$. In other words, the chemical potential for an ideal gas is *negative*. There is nothing wrong with it, though in general μ can be both positive and negative, depending on the system.

To derive the equation of state, we use the Landau potential, from Eq. (2.114) and Eq. (1.80),

$$\Psi = -k_b T \ln \mathcal{Z} = -PV \tag{3.51}$$

but $\ln \mathcal{Z} = V e^{\beta \mu} \lambda^{-3} = \langle N \rangle$ from Eq. (3.49), and the equation of state immediately follows.

3.5 Non-ideal gas

We have so far considered ideal gasses, of which the particles do not interact. They are very good approximations for situations when the gas density is low. In this section, we will discuss how we can model “real gasses”, which can have various forms of interactions.

3.5.1 Interacting gasses

To begin, let's consider a system of N *indistinguishable* particles of mass m which interact with one another. As should be familiar by now, we want to construct its partition function. The Hamiltonian (or energy) of this system is

$$H = \underbrace{\sum_i \frac{\mathbf{p}_i^2}{2m}}_{\text{momenta only}} + \sum_{i>j} \underbrace{U(r_{ij})}_{\text{position only}}, \quad (3.52)$$

where $U(\mathbf{x}_1, \mathbf{x}_2)$ is the **interacting potential** between any two particles with position \mathbf{x}_i and \mathbf{x}_j , which depends on the distance between the particles

$$r_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j|. \quad (3.53)$$

Notice that the Hamiltonian Eq. (3.52) is a sum of terms that depends on momentum and terms that depend on position, and we sum over all i and j with the condition $i > j$ so that we avoid overcounting.

The partition function is in general an integral over all the momenta and coordinates,

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \int \prod_i d^3 p_i \int \prod_j d^3 x_j e^{-\beta H}. \quad (3.54)$$

The product integral measures $\prod_i d^3 x_i$ and $\prod_i d^3 p_i$ appear so often that it is very convenient to introduce a shorthand

$$\prod_i d^3 x_i \equiv \mathcal{D}x, \quad \prod_i d^3 p_i \equiv \mathcal{D}p. \quad (3.55)$$

Now since we can split the Hamiltonian into momentum only and position only parts, we can separate the integrals (using the shorthand $U(r_{ij}) = U_{ij}$)

$$\begin{aligned} Z &= \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \left[\int \mathcal{D}p e^{-\beta \sum_i \mathbf{p}_i^2 / 2m} \right] \times \left[\int \mathcal{D}x e^{-\beta \sum_{j>k} U_{jk}} \right] \\ &= \frac{1}{N!} \frac{1}{\lambda^{3N}} \left[\int \mathcal{D}x e^{-\beta \sum_{j>k} U_{jk}} \right]. \end{aligned} \quad (3.56)$$

We have used the ideal gas result Eq. (3.9), but without the “trivial” position integral as it is no longer trivial in the presence of the potential $U(r_{ij})$. Now the Helmholtz free energy for the ideal gas is Eq. (2.74)

$$\begin{aligned} F_{\text{id}} &= -k_b T \ln Z_{\text{id}} \\ &= -k_b T \ln \left(\frac{V^N}{\lambda^{3N} N!} \right) \\ &= -k_b T \left[\ln \left(\frac{1}{\lambda^{3N} N!} \right) + \ln V^N \right]. \end{aligned} \quad (3.57)$$

The Helmholtz free energy for the interacting gas is then

$$\begin{aligned} F &= -k_b T \ln Z \\ &= -k_b T \left[\ln \left(\frac{1}{\lambda^{3N} N!} \right) + \ln \int \mathcal{D}x e^{-\beta \sum_{j>k} U_{jk}} \right] \\ &= F_{\text{id}} - k_b T \ln \left[\frac{1}{V^N} \int \mathcal{D}x e^{-\beta \sum_{j>k} U_{jk}} \right] \\ &= F_{\text{id}} - k_b T \times I, \end{aligned} \quad (3.58)$$

where we have expressed the remaining integral as

$$I \equiv \ln \left[\frac{1}{V^N} \int \mathcal{D}x e^{-\beta \sum_{j>k} U_{jk}} \right]. \quad (3.59)$$

This integral encodes the change to the system due to the presence of the interactions. In general, it is an incredibly difficult integral to perform since all the particles may interact with every other particles. To proceed, we want to understand the nature of the interactions, so let's look at U_{ij} closely.

3.5.2 Van der Waals forces

Consider two particles (say the molecules of some gas), the Hamiltonian is $(\mathbf{p}_1^2 + \mathbf{p}_2^2)/2m + U(r_{12})$. $r_{12} = |\mathbf{x}_1 - \mathbf{x}_2| \equiv r$ is the distance between the particles. Physically, we know that the particles cannot be infinitesimally close to each other, since Pauli's exclusions principle will prevent them from occupying the same space. Suppose r_0 is roughly the radius of the particle, then we can roughly model this behavior as

$$U(r) \rightarrow \infty \text{ for } r < r_0, \quad (3.60)$$

i.e. it is infinitely expensive energetically for the particles to overlap $r < r_0$ – hence making the potential *repulsive* at short distances. Such an infinite core is called a **hard core**.

Meanwhile, from experiments, we notice that there exists a very weak molecular *attractive* force between molecules that are neither ionic or covalent, called **Van der Waal's forces**. This force vanishes at as $r \rightarrow \infty$, so we can model it as a potential

$$U = -U_0 \left(\frac{r_0}{r}\right)^6, \quad (3.61)$$

which is sometimes called the **London potential**. Van der Waal's forces, as you studied in your high school days, describe the very weak but present forces between the molecules of a gas. The origins of the Van der Waals forces are quantum mechanical – technically, they are a sum of all vacuum polarizations multipoles between molecules. Combining Eq. (3.60) and Eq. (3.61), we get

$$U(r) = \begin{cases} \infty & , \quad r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & , \quad r > r_0 \end{cases}. \quad (3.62)$$

This potential is sketched in Fig. 3.5.

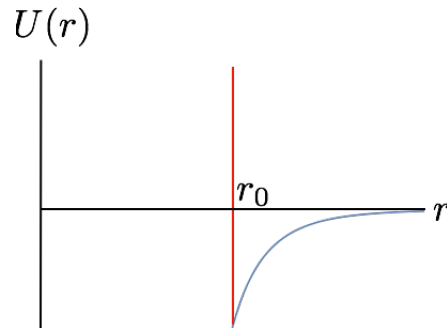


Figure 3.5: The potential for the Van der Waal's forces which consists of a hard core model with weak attractive London interaction.

Given this potential, let's see how we can perform the integral Eq. (3.59) using a very clever trick. The exponent $e^{-\beta U}$ contains *all the possible interactions between all the particles*, but we can make use of the fact that since we are dealing with gasses with low densities, the most likely interaction is a single interaction between two particles, followed by the less likely *two simultaneous interactions* either between 3 particles or between two pairs of particles, and even rarer $n > 3$ simultaneous interactions. So what we want is some kind of formal expansion of the integrand which will allow us arrange the integration along such n -interactions. We implement this trick by introducing the following change of variables

$$f(r_{ij}) \equiv e^{-\beta U(r_{ij})} - 1. \quad (3.63)$$

This is a very clever function³. Notice that for any pair of particles labeled i and j , if they are *very weakly interacting* when they are far away (at $r_{ij} \rightarrow \infty$), then since $U_{ij} \rightarrow 0$, $f(r_{ij}) = e^0 - 1 \rightarrow 0$. If they are close $r_{ij} \rightarrow 0$ and strongly interacting, then $U_{ij} \rightarrow \infty$, and $f(r_{ij}) \rightarrow -1$. This means that when we do the $\int \prod_i d^3x_i$ integral over all the coordinates, they will only contribute when around the domain where $\mathbf{x}_i \approx \mathbf{x}_j$ – a fact we will make use of very soon. Using this function, we can then expand the exponent as (using the shorthand $f_{ij} \equiv f(r_{ij})$)

$$\begin{aligned}
e^{-\beta \sum_{j>k} U_{jk}} &= \prod_{j>k} (1 + f_{jk}) \\
&= 1 + \sum_{j>k} f_{jk} + \sum_{j>k, l>m} f_{jk} f_{lm} + \sum_{j>k, l>m, q>w} f_{jk} f_{lm} f_{qw} + \dots \\
&= 1 + (f_{12} + f_{13} + \dots + f_{23} + f_{24} \dots) \\
&\quad + (f_{12}f_{23} + f_{13}f_{34} + \dots) + (f_{13}f_{23}f_{34} + \dots) + \dots
\end{aligned} \tag{3.64}$$

Thus one can interpret f_{ij} as the contribution to the partition function of the interaction between particle i and j . The linear terms $f_{12} + f_{23} + \dots = \sum_{j>k} f_{jk}$ are the interactions of two particles, and as the sum makes clear, there are $N(N-1)/2$ pairs of these. The next to leading order term $f_{12}f_{23} + f_{13}f_{34} + \dots = \sum_{j>k, l>m} f_{jk} f_{lm}$ are the interactions of either 3 particles or simultaneous interactions of two pairs of particles (e.g. $f_{12}f_{34}$) etc. Such an expansion is called a **cluster expansion** and is a very useful device which you will see again and again in any calculations involving the partition functions (e.g. in quantum field theory).

Using our intuition that the most dominant interactions will be for a single pair of particles⁴, we will drop all the higher order f terms and keep just the linear term. The integral I then is

$$\begin{aligned}
I &= \ln \left[\frac{1}{V^N} \int \mathcal{D}x e^{-\beta \sum_{j>k} U(r_{jk})} \right] \\
&= \ln \left[\frac{1}{V^N} \int \mathcal{D}x \prod_{j>k} (1 + f_{jk}) \right] \\
&= \ln \left[\frac{1}{V^N} \int \mathcal{D}x \left(1 + \sum_{j>k} f_{jk} + \dots \right) \right]
\end{aligned} \tag{3.65}$$

The “1” integral is trivial $\int \mathcal{D}x = V^N$. Our introduction of the f expansion has cleverly changed our integrand from a crazy product of many exponents into a *sum* of linear f_{jk} terms – where each f_{jk} is the contribution of the interaction of a single pair. Better still, each pair interaction is exactly identical as any other pairs, and the sum gives us $N(N-1)/2$ such pairs in the entire integrand, with the total

$$\int \mathcal{D}x \sum_{j>k} f_{jk} \rightarrow \frac{N(N-1)}{2} \int \left(\prod_i d^3x_i \right) f_{jk},$$

for *any* choice of j and k . Since N is very large, we can simply approximate $N(N-1) \approx N^2$. Now each interaction, $f_{jk} = f(r_{jk})$ only depends on the coordinates of two particles, we can trivially integrate all the coordinates x_i except for when $i = j, k$ giving us a factor of V^{N-2} . Putting everything back together, the integral I is

$$I = \ln \left[1 + \frac{N^2}{2V^2} \int d^3x_j d^3x_k f_{jk} \right]. \tag{3.66}$$

Since we can always fix the coordinate of one of the particle, say the k particle, and express the j particle as distance from k , $r = |\mathbf{x}_j - \mathbf{x}_k|$ then $\int d^3x_j \int d^3x_k \rightarrow V \int_0^\infty d^3r$, where the factor of V comes from the

³It's called the *Mayer f function* for those who likes fancy names.

⁴If you have spotted that we have brazenly ignored simultaneous interactions of 2 pairs of particles, e.g. $f_{12}f_{34}$, then well done. This is an important point we will come back to a bit – see footnote 5.

fact that we integrate over all possible locations for the k particle, we can further reduce I into a single integral

$$I = \ln \left[1 + \frac{N^2}{2V} \int_0^\infty d^3r f(r) \right] . \quad (3.67)$$

We can proceed with this integral if we like, but now is a worthwhile time to stop doing math, and think about physics a bit. As we said earlier, $f(r)$ only contributes to the integral when the particles are near each other. Looking at the potential in fig. 3.5, it's clear that f only contribute when $r \lesssim r_0$, so the volume integral $\int d^3r f(r) \sim -r_0^3$ (recall that $f(r) \rightarrow -1$ at small distances). This means that (ignoring signs)

$$\frac{N^2}{2V} \int d^3r f(r) \sim \frac{N^2 r_0^3}{V} . \quad (3.68)$$

Now N/V is the **number density** of the gas, and since r_0^3 is roughly the *volume* of the particle or molecule, $1/r_0^3$ must be the number density of the particles *if we pack them together touching each other!* Thus the combination

$$\frac{N r_0^3}{V} \ll 1 , \quad (3.69)$$

must be true – it's just the statement that particles of a gas are not packed edge-to-edge. But, we further *assert* that the combination

$$\frac{N^2 r_0^3}{V} \ll 1 , \quad (3.70)$$

is *also* true. This is less obvious – why are we allowed to do this? Indeed, at first glance, it seems wrong. For example, a mol of hydrogen occupy 22.4 m^3 as usual, while molecular hydrogen has the radius $r_0 = 1.2 \times 10^{-10} \text{ m}$. $N = 6.02 \times 10^{23}$ for a mol, so $NV/r_0^3 = 4.6 \times 10^{-8}$. But then $N^2V/r_0^3 \sim 10^{15}$, which is very large! What gives?

The “formal” answer is that we *assert* that we are only doing this integral for *small quantities of gas*, i.e. when $N \ll 10^8$. The reason we are allowed to do this is because we know that the *free energy is extensive*, i.e. they are additive $F_{\text{total}} = F_1 + F_2$, as we have seen in section 1.5. Thus, once we have computed F for a small quantity of gas, it's easy to simply sum them up⁵.

With this further assumption, we can then use the expansion $\ln(1+x) \approx x$ for $x \ll 1$ to finally write down the integral we have to do

$$I = \frac{N^2}{2V} \int d^3r f(r) . \quad (3.71)$$

This is now looking much more promising! Recalling that the f function has the property $f(r) \rightarrow -1$ at $r \lesssim r_0$ while $f(r) \rightarrow 0$ at large r , we break the integral into two parts

$$\begin{aligned} I &= \frac{N^2}{2V} \int d^3r f(r) \\ &= \frac{N^2}{2V} \left(\int_0^{r_0} d^3r f(r) + \int_{r_0}^\infty d^3r f(r) \right) . \end{aligned} \quad (3.72)$$

For the Van der Waals potential Eq. (3.62), the 1st integrand above is $f(r < r_0) = -1$ since $U(r < r_0) \rightarrow \infty$, we get

$$\int_0^{r_0} d^3r f(r) = \int_0^{r_0} 4\pi r^2 (-1) dr = -\frac{4\pi r_0^3}{3} . \quad (3.73)$$

⁵We have to assume that the subsystems do not interact of course, but this is explained by something we have swept under the rug when we do the expansion in Eq. (3.64). Some of you might have noticed that some 2nd order terms (e.g. $f_{12}f_{34}$) interactions are actually between 2 pairs of interactions. Now, these are rare as we asserted, but in a sufficiently large volume of gas, they can occur. Since F is extensive, we are in danger of undercounting the number of interactions. The solution is simply to restrict the volume (and hence the number of particles N) such that we are safe to assume that there is only *a single* interaction in the entire volume at any one time. This restriction is equivalent to our assumption that $N^2 r_0^3/V \ll 1$.

Meanwhile, the third term $f(r \gg r_0) = e^{-\beta U(r \gg r_0)} - 1$, and assuming (see below) βU is small in this range, we *can* expand $e^{-\beta U} - 1 \approx (1 - \beta U + \dots) - 1 = -\beta U + \dots$ where the dots denote terms of $\mathcal{O}(\beta^2 U^2)$ and higher. The 3rd integral then becomes

$$\beta U_0 \int_{r_0}^{\infty} 4\pi r^2 \left(\frac{r_0}{r}\right)^6 dr = \beta U_0 \frac{4\pi r_0^3}{3}. \quad (3.74)$$

Putting everything together, the final integral is then

$$I = \frac{N^2}{2V} \frac{4\pi r_0^3}{3} (\beta U_0 - 1). \quad (3.75)$$

Inserting this back into Eq. (3.58), we obtain the final answer for the Helmholtz free energy

$$F = F_{\text{id}} - \frac{N^2 k_b T}{V} \frac{2\pi r_0^3}{3} (\beta U_0 - 1). \quad (3.76)$$

To find the equation of state, we use Eq. (1.32), $P = -(\partial F / \partial V)_T$,

$$P = \frac{N k_b T}{V} \left[1 - \frac{N}{V} \left(\frac{a}{k_b T} - b \right) \right], \quad (3.77)$$

where we have defined the coefficients

$$a \equiv \frac{2\pi r_0^3 U_0}{3}, \quad b \equiv \frac{2\pi r_0^3}{3}. \quad (3.78)$$

Rearranging Eq. (3.77),

$$k_b T = \frac{V}{N} \left(P + \frac{N^2}{V^2} a \right) \left(1 + \frac{N}{V} b \right)^{-1} \approx \left(P + \frac{N^2}{V^2} a \right) \left(\frac{V}{N} - b \right) \quad (3.79)$$

where we have expanded the last term, again using the fact that $Nb/V \sim Nr_0^3/V \ll 1$ to Taylor expand the second bracket. Eq. (3.79) is the famous **Van Der Waals equation of state**, which you may have encountered in high school.

We have glossed over a few things in the derivation, so let's make some parenthical remarks here:

- **High temperatures:** In deriving Eq. (3.74), we have assumed that $\beta U_0 = U_0/(k_b T) \ll 1$. This means that the temperature $T \gg U_0/k_b$. As an example, for Argon gas interactions, $U_0/k_b \sim 400$ Kelvins.
- **Short range forces only:** When we integrate the potential in Eq. (3.74), $\int_0^\infty r^2 (r_0/r)^6 dr$, the London potential scales as $1/r^6$, while the integral scales as r^3 . This means that when we take the upper limit $r = \infty$, it is zero and hence the integral converges. However, it is clear that if the potential has been longer range, i.e. $U(r) \propto r^{-n}$ where $n \leq 3$, then the integral diverges. For example, the Coulomb potential scales like $1/r$ so this derivation will not work.
- **Low densities:** As we have explained earlier, we have used the fact the following low density assumption

$$\frac{N}{V} \ll \frac{1}{r_0^3}. \quad (3.80)$$

This suggests that we can use the parameter N/V an *expansion* parameter, where higher order effects are proportional to $\mathcal{O}(N/V)^n$. This allows us to motivate the following **virial expansion** of the equation of state

$$\frac{P}{k_b T} = \frac{N}{V} \left[1 + \frac{N}{V} B_1(T) + \left(\frac{N}{V}\right)^2 B_2(T) + \left(\frac{N}{V}\right)^3 B_3(T) + \dots \right], \quad (3.81)$$

where $B_i(T)$ are known as **virial coefficients**. For the Van Der Waals gas above, we see that $B_1(T) = -(a/k_bT - b)$. These coefficients can be calculated theoretically, for a given potential, by taking into account higher order interactions. For those interested can check out Goodstein, section 4.4. In practice though, the virial coefficients are usually measured from experiments.

- **The Lennard-Jones Potential.** In the literature, especially in chemistry texts, instead of the hard core + London potential we used Eq. (3.62), the so-called Lennard-Jones potential or the **12-6 potential**, is often used

$$U = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (3.82)$$

where ϵ and σ are the *Lennard-Jones coefficient* and effective radius of the molecules respectively. These coefficients are usually measured experimentally. You will show in a homework problem we will recover the same results in this section using this potential.

Chapter 4

Quantum Gas

So far, we have considered classical systems. Even so, the universe is actually quantum, and hence in a couple of places, we have leaned on quantum mechanics to motivate some otherwise unexplained assertions. Firstly, we have argued in section 2.5.2 that the correct normalization factor when we compute the continuous partition function is $1/(2\pi\hbar)$ per spatial dimension. Secondly, in section 3.3, we have argued that quantum mechanically particles are indistinguishable.

Nevertheless, in those sections, we have not fully embraced quantum mechanics. In this chapter, we take the plunge into the quantum world.

4.1 Quantum states vs classical particles

Consider a quantum particle of mass m in a 3 dimensional box with equal sides a , and volume $V = a^3$, and periodic boundary conditions. Extending the 1-D derivation in section 2.5.2 to 3-D, the eigenfunction for the time-independent Schrodinger's equation is the plane wave solution in 3-D,

$$\psi(\mathbf{x}) = \mathcal{A}e^{i\mathbf{k}\cdot\mathbf{x}} \quad (4.1)$$

with the wavenumbers $\mathbf{k} = (k_x, k_y, k_z)$ quantized as

$$k_i = \frac{2\pi n_i}{a}, \quad n_i = 0, \pm 1, \pm 2, \dots, \quad (4.2)$$

so the energy of the particle is

$$E_{\mathbf{n}} = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2), \quad k \equiv \sqrt{k_x^2 + k_y^2 + k_z^2}. \quad (4.3)$$

The **quantum numbers** n_i labels the **quantum state** of the particle.

4.1.1 Density of states

So far this is simply a review of quantum mechanics. Bringing in the machinery of statistical mechanics, we make the connection that *each quantum state of the particle represents a possible microstate*, and hence the partition function for a single quantum mechanical particle is then given by Eq. (2.43)

$$Z_1 = \sum_{\mathbf{n}} e^{-\beta E_{\mathbf{n}}}, \quad (4.4)$$

where the sum is over all possible quantum numbers

$$\mathbf{n} \equiv (n_x, n_y, n_z). \quad (4.5)$$

Recall that the lengthscale when quantum mechanics is important is given by the de Broglie wavelength, or as we have discussed in section 3.1, the thermal de Broglie wavelength Eq. (3.12)

$$\lambda \equiv \sqrt{\frac{2\pi\hbar^2}{mk_bT}} . \quad (4.6)$$

As long as the box size is much, much greater than this wavelength, $a \gg \lambda$, the number of possible states \mathbf{n} is super-duper large, so we can approximate the sum over all \mathbf{n} as an integral

$$\sum_{\mathbf{n}} \rightarrow \int dn_x dn_y dn_z . \quad (4.7)$$

Following the arguments in section 2.5.2, the measure dn_i is

$$dn_i = \frac{a}{2\pi} dk_i , \quad (4.8)$$

so

$$\int dn_x dn_y dn_z = \frac{V}{(2\pi)^3} \int d^3k = \frac{4\pi V}{(2\pi)^3} \int_0^\infty k^2 dk \quad (4.9)$$

where we have used isotropy to turn the $dk_x dk_y dk_z$ integral into a volume integral over the 2-sphere. The partition function Eq. (4.4) is then

$$Z_1 = \frac{4\pi V}{(2\pi)^3} \int_0^\infty k^2 e^{-\beta E_{\mathbf{n}}(k)} dk , \quad (4.10)$$

where we have explicitly specified the k dependence of $E_{\mathbf{n}}$ to be clear. We can easily convert the dk measure into an energy measure dE by using Eq. (4.3)

$$dE = \frac{\hbar^2 k}{m} dk , \quad (4.11)$$

so

$$\begin{aligned} Z_1 &= \frac{4\pi V}{(2\pi)^3} \int_0^\infty \frac{2mE}{\hbar^2} \frac{m}{k\hbar^2} e^{-\beta E_{\mathbf{n}}} dE \\ &= \frac{4\pi V}{(2\pi)^3} \int_0^\infty \sqrt{\frac{2mE}{\hbar^2}} \frac{m}{\hbar^2} e^{-\beta E_{\mathbf{n}}} dE \\ &= \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} \int_0^\infty m^{3/2} E^{1/2} e^{-\beta E_{\mathbf{n}}} dE \\ &\equiv \int_0^\infty e^{-\beta E} g(E) dE , \end{aligned} \quad (4.12)$$

where the measure

$$g(E) dE = \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{1/2} dE , \quad (4.13)$$

quantifies the *density* of possible microstates of a single particle between E and $E + dE$. This measure is called the **density of states**. Since the factor $e^{-\beta E_{\mathbf{n}}}$ just came along for the ride, in general we can use this measure for any distribution $f(E)$ – we simply replace the sum over quantum states \mathbf{n} with the density of states

$$\boxed{\sum_{\mathbf{n}} f(E) \rightarrow \int_0^\infty g(E) f(E) dE .}$$

Notice that we have obtained the correct normalization factor $(2\pi\hbar)^{-3}$ for the partition function, which is not surprising since we followed the same arguments. Also not surprising is that the quantum single particle partition function Eq. (4.12) is the same as its “classical” counterpart Eq. (3.4) – which we have derived with quantum mechanical input to “make it right”.

4.1.2 Relativistic vs non-relativistic particles

So far we have worked with non-relativistic particles, where the energy $E = \hbar^2 k^2 / 2m$. But of course, Einstein told us that, when a particle is moving a close to the speed of light, the energy is given by the relativistic formula

$$E^2 = \hbar^2 k^2 c^2 + m^2 c^4 . \quad (4.14)$$

The measure in this case is then

$$E dE = \hbar^2 k c^2 dk . \quad (4.15)$$

You will show in a homework problem that, this leads to the following relativistic version of the density of states

$$g(E) dE = \frac{4\pi V}{(2\pi\hbar)^3} \frac{E}{c^3} \sqrt{E^2 - m^2 c^4} dE . \quad (4.16)$$

For massless particles $m = 0$, say like the photon, this becomes

$$g(E) dE = \frac{4\pi V}{(2\pi\hbar)^3} \frac{E^2}{c^3} dE . \quad (4.17)$$

We should come clean and point out that we have sort off cheated by using a result we have derived using the Schrodinger's equation (valid only for non-relativistic particles) to obtain a relation for relativistic particles. In this case, this is actually fine, because the eigenfunctions are plane waves, which also happens to be solutions to the relativistic equations (e.g. the free Klein-Gordon equation).

4.1.3 Many particles vs many quantum states

What about a system of many quantum particles?

As usual, we will take advantage of the fact that the partition function of a non-interacting composite system multiply,

$$Z = \prod Z_1 ,$$

but we can choose how to label the microstates we take the product \prod over. Since particles are in general not conserved and can be created/destroyed, the product is “over all possible configurations over all possible particle numbers”. In other words, we are really working with a grand canonical ensemble $Z \rightarrow \mathcal{Z}$. When we previously studied the grand canonical ensemble in section 2.4, we introduced a new pair of conjugate variables: the total particle number N and the chemical potential μ per particle.

While we can do the same here, we can actually do better! We take advantage of the fact that, for a particle with a definite quantum state \mathbf{n} , we already know the entire solution for its evolution, i.e. every particle with quantum number \mathbf{n} is exactly described by the wavefunction Eq. (4.1) with the energy Eq. (4.3) – they are completely indistinguishable, so it doesn't make sense to label them individually. So instead of making a single particle a subsystem, and then taking the product of all such single particle subsystems to construct the grand partition function, we *choose to partition the system up into subsystems of constant quantum number \mathbf{n}* . Each of this constant \mathbf{n} subsystem can have no particles, one particle, two particles etc as microstates. So the sum over all possible microstates of such a subsystem is over its *occupation*.

Thus, instead of an all-inclusive N , we introduce $f_{\mathbf{n}}$, which is the **occupation number** for the quantum state \mathbf{n} . $f_{\mathbf{n}}$ expresses the *number¹ of particles with quantum number \mathbf{n}* . The grand partition

¹Ideally, we would have liked to use n to express the occupation number, but we have already used \mathbf{n} as the quantum number, so $n_{\mathbf{n}}$ would be rather silly. This is the point when the literature diverges in their solution to this terrible notational problem.

function of the quantum state \mathbf{n} is then given by the sum over all possible microstates of occupation number $f_{\mathbf{n}}$,

$$\mathcal{Z}_{\mathbf{n}} \equiv \sum_{f_{\mathbf{n}}} e^{-f_{\mathbf{n}}\beta(E_{\mathbf{n}}-\mu)} . \quad (4.18)$$

If you like, Eq. (4.18) is the grand canonical partition for a subsystem with quantum state \mathbf{n} . The grand partition function for the entire system is then the product over all possible subsystems of quantum states

$$\mathcal{Z} = \prod_{\mathbf{n}} \mathcal{Z}_{\mathbf{n}} . \quad (4.19)$$

You should take a moment to convince yourself that the grand canonical partition function Eq. (4.19) really did capture all the possible configurations of all possible particle number of the system.

Let's summarize what we have done. The (grand) partition function is a sum over all possible microstates of the system. We get to choose how we want to execute this sum. Instead of a particle centric view where we “sum over all possible particle configurations, and over all possible particle numbers”, we take a state-centric view, where we “sum over all possible occupation numbers of state \mathbf{n} , considering that as a subsystem. The total partition function is then the product over all possible quantum state \mathbf{n} subsystems”. The beauty of this state-centric view is that the product over all the subsystems has no free parameters – the entire system is described by the set of occupation numbers $f_{\mathbf{n}}$.

This shedding of the particle-centric notion, and focusing on the state-centric notion will pay even greater dividends in the coming sections.

4.1.4 Indistinguishability part deux

In section 3.3, we argued that at the quantum level, particles are indistinguishable, and hence we should not overcount them when we calculate the partition function. However, the consequences of indistinguishability go far beyond simple overcounting. As we will see, it ultimately allows us to separate particles into two major types, **bosons** and **fermions**. So it is worth exploring the notion.

Consider a scattering experiment, with two particles A and B fired at each other, and scattering into two separate detectors 1 and 2, see fig. 4.1. Let's define the probability of particle X to be detected in detector Y as $P(X|Y)$. Suppose, *the probability amplitude* for detector Y to detector particle X is $\langle X|Y \rangle$, then as you have learned from quantum mechanics, the probability is its square,

$$P(X|Y) = |\langle X|Y \rangle|^2 . \quad (4.20)$$

Note that since the detectors do not cover all the angles, there is a non-zero chance that no particles were detected at either detectors. Suppose particle A and particle B are different, say A is an oxygen nucleus and B is deuterium nucleus, then the probability of finding some particle (either A or B) in detector 1 is given by

$$P(1|\text{some particle}) = P(1|A) + P(1|B) = |\langle 1|A \rangle|^2 + |\langle 1|B \rangle|^2 \quad (4.21)$$

which is not surprising.

On the other hand, if A and B are indistinguishable (i.e. identical), then there is no way of telling which of the process in Fig. 4.1 actually occurs. Quantum mechanics tells us that we have to consider the entire process as a quantum state, say $|A, B \rangle$. After the scattering has occurred, both detectors saw some of the particles. Since we have no way of distinguishing either which particles are detected, the probability of detecting A and B in detectors 1 and 2 must be equal as if the particles are swapped, i.e.

$$|\langle 1, 2|A, B \rangle|^2 = |\langle 1, 2|B, A \rangle|^2 , \quad (4.22)$$

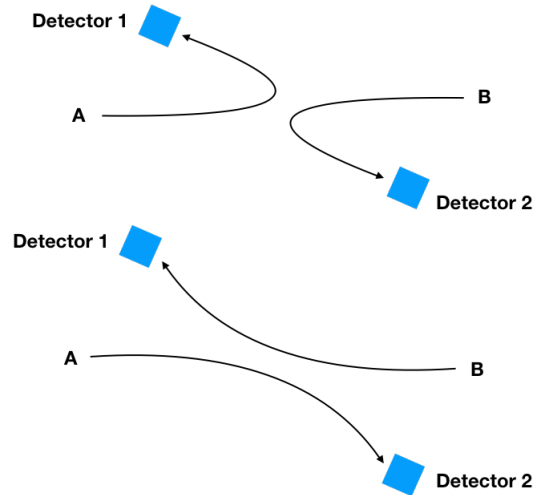


Figure 4.1: Two particles A and B fired at each other, with detectors 1 and 2. If particles A and B are indistinguishable then there for each detection event where *both* detectors saw a particle, the sequence of events can be either of the two shown in this figure – we have no way of distinguishing them.

since if they are not equal, we can use the inequality to identify the particles. It follows from Eq. (4.22) that

$$\langle 1, 2|A, B \rangle = \pm \langle 1, 2|B, A \rangle . \quad (4.23)$$

Since if detector 1 sees particle A , detector 2 must see particle B and *vice versa*, there are only two possible contributions to the final wave function $\langle 1|A \rangle \langle 2|B \rangle$ and $\langle 1|B \rangle \langle 2|A \rangle$. Quantum mechanics tell us that the total probability amplitude is a linear combination of these two possibilities, so since the actual state must obey the indistinguishability condition Eq. (4.22), and thus it must either be **symmetric**

$$\langle 1, 2|A, B \rangle = \langle 1|A \rangle \langle 2|B \rangle + \langle 1|B \rangle \langle 2|A \rangle , \quad (4.24)$$

or be **antisymmetric**

$$\langle 1, 2|A, B \rangle = \langle 1|A \rangle \langle 2|B \rangle - \langle 1|B \rangle \langle 2|A \rangle , \quad (4.25)$$

under the interchange of A and B .

This is a remarkable result. If the wavefunction is anti-symmetric, then if we move detector 2 to the same place as detector 1, or more simply, ask whether detector 1 sees *both* particles, Eq. (4.25) tells us that

$$\langle 1, 1|A, B \rangle = \langle 1|A \rangle \langle 1|B \rangle - \langle 1|B \rangle \langle 1|A \rangle = 0 , \quad (4.26)$$

there is zero probability as the wavefunction vanishes.

In other words, particles with anti-symmetric wavefunctions cannot be in the same place. In fact, if we drop the whole scaffolding of talking about scattering and detectors, and let 1, 2 be some arbitrary states (say the particle's quantum number), Eq. (4.22) and Eq. (4.25) tells us that *no two anti-symmetric particles can be in the same state*. This is the **Pauli Exclusion Principle**.

Particles which have anti-symmetric wavefunctions are called **fermions**, and those with symmetric wavefunctions are called **bosons**. It can be shown that particles with half-integer spins, e.g. $1/2, 3/2, 5/2$ etc (such as electrons) are fermions, while particles with integer spins (such as photons) are bosons. This is known as the **Spin-statistics theorem** and it was proven by Pauli with some reasonable assumptions such as that theory must obey special relativity etc, although we will leave it for another course.

Whether particles are bosons or fermions have a dramatic effect on the property of the system. If the particles are fermions, then the occupation number can only be empty, or has exactly one particle,

$f_{\mathbf{n}} = 0, 1$. On the other hand, if the particles are bosons, there are no such restriction. We will separately study the particle distributions in what follows.

Finally, what is the origin of indistinguishability? There are roughly two methods of distinguishing two particles. The obvious one is to use some physical properties, such as its mass, its spins, its charges etc – it's easy to tell apart an electron and a neutrino, even if both are fermions. What if both particles are the same, for example, both Helium nuclei? One possibility is to keep track of the trajectory of the particles, but this requires us to keep track of the exact position *and* momentum of the particle, which is of course not possible due to the Heiserberg Uncertainty Principle.

4.2 Bosons

In the case of bosons, there are no restrictions on $f_{\mathbf{n}}$. The sum Eq. (4.18),

$$\mathcal{Z}_{\mathbf{n}} \equiv \sum_{f_{\mathbf{n}}=0}^{f_{\mathbf{n}}=\infty} e^{-f_{\mathbf{n}}\beta(E_{\mathbf{n}}-\mu)} , \quad (4.27)$$

has the form of a geometric series you learned in high-skool

$$\sum_{p=0}^{p=\infty} x_{\mathbf{n}}^p = \frac{1}{1-x_{\mathbf{n}}} , \quad x_{\mathbf{n}} = e^{-\beta(E_{\mathbf{n}}-\mu)} , \quad (4.28)$$

and hence

$$\mathcal{Z}_{\mathbf{n}} = \frac{1}{1-e^{-\beta(E_{\mathbf{n}}-\mu)}} . \quad (4.29)$$

For this sum to converge, we must have $x_{\mathbf{n}} < 1$, which means that $\mu < E_{\mathbf{n}}$ for all \mathbf{n} . But since $E_{\mathbf{n}}$ only increases as \mathbf{n} increases, we require that the chemical potential must be less than the ground state energy

$$\mu \leq E_0 . \quad (4.30)$$

But E_0 is the lowest energy state, i.e. $E_0 = 0$ and hence $\mu \leq 0$.

We can compute the mean particle number for each state \mathbf{n} , by using Eq. (2.108)

$$\begin{aligned} \langle N_{\mathbf{n}} \rangle &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_{\mathbf{n}}}{\partial \mu} \\ &= \frac{1}{e^{\beta(E_{\mathbf{n}}-\mu)} - 1} , \end{aligned} \quad (4.31)$$

which is known as the **Bose-Einstein distribution**.

The grand partition function for bosons is then the product, Eq. (4.19),

$$\mathcal{Z} = \prod_{\mathbf{n}} \frac{1}{1-e^{-\beta(E_{\mathbf{n}}-\mu)}} . \quad (4.32)$$

The log of \mathcal{Z} is usually the more useful quantity as the log converts the product into a sum,

$$\ln \mathcal{Z} = - \sum_{\mathbf{n}} \ln \left(1 - e^{-\beta(E_{\mathbf{n}}-\mu)} \right) . \quad (4.33)$$

The total mean particle number of a boson gas is given by Eq. (2.108),

$$\begin{aligned} \langle N \rangle &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \\ &= \sum_{\mathbf{n}} \frac{1}{e^{\beta(E_{\mathbf{n}}-\mu)} - 1} \\ &= \sum_{\mathbf{n}} \langle N_{\mathbf{n}} \rangle , \end{aligned} \quad (4.34)$$

which is simply the sum over the mean particle numbers per state \mathbf{n} – the magic of taking logs. The Landau potential is then

$$\Psi = -k_b T \ln \mathcal{Z} = k_b T \sum_{\mathbf{n}} \ln \left(1 - e^{-\beta(E_{\mathbf{n}} - \mu)} \right) . \quad (4.35)$$

4.2.1 The Blackbody Radiation

We will now use our results to consider a critically important case – a gas of photons, or a gas of electromagnetic waves. The motion of the photons or electromagnetic waves is governed by the (quantized) Maxwell equations, so we have the following properties:

- **Quantum states of photons** : In vacuum, there are no charges or currents. In this case, the Maxwell equation is a Wave equation,

$$\frac{\partial^2 \mathbf{E}}{\partial t^2} - c^2 \nabla^2 \mathbf{E} = 0 , \quad (4.36)$$

with solutions

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} , \quad (4.37)$$

where

$$\omega = \pm |\mathbf{k}|c . \quad (4.38)$$

Since the free Maxwell equation is linear, it obeys the superposition principle, and hence we can solve the equation mode by mode, and obtain its **spectrum**

$$\mathbf{k} = (k_x, k_y, k_z) , \quad k_i = \frac{2\pi}{L} n_i , \quad n_i = 0, \pm 1, \pm 2, \dots \quad (4.39)$$

We see that the spectrum is identical to that of the quantum mechanical case we consider in section 4.1 earlier. Of course, the Maxwell equation is completely classical, so this fact is simply the result that both the quantum mechanical case in 4.1 and the Maxwell solutions are *waves*. The true content of quantum mechanics in section 4.1 is the quantized energy spectrum, Eq. (4.3). For photons, the analogous quantum mechanical energy is given by the Einstein quantization relation

$$E_{\omega} = \hbar \omega . \quad (4.40)$$

Notice that both Eq. (4.3) and Eq. (4.40) contain the crucial tell-tale constant \hbar that indicates their quantum mechanical nature.

Finally, there is another difference – for each wave number \mathbf{k} , electromagnetic waves possess *two* traverse polarization modes, so we have to take this into account.

- **Non-interaction in vacuum**: As we mentioned above, the vacuum Maxwell is linear, and obey the law of superposition. This means that *photons do not interact* since each wave doesn't care how many other waves are around, and hence behave like an ideal gas².
- **Zero chemical potential $\mu = 0$** : On the other hand, the photons can interact with other kind of matter via absorption and reemission (say on the walls of the box which the photons are contained), so *their number is not a conserved quantity*. This occurs even when the photons are in equilibrium with the box – i.e. no energy is lost or gained during this absorption and emission process (for example, a high energy photon can be absorbed with the emission of two lower energy photons).

²Actually, this is not quite true, as there exists some very weak interactions due to quantum fluctuations. This *photon-photon scattering* is mediated by the virtual production of electron-positron pairs, and is a purely quantum mechanical effect.

More explicitly, consider a system with fixed T and V , but with the number of particles N allowed to vary as we had argued. But the Helmholtz free energy F is minimum in equilibrium and hence a constant, so $dF/dt = 0$ or $dF = 0$ (see section 1.3.1), thus from Eq. (1.59)

$$dF = -SdT - PdV + \mu dN , \quad (4.41)$$

we see that since $dF = 0$, and $dT = dV = 0$ (for fixed T and V) implies that

$$\mu = 0 , \quad (4.42)$$

for all possible dN .

Given these conditions, using the Bose-Einstein distribution Eq. (4.31) and setting $\mu = 0$, we have

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta E_{\mathbf{n}}} - 1} . \quad (4.43)$$

To count the quantum states \mathbf{n} of photons, we recall Einstein taught us that for an electromagnetic wave of wavelength λ and hence has frequency $\omega = 2\pi c/\lambda$, its energy is given by Eq. (4.40), and hence we obtained the famous **Planck Distribution**,

$$\boxed{\langle N_{\omega} \rangle = \frac{1}{e^{\frac{\hbar\omega}{k_b T}} - 1}} , \quad (4.44)$$

where we have restored $\beta = (k_b T)^{-1}$. The Planck distribution is usually expressed as a *spectral energy of a unit volume of radiation*, i.e. the energy per unit volume per unit frequency $d\omega$, or $E(\omega)d\omega$. To calculate this, we note that the mean energy is given by Eq. (2.107), which with $\mu = 0$, is

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ &= \sum_{\mathbf{n}} \frac{E_{\mathbf{n}}}{e^{\beta E_{\mathbf{n}}} - 1} . \end{aligned} \quad (4.45)$$

Now the sum over all quantum states \mathbf{n} is something we have learned how to do, when we discussed the density of states in section 4.1.1. There, we learned that the density of states for a system whose quantum states are labeled by \mathbf{n} is given by Eq. (4.17)

$$g(E)dE = \frac{4\pi V}{(2\pi\hbar)^3} \frac{E^2}{c^3} dE \quad (4.46)$$

where we have used the relativistic version since photons travel at the speed of light. However, there is an additional wrinkle – for each mode \mathbf{n} , each photon possesses *two polarization modes*. This means that the correct density of states for photons is doubled that of Eq. (4.17), i.e.

$$g_{\gamma}(E)dE = 2 \times \frac{4\pi V}{(2\pi\hbar)^3} \frac{E^2}{c^3} dE . \quad (4.47)$$

Using this $g_{\gamma}(E)$, we can then express the sum Eq. (4.45) as an integral over the density of states

$$\begin{aligned} \langle E \rangle &= \sum_{\mathbf{n}} \frac{E_{\mathbf{n}}}{e^{\beta E_{\mathbf{n}}} - 1} \\ &= \int_0^{\infty} \frac{g_{\gamma}(E)E}{e^{\beta E} - 1} dE \\ &= \int_0^{\infty} \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \\ &\equiv \int_0^{\infty} E(\omega)d\omega , \end{aligned} \quad (4.48)$$

where

$$E(\omega, T) = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{k_b T}} - 1} . \quad (4.49)$$

is the Planck distribution in a more familiar form. We have made explicit the fact that the distribution depends on the temperature T (or β).

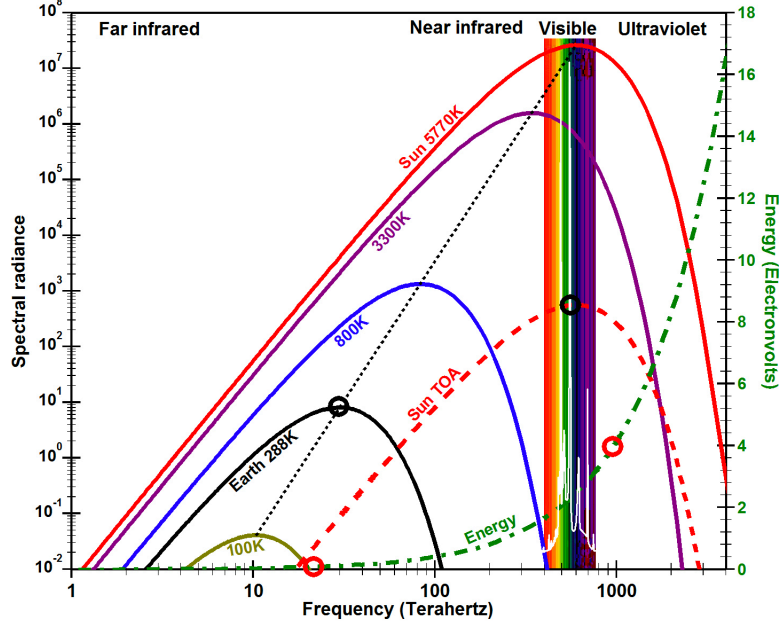


Figure 4.2: The Planck distribution as a function of frequency.

With this distribution (see Fig. 4.2), we can derive several well known laws. Notice that at small ω or high temperatures, $\omega \ll k_b T / \hbar$, the exponential $e^{\hbar\omega/k_b T} \ll 1$, we can expand (homework)

$$\frac{1}{e^{\hbar\omega/k_b T} - 1} \approx \frac{k_b T}{\hbar\omega} + \dots \quad (4.50)$$

so we obtain the **Rayleigh-Jeans law**

$$E_{RJ}(\omega) = \frac{V k_b T}{\pi^2 c^3} \omega^2, \quad \omega \ll k_b T / \hbar, \quad (4.51)$$

where the distribution rises as ω^2 . Notice that this law has no \hbar – it has no quantum mechanics in it. Indeed, this was first derived classically by Rayleigh and Jeans, and was successful at reproducing experimental results at low frequencies. However, since the distribution rises without bound at high frequencies, the integral $\int_0^\infty E_{RJ}(\omega) d\omega \rightarrow \infty$. This is known as the **Ultraviolet Catastrophe**, and is instrumental in guiding physicists towards the realization that physics is quantum mechanical in nature.

Coming back to the Planck distribution, at high frequencies, the $(e^{\hbar\omega/k_b T} - 1)^{-1}$ term will start to dominate at larger $\omega \gg k_b T / \hbar$, so the distribution becomes highly suppressed, behaving as

$$E_{WL}(\omega) = \frac{V\hbar}{\pi^2 c^3} \omega^3 e^{-\hbar\omega/k_b T}, \quad (4.52)$$

which is sometimes known as the “Wien’s Law” (not to be confused with the more famous Wien’s displacement law below). Thus there exists a maximum ω_{\max} , which we can compute as usual

$$\frac{dE}{d\omega}(\omega_{\max}) = 0 \quad (4.53)$$

which gives us the implicit formula (homework)

$$3 + e^{\frac{\hbar\omega_{\max}}{k_b T}} \left(\frac{\hbar\omega_{\max}}{k_b T} - 3 \right) = 0.$$

By setting $x \equiv \hbar\omega_{\max}/k_b T$, the equation becomes

$$x - 3 = -3e^{-x} \quad (4.54)$$

which can be numerically solved to get us $x \approx 2.8$, giving us the **Wien's Displacement Law**

$$\boxed{\omega_{\max} = 2.8 \frac{k_b T}{\hbar}}. \quad (4.55)$$

Since k_b and \hbar are fundamental constants, this means that $\omega_{\max} \propto T$.

Let us now compute the thermodynamics quantities of blackbody radiation.

- **Free energy:** Since the chemical potential $\mu = 0$, the Helmholtz free energy $F = E - TS$ and the Landau potential $\Psi = E - TS + \mu N$ coincides, so we can use Eq. (2.114) to compute

$$F = \Psi = -k_b T \ln \mathcal{Z} \quad (4.56)$$

which from Eq. (4.35),

$$\begin{aligned} F &= k_b T \sum_{\mathbf{n}} \ln(1 - e^{-\beta E_{\mathbf{n}}}) \\ &= k_b T \int_0^{\infty} g_{\gamma}(E) \ln(1 - e^{-\beta E}) dE \\ &= k_b T \int_0^{\infty} \frac{\pi V}{(\pi \hbar)^3} \frac{E^2}{c^3} \ln(1 - e^{-\beta E}) dE, \end{aligned} \quad (4.57)$$

where we have used the density of states for photons Eq. (4.47) to convert the sum over states into an integral over E . This integral is actually doable analytically. First defining $x \equiv \beta E$, we have

$$F = \frac{V}{\pi^2 (\hbar c)^3 \beta^4} \int_0^{\infty} x^2 \ln(1 - e^{-x}) dx, \quad (4.58)$$

then we integrate by parts,

$$\int_0^{\infty} x^2 \ln(1 - e^{-x}) dx = \frac{x^3}{3} \ln(1 - e^{-x}) \Big|_0^{\infty} - \int_0^{\infty} \frac{x^3}{3} \frac{1}{e^x - 1} dx \quad (4.59)$$

where the first term vanishes, leaving us with the 2nd term. This horrible looking integral actually has a solution³

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}. \quad (4.61)$$

The free energy is then

$$F = -\frac{V \pi^2 (k_b T)^4}{45 (\hbar c)^3}. \quad (4.62)$$

Meanwhile, the entropy S is given by Eq. (1.32)

$$S = -\left(\frac{\partial F}{\partial T} \right)_V = \frac{4V \pi^2 k_b^4 T^3}{45 (\hbar c)^3}. \quad (4.63)$$

³Integrals of the form

$$\int_0^{\infty} \frac{x^p}{e^x \pm 1} dx, \quad (4.60)$$

occur frequently in statistical mechanics, and we will see them again soon. See Appendix A.2 for the formulas.

The total internal energy is then,

$$E = F + TS = \frac{V\pi^2(k_bT)^4}{15h^3c^3}. \quad (4.64)$$

Of course you can obtain the same exact answer if you integrate the Planck distribution Eq. (4.49) directly $E = \int_0^\infty E(\omega)d\omega$, which you will do in a homework problem. If we define the **Stefan-Boltzmann constant**

$$\sigma \equiv \frac{\pi^2 k_b^4}{60h^3c^2} = 5.67 \times 10^{-5} \text{ g s}^{-3} \text{ deg}^{-4}, \quad (4.65)$$

then we recover the **Stefan-Boltzmann Law** of radiation energy as a function of T ,

$$\boxed{\frac{E}{V} = \rho_{\text{rad}} = \frac{4\sigma}{c}T^4}. \quad (4.66)$$

Eq. (4.66) tells us that the energy density of blackbody radiation scales as T^4 .

- **Radiation Pressure:** Using the relationship between the Landau potential and the pressure, Eq. (1.80), we have

$$F = \Psi = -PV \quad (4.67)$$

or

$$\boxed{P = \frac{4\sigma T^4}{3c} = \frac{1}{3}\rho_{\text{rad}}}, \quad (4.68)$$

which expresses the well-known result that radiation pressure is a third of its energy density.

- **Heat capacity:** We can compute the heat capacity of radiation using Eq. (1.50)

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{16\sigma T^3 V}{c}. \quad (4.69)$$

This result, while innocuous, tells us that the hotter the gas is, the harder it is to heat it up, since $C_V \propto T^3$. Since the spectrum of accessible modes increases with increasing T , this tells us that *higher frequency modes are harder to “activate”*. We will come back to this point in section 4.2.3

The Cosmic Microwave Background

One of the most important application of the blackbody radiation is the **Cosmic Microwave Background**. If we point a radio telescope at a random direction in the sky, you will find a stream of photons, with a number density that is a function of the frequency ω , i.e. a spectrum. The spectrum of this stream of photons *almost* exactly matches that of the Planck distribution Eq. (4.44), with a temperature of $T = 2.725$ K. The remarkable thing about this radiation is that it is isotropic – it doesn’t matter where you point that telescope.

In the old days, when you still get your television from terrestrial broadcasts, your television set’s aerial receiver would pick up some of this radiation, and you can literally visually see this radiation. Nowadays of course, you get everything on the internet, so to see this radiation, you google and you will get a plot like Fig. 4.3. The CMB is the afterglow of the Big Bang – the universe started out very hot, and cools down as it expands. Throughout its evolution, the radiation component of the matter in the universe behaves like blackbody radiation.

This radiation was first detected by Penzias and Wilson in 1964, rather accidentally. A spacecraft, *COBE*, was launched in 1990 to measure this spectrum more precisely, and the result is shown in Fig. 4.3. Remarkably, while the radiation is extremely uniform and isotropic across the sky, it is *not exactly* isotropic – it turns out that there is an average fluctuation $\Delta T/T \sim 10^{-5}$, i.e. about 1 part in 100000. This **CMB anisotropy** is the seed of all the structure that we see in the universe today – galaxies, stars, planets, cats, physics students etc. The question is then “where did that come from?”. The study of the origins of structure is an active field of research today.

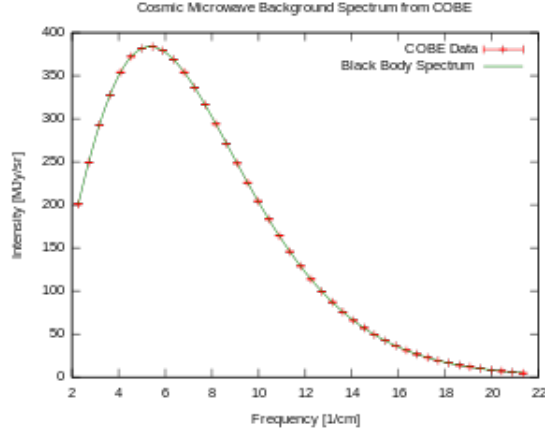


Figure 4.3: The Cosmic Microwave Spectrum, as measured by the satellite *COBE* in 1990. The data fits almost exactly on the theoretical curve for a Planck spectrum of $T = 2.725$ K.

4.2.2 Phonons in solids : the Debye Model

For most solids (say pure silver), the heat capacity C_V behaves as shown in Fig. 4.4. At high temperatures, the heat capacity is a fixed number that doesn't depend on the material,

$$\text{High temperature : } C_V = 3Nk_b \quad (4.70)$$

where N is the total number of particles in the solid, known as the **Dulong-Petit Law**. At low temperatures, we find that its heat capacity scales like

$$\text{Low temperature : } C_V = \alpha T^3 + \gamma T \quad (4.71)$$

where α and γ are usually obtained from experiments. Remarkably, this behaviour is true for most solids! How does this come about? The answer to this question is actually in two part – the αT^3 and γT contributions comes from different physics. We will focus on the first term, and postpone the γT term – which comes from the free electrons – to section 4.3.4 when we study fermions.

We first note that the low temperature scaling $C_V \propto T^3$ is the same as the heat capacity for blackbody radiation Eq. (4.69). As we will see in this section, this is not a coincidence – the behaviour of vibration modes of a solid very closely mimics that of a gas of photons! Let's see how this can be true.

A solid can be modeled as a 3-dimensional lattice of masses, connected to each other by a spring as in Fig. 4.5. While the individual masses are restricted to more or less their location in the lattice, they can vibrate against each other. These vibration modes, as you have studied in the Fields and Waves course, are the **sound waves**. Like all waves, these vibration modes which are *density perturbations* $v(\mathbf{x}, t) \equiv \delta\rho(\mathbf{x}, t)$ of the solid itself, evolve according to the Wave equation

$$\frac{\partial^2 v}{\partial t^2} - c_s^2 \nabla^2 v = 0, \quad (4.72)$$

where c_s^2 is the **sound speed squared** of the vibration modes. We can consider a traveling wave in the x direction, the solution is then

$$v(x, t) = v_0 e^{i(k_x x - \omega t)}, \quad (4.73)$$

where

$$\omega = \pm k_x c_s. \quad (4.74)$$

Suppose now the lattice is a cube with length L , then imposing periodic boundary conditions

$$\delta\rho(x = L) = \delta\rho(x = 0),$$

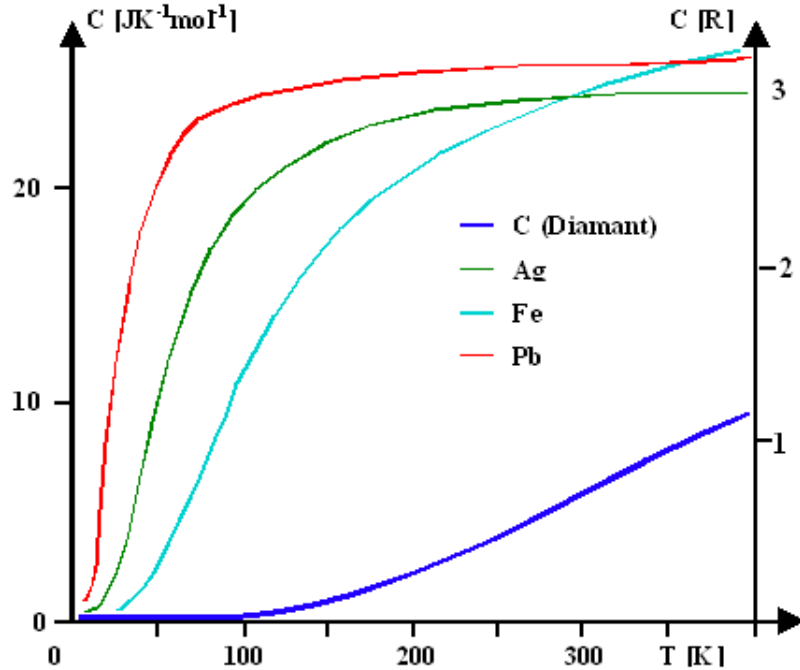


Figure 4.4: Experimentally measured values of C_V for various solids. At low temperatures, $C_V = \alpha T^3 + \gamma T$, while at high temperatures it asymptotes to the classically expected value of $C_V = 3Nk_b$.

means that the solution has a *discrete* spectrum

$$k_x = \frac{2\pi}{L} n_x, \quad n_x = 0, \pm 1, \pm 2, \dots \quad (4.75)$$

Since the Wave equation is linear and thus its solutions obey the principle of superposition, we can solve a single wave in a single direction, and then sum up the results WLOG. The solutions span the following parameter space

$$\mathbf{k} = (k_x, k_y, k_z), \quad k_i = \frac{2\pi}{L} n_i. \quad (4.76)$$

This is beginning to look very familiar – they are like the photons we just studied! Indeed, it shouldn't be surprising since photons are electromagnetic waves which also obey the wave equation! As in the photons case, this is all classical – the solutions simply describe propagating sound waves. Now we make the somewhat reckless assumption that these waves can be *quantized* just like their electromagnetic counterparts with the Einstein quantization relationship

$$E_\omega = \hbar\omega = \hbar kc_s. \quad (4.77)$$

A “quantized” sound wave is called a **phonon**, just like a quantized electromagnetic wave is called a photon⁴. Indeed, with this quantization, all the machinery we have developed for studying the photon gas can be imported directly to the study of vibrations in solids, with two important exceptions.

- **3 vs 2 polarization modes:** There are *three* polarization phonon modes per wave mode, instead of two for electromagnetic waves. This is due to the fact that sound waves travel at less than the speed of light $c_s < c$, so there exists a longitudinal mode in addition to the two traverse modes. In general, the longitudinal mode and the traverse mode may possess different sound speeds – we have assumed that they are the same for simplicity.

⁴The “phon” in phonon comes from the Greek word *phonetikus*, which means sound.

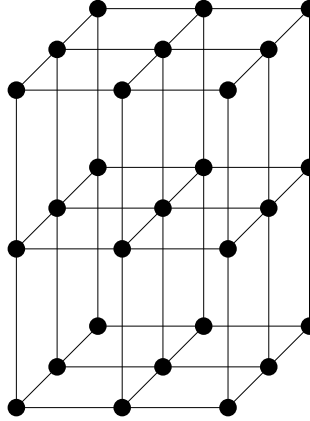


Figure 4.5: A model of a solid, with masses connected to each other with springs.

- **Maximum frequency ω_D :** Unlike electromagnetic waves which can take arbitrary high frequencies, phonons cannot take arbitrary high frequencies, since the vibrational wavelength is limited by the spacing between the lattice points. If N is the number of particles and λ_D is the distance between two particles, then

$$\lambda_D \sim \left(\frac{V}{N}\right)^{1/3}, \quad (4.78)$$

and hence the maximum frequency $\omega_D \sim c_s/\lambda_D$ before the wave approximation breaks down. The subscript “ D ” stands for **Debye**, after Peter Debye, of which this model of phonons is named after. We will calculate exactly what this value is later.

In the case of low temperatures, $T \ll \hbar\omega_D/k_b$, then we can see from the mean particle per mode Eq. (4.31)

$$\langle N_\omega \rangle = \frac{1}{e^{\hbar\omega/k_b T} - 1} \quad (4.79)$$

that in low temperatures, most of the high frequency modes are not activated, so we can safely integrate the energy $\langle E \rangle = \int_0^\infty E(\omega)d\omega$ as we have done in section 4.2.1. All the results follow then by simply making the replacement

$$\frac{2}{c^3} \rightarrow \frac{3}{c_s^3}, \quad (4.80)$$

which you can see easily by observing the density of states Eq. (4.47).

Harking back to the question about the heat capacity, we can immediately use Eq. (4.69), and convert it with Eq. (4.80) to get (don’t forget that σ contains a factor of c^{-2} !)

$$C_V = \frac{2\pi^2 k_b^4 V}{5\hbar^3 c_s^3} T^3 \propto T^3, \quad (4.81)$$

as was found by experiment for low temperatures.

What about the high temperature limit, where $T \gg \hbar\omega_D/k_b$? In this case, we cannot integrate from the frequencies from zero to infinity, since high frequency modes no longer behave like the sound waves. In this case, instead of integrating the frequencies all the way to $\omega \rightarrow \infty$, Debye proposed that *the total number of modes from $\omega = 0$ to $\omega = \omega_D$ is exactly equal to the three times the number of particles $3N$* , or

$$\int_0^{\omega_D} g_D(\omega)d\omega = 3N, \quad g_D(\omega) = \frac{12\pi V \omega^2}{(2\pi)^3 c_s^3}. \quad (4.82)$$

Here we have used $E = \hbar\omega$ to convert the relativistic density of states for photons Eq. (4.47), and used the replacement $2/c^3 \rightarrow 3/c_s^3$ as usual. This integral is easy to do, and we get

$$3N = \frac{4\pi V \omega_D^3}{(2\pi)^3 c_s^3}, \quad (4.83)$$

which gives us the cut-off ω_D ,

$$\omega_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} c_s. \quad (4.84)$$

This frequency is known (unsurprisingly) as the **Debye frequency**.

To compute the heat capacity C_V , again we follow the derivation in the black body case except the point when we perform the horrible integral Eq. (4.61), we only integrate up to a finite value $x_D \equiv \beta\hbar\omega_D$, i.e.

$$\int_0^\infty \frac{x^3}{e^x - 1} dx \rightarrow \int_0^{x_D} \frac{x^3}{e^x - 1} dx.$$

But since we are considering high temperatures $T \gg \hbar\omega_D/k_b$, this means that $x_D \ll 1$, and hence we can Taylor expand the integrand

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \approx \int_0^{x_D} (x^2 + \dots) dx = \frac{x_D^3}{3} + \dots. \quad (4.85)$$

With this result, we can obtain the total internal energy of phonons of solids at high temperature by taking Eq. (4.64), and replacing $2/c^3 \rightarrow 3/c_s^3$ and $\pi^4/15 \rightarrow x_D^3/3$, to get

$$E = \frac{V k_b T}{2\pi^2 c_s^3} \omega_D^3. \quad (4.86)$$

The heat capacity is then, using and the Debye frequency Eq. (4.84),

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N k_b, \quad (4.87)$$

which is exactly as experimentally observed.

We should pause and admire how crazy this simple model works so well. The reckless quantization condition Eq. (4.77) works because ultimately, the constituents of the solid are particles which interact quantum mechanically. The Debye proposal Eq. (4.83) requires more exposition which unfortunately we don't have time for, but roughly it says that the total number of phonon states is equal to the number of ways you can excite a lattice of N particles which is $3N$ for three degrees of freedom per particle. You will learn about this in the Solid State Physics module next term.

4.2.3 Mode freeze-out

Most interestingly, the Debye model captures the physics where the total number of accessible states (see section 2.1 for a refresher on accessible states) *changes with temperature*. Here, the Debye frequency ω_D sets a temperature scale

$$T_D \equiv \frac{\hbar\omega_D}{k_b}, \quad (4.88)$$

which is known as the **Debye temperature**. Above $T > T_D$, the solid's heat capacity obeys the Dulong-Petit limit of $C_V = 3k_b N$. Below $T < T_D$, the heat capacity is reduced, when compared to the Dulong-Petit limit. In our discussion above, we argue that this is due to the fact that high frequency modes are not activated. In other words, at low temperatures, *not all modes are active*. This behaviour is colloquially called a "freezing-out" of modes. Indeed, we already see this effect when we studied the black body radiation. The heat capacity is given by Eq. (4.69), or $C_V \propto T^3$, as we argued this means that higher frequencies are harder to excite.

Harking back to our discussion on the heat capacity of the diatomic gas, recall that modeling it as a classical gas suggests that $C_V = 7/2k_bT$, while experiments show that C_V increases with temperature as shown in Fig. 3.2. Let's see how this works using our newfangled quantum mechanical understanding explains the behaviour.

In your homework problem, you showed that the diatomic gas can be modeled as a gas of dumbbells connected by springs. Its energy contribution can be split into translation kinetic energy $E_{\text{kin}} = 3/2k_bT$, rotational energy $E_{\text{rot}} = k_bT$ and vibration energy $E_{\text{vib}} = k_bT$, per particle. Classically, all these degrees of freedom should contribute to the heat capacity, but as shown in Fig. 3.2, it turns out that at low temperatures, only E_{kin} is present, while at some intermediate temperature $E_{\text{rot}} = k_bT$ starts to contribute and at high temperatures $E_{\text{vib}} = k_bT$ finally kicks in.

The explanation for this is rotation and vibration modes are “harder” to activate. Consider the vibration mode. Classically, we model it as a harmonic oscillator. Quantum mechanically, it is also a harmonic oscillator, but as you have learned in your Quantum Mechanics course, the quantum simple harmonic oscillator has a quantized energy spectrum

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad (4.89)$$

where again ω is the natural frequency of oscillation which depends on the atomic bond (i.e. the “spring” of the dumbbell) so is a constant of the model. The canonical partition function for a single particle is given by Eq. (4.4),

$$\begin{aligned} Z_{\text{vib}} &= \sum_n e^{-\beta E_n} \\ &= \sum_n e^{-\beta \hbar\omega (n+1/2)} \\ &= e^{-\beta \hbar\omega / 2} \sum_n e^{-\beta \hbar\omega n} \\ &= \frac{e^{-\beta \hbar\omega / 2}}{1 - e^{-\beta \hbar\omega}} \\ &= \frac{1}{2 \sinh(\hbar\omega / 2k_bT)} \end{aligned} \quad (4.90)$$

where we have again used the geometric sum in line 3. At high temperatures, $T \gg \hbar\omega/k_b$, $\sinh(\hbar\omega/2k_bT) \approx \hbar\omega/2k_bT$ so $Z_{\text{vib}} = k_bT/\hbar\omega = 1/\beta\hbar\omega$. The average energy is then

$$E_{\text{vib}} = -\frac{\partial}{\partial\beta} \ln Z_{\text{vib}} = k_bT, \quad (4.91)$$

which is the classical result.

On the other hand, at low temperatures $T \ll \hbar\omega/k_b$, the partition function becomes $Z_{\text{vib}} \approx e^{-\beta\hbar\omega/2}$, and then

$$E_{\text{vib}} = -\frac{\partial}{\partial\beta} \ln Z_{\text{vib}} = \frac{\hbar\omega}{2}, \quad (4.92)$$

which is just the vacuum energy of the harmonic oscillator. In other words, the oscillator is not oscillating, and not active. The contribution to the heat capacity is $C_V = (\partial E/\partial T)_V = 0$, as experiments confirmed.

What determines the temperature where these modes get “activated” or “accessed”? For the vibration modes, since the condition for high T and low T is compared to $\hbar\omega/k_b$, it is the natural frequency ω of the diatom, thus the transition temperature is then $T_{\text{vib}} \equiv \hbar\omega/k_b$. You will show in a homework problem that for rotational modes, the transition temperature $T_{\text{rot}} = \hbar^2/2Ik_b$ where I is the moment of inertia of the particle. Thus, these modes get “activated” at different temperatures, resulting in the step-like behaviour of the C_V as a function of temperature we see experimentally.

Finally, what about non-relativistic bosons with $\mu < 0$? In this case, we will use the non-relativistic version of the density of states Eq. (4.13) when performing the integrals over the energy E . As it turns out, the calculation that follows will be very similar to the fermionic case section 4.3. We will postpone it for now, and let you do all the hard work in a homework problem.

4.3 Fermions

For fermions, the occupation number $f_{\mathbf{n}}$ can only be 0 or 1, due to the Pauli Exclusion Principle. So the sum Eq. (4.18) truncates, giving us the state subsystem partition function

$$\mathcal{Z}_{\mathbf{n}} = \sum_{f_{\mathbf{n}}} e^{-f_{\mathbf{n}}\beta(E_{\mathbf{n}}-\mu)} = 1 + e^{-\beta(E_{\mathbf{n}}-\mu)}. \quad (4.93)$$

The chemical potential μ can take both positive and negative (and zero) values.

Turning the crank, we can compute all the relevant quantities. The mean particle number for each state \mathbf{n} is (using Eq. (2.108),

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_{\mathbf{n}}}{\partial \mu} = \frac{1}{e^{\beta(E_{\mathbf{n}}-\mu)} + 1}, \quad (4.94)$$

which differs from its Bosonic counterpart Eq. (4.31) by a + sign. This distribution Eq. (4.94) is known as the **Fermi-Dirac distribution**.

The grand partition function for fermions is then the product, Eq. (4.19)

$$\mathcal{Z} = \prod_{\mathbf{n}} \left(1 + e^{-\beta(E_{\mathbf{n}}-\mu)} \right). \quad (4.95)$$

As usual, the log of \mathcal{Z} is the more useful quantity as the log converts the product into a sum,

$$\ln \mathcal{Z} = \sum_{\mathbf{n}} \ln \left(1 + e^{-\beta(E_{\mathbf{n}}-\mu)} \right). \quad (4.96)$$

The total mean particle number of a fermion gas is given by Eq. (2.108),

$$\begin{aligned} \langle N \rangle &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} \\ &= \sum_{\mathbf{n}} \langle N_{\mathbf{n}} \rangle, \end{aligned} \quad (4.97)$$

which, as in the case of the bosons, is the sum over the mean particle number state \mathbf{n} . The Landau potential is then

$$\Psi = -k_b T \ln \mathcal{Z} = -k_b T \sum_{\mathbf{n}} \ln \left(1 + e^{-\beta(E_{\mathbf{n}}-\mu)} \right), \quad (4.98)$$

which differs from that of the bosons Eq. (4.35) by both signs being flipped. This similarity in equations means that a lot of the mathematics we have developed for the bosons will be recycled for what comes next.

4.3.1 Non-relativistic fermion gas

As usual, to compute the grand partition function, we need to know how to count the quantum state \mathbf{n} . Non-relativistic fermions with mass m obey the Schrodinger's equation, and hence their spectrum of states is exactly as discussed in section 4.1.1. We asserted previously that fermions have half-integer spins, $s = 1/2, 3/2, 5/2, \dots$. As you have learned in your quantum mechanics module, spin s fermions have a degeneracy of

$$\tilde{g} = 2s + 1. \quad (4.99)$$

For example, electrons are spin-1/2 particles, thus has a degeneracy of 2, i.e. the spin “up” and spin “down” states.

Thus for each principal quantum number \mathbf{n} , we need to count \tilde{g} time, so the density of states for non-relativistic fermions is \tilde{g} times Eq. (4.13)

$$g_f(E)dE = \tilde{g} \times \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{1/2} dE , \quad (4.100)$$

Using this, and the by now familiar substitution $x \equiv \beta E$, the mean particle number is given by Eq. (4.97),

$$\begin{aligned} \langle N \rangle &= \sum_{\mathbf{n}} \langle N_{\mathbf{n}} \rangle \\ &= \int_0^\infty \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{1/2}}{e^{\beta(E_{\mathbf{n}}-\mu)} + 1} dE \\ &= \int_0^\infty \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} \frac{m^{3/2}}{\beta^{3/2}} \frac{x^{1/2}}{e^{x-\beta\mu} + 1} dx , \end{aligned} \quad (4.101)$$

while the mean energy is given by

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu \langle N \rangle \\ &= \sum_{\mathbf{n}} \frac{E_{\mathbf{n}}}{e^{\beta(E_{\mathbf{n}}-\mu)} + 1} \\ &= \int_0^\infty \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{3/2}}{e^{\beta(E_{\mathbf{n}}-\mu)} + 1} dE \\ &= \int_0^\infty \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} \frac{m^{3/2}}{\beta^{5/2}} \frac{x^{3/2}}{e^{x-\beta\mu} + 1} dx . \end{aligned} \quad (4.102)$$

In both cases, we get integrals of the form

$$\int_0^\infty \frac{x^p}{e^{x-\beta\mu} + 1} dx$$

which are actually quite tricky to do in general. But as you might have guessed by now, things simplify when we consider the high temperature or low temperature limit.

4.3.2 The classical limit : high temperature and low density

Note that the derivation in this section is very similar for the classical limit of bosons, which you will solve in a homework set.

Since we know that classical physics do work most of the time, there must be some limit where we recover the classical gas we studied in Chapter 3. Heuristically, from our understanding of mode freeze-out in section 4.2.3, we expect this to be the at *high temperature* when all the modes are activated and the classical counting works. Furthermore, if we pack too many particles close together, we expect quantum effects to start to be important, so the classical limit should also correspond to the *low density* limit. With these two **classical limits**, we should be able to recover the ideal gas law $PV = Nk_bT$, that we derived earlier. Let’s see how this works.

Now we shall make an assertion. The high temperature limit ($\beta \rightarrow 0$ or $T \rightarrow \infty$) corresponds to

$$e^{\beta\mu} \ll 1 . \quad (4.103)$$

This seems counter-intuitive – at $\beta \rightarrow 0$, surely $e^0 \rightarrow 1$? It turns out that this is too quick – if we fixed N , then Eq. (4.97)

$$\langle N \rangle = \int_0^\infty \frac{g_f(E)}{e^{-\beta\mu+\beta E} + 1} dE \quad (4.104)$$

tells us that μ must also change as we take $T \rightarrow \infty$. Now, we have argued that $\mu < 0$ for most cases in the classical limit (it will turn out that $\mu > 0$ for the quantum limit for fermions, which we will see in the next section). It will turn out that $\mu \rightarrow -\infty$ quicker than $T \rightarrow \infty$ – indeed we will show later that $e^{\beta\mu} \propto T^{-3/2}$, so it makes sense to take the limit Eq. (4.103).

Thus, we can Taylor expand the integral

$$\begin{aligned} \int_0^\infty \frac{x^p}{e^{x-\beta\mu} + 1} dx &\approx e^{\beta\mu} \int_0^\infty x^p e^{-x} (1 - e^{\beta\mu} e^{-x} + \dots) dx \\ &= e^{\beta\mu} \left[\Gamma(p+1) - \frac{1}{2^{p+1}} \Gamma(p+1) e^{\beta\mu} + \dots \right] \end{aligned} \quad (4.105)$$

where we have used the definition of the gamma function Eq. (A.9) to do the integrals⁵. For now, let's ignore the 2nd term in the integrals since at high temperatures $e^{\beta\mu} \ll 1$. The energy $\langle E \rangle$ and particle number $\langle N \rangle$ are then (with $p = 3/2$ and $p = 1/2$ respectively),

$$\langle E \rangle \approx \tilde{g}V \frac{3}{2\beta} \frac{e^{\beta\mu}}{\lambda^3}, \quad \langle N \rangle \approx \tilde{g}V \frac{e^{\beta\mu}}{\lambda^3} \quad (4.106)$$

where we have used the thermal de Broglie wavelength Eq. (3.12), $\lambda = \sqrt{2\pi\hbar^2/mk_bT}$ to express the results in a more suggestive form. This gives us the very familiar result

$$\langle E \rangle = \frac{3}{2} k_b T \langle N \rangle, \quad (4.107)$$

which, according to the Equipartition theorem Eq. (3.16), tells us that the fermion has 3 d.o.f. This is exactly what we should expect, since we are using the Schrodinger's equation to describe the translational motion of the particles!

From $\Psi = -PV$, we can integrate the Landau potential Eq. (4.98),

$$\begin{aligned} \Psi &= -\frac{1}{\beta} \int_0^\infty \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{1/2} \ln(1 + e^{-\beta(E-\mu)}) dE \\ &= -\frac{1}{\beta} \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} \left(\frac{m}{\beta}\right)^{3/2} \int_0^\infty x^{1/2} \ln(1 + e^{-x+\beta\mu}) dx \end{aligned} \quad (4.108)$$

using $x = \beta E$ which you should be doing it in your sleep by now. We have seen this kind of log integral before when we studied bosons – we can integrate by parts (see Eq. (4.59))

$$\int_0^\infty x^{1/2} \ln(1 + e^{-x+\beta\mu}) dx = \frac{2x^{3/2}}{3} \ln(1 + e^{-x+\beta\mu}) \Big|_0^\infty + \frac{2}{3} \int_0^\infty x^{3/2} \frac{1}{e^{x-\beta\mu} + 1} dx. \quad (4.109)$$

The first term vanishes, and the second term then has the form of the energy integral Eq. (4.102), except with an extra factor of 2/3, so

$$\boxed{PV = -\Psi = \frac{2}{3} \langle E \rangle}. \quad (4.110)$$

Note that Eq. (4.110) is very general – it is valid for all non-relativistic gas, not just those in the classical limit, for both bosons and fermions. This is because we have not performed the integral.

Combining this result with the Eq. (4.107), we recover the ideal gas law

$$PV = Nk_bT, \quad (4.111)$$

as we asserted.

But wait! We also said that the classical limit requires *low density*! Where have we sneaked this argument in? The place is when we computed the particle number Eq. (4.106), where we can express as

$$\frac{\langle N \rangle}{\tilde{g}} \lambda^3 = e^{\beta\mu} \ll 1. \quad (4.112)$$

⁵The second term of the integral can be obtained by making the substitution $y = 2x$

Since $N\lambda^3/\tilde{g}$ is the total volume of taken by the particles, then $N\lambda^3/V\tilde{g}$ is the fraction of space occupied by the particles themselves (notice that we divide N by \tilde{g} because degeneracy means that \tilde{g} particles can occupy the same state). Imposing the high temperature limit means that this fraction is very small – i.e. the density is small. In other words, the two limits are equivalent. Finally, notice that if we keep N/V fixed, then

$$e^{\beta\mu} \propto T^{-3/2} . \quad (4.113)$$

which justifies our assertion earlier Eq. (4.103).

In general, since the factor $e^{\beta\mu} \ll 1$ is small, we can use it as an expansion parameter – indeed you can see from our expansion Eq. (4.105), that the next to leading order term is $e^{\beta\mu}$. In a homework problem, you will be asked to compute the leading order corrections to the classical ideal gas law $PV = Nk_bT$, and show that, for *both bosons and fermions*, the ideal gas law is given by

$$PV = Nk_bT \left[1 \pm 2^{-5/2} \frac{N/\tilde{g}}{V} \lambda^3 + \dots \right] , \quad (4.114)$$

where the $+$ sign is for fermions while the $-$ sign is for bosons. You will notice that it is again an expansion in the density parameter N/V , just like the virial expansion that we discussed in section 3.5.2 for the Van der Waals forces⁶. An easy mnemonic to remember the signs is to realize that bosons want to “stay together” while fermions want to “stay apart”, so the correction to the pressure decreases and increases respectively. The fact that both fermions and bosons reduce to the classical ideal gas law in the classical limit is not surprising, since classical physics do not distinguish between fermions or bosons.

4.3.3 Low temperature fermions : degenerate fermion gas

What happens if we move away from the classical limit, i.e. what happens at low temperatures and high densities? In this limit, quantum mechanics will begin to dominate, and we expect the fermionic or bosonic nature of the particles to become important. This is exactly what happens – bosons and fermions behave drastically differently. We will postpone the study low temperature/high density bosons to the next Chapter, and focus on the physics of fermions in this section.

Consider the Fermi-Dirac distribution Eq. (4.94),

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} + 1} .$$

At very low temperatures, $\beta = (k_bT)^{-1} \gg 1$, and now $\langle N_{\mathbf{n}} \rangle$ depends on the sign of $E_{\mathbf{n}} - \mu$,

$$\begin{aligned} E_{\mathbf{n}} < \mu & \quad , \quad \langle N_{\mathbf{n}} \rangle \rightarrow 1 \\ E_{\mathbf{n}} > \mu & \quad , \quad \langle N_{\mathbf{n}} \rangle \rightarrow 0 . \end{aligned} \quad (4.115)$$

In words, states with energies smaller than μ will be occupied, while states with energies bigger than μ will be unoccupied. The Fermi-Dirac distribution then looks like a step function, Fig. 4.6. The point where the step is, $E_{\mathbf{n}} = \mu \equiv E_F$, is called the **Fermi Energy**. The associated momentum

$$p_F \equiv \sqrt{2mE_F} , \quad (4.116)$$

is called the **Fermi momentum**. We emphasise that since μ is a conjugate variable to the total particle number N (see section 1.5), μ and hence E_F in general depends on N .

Physically we can understand this as follows. At very low temperatures, the fermions are more likely to possess low momentum than high momentum, so would prefer to occupy the low momentum states.

⁶While both corrections are due to quantum mechanical forces, they are not the same kind of corrections.

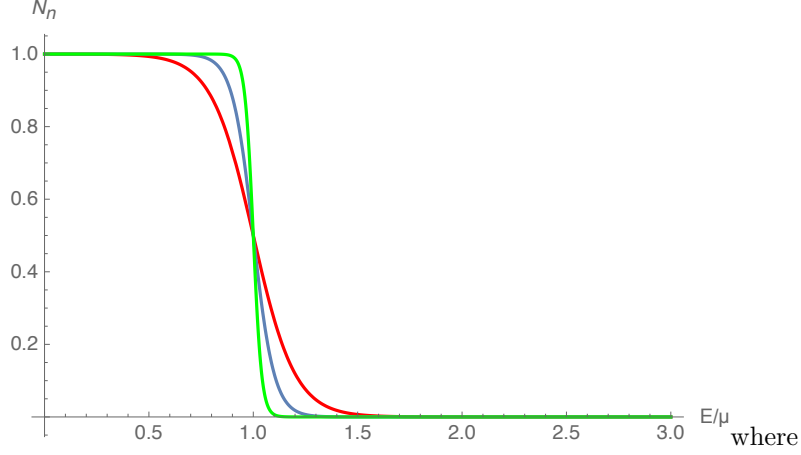


Figure 4.6: The Fermi-Dirac distribution at very low temperatures, with $\beta = 10, 20, 50$ (red, blue, green). As β increases, i.e. temperature decreases, the distribution becomes more and more step function like, with the step being at the Fermi energy $E_{\mathbf{n}} = \mu \equiv E_F$.

However, since fermions obey the Pauli Exclusion Principle, they cannot all occupy the same lowest momentum states. So they start to fill up spectrum by occupying all the available states from the lowest energy, to the next lowest energy and then to the third lowest energy and so on and so forth. Now due to the degeneracy of spins, each principal state \mathbf{n} possess a degeneracy of $\tilde{g} = 2s + 1$ fermions. This continue until we reached the Fermi energy E_F . So one can picture a low temperature fermion gas as a “sea” of degenerate fermions, with the surface defined by the Fermi energy E_F . This is known as the **Fermi sea**. A fermion gas at this very low temperature is called a **degenerate gas**, as deep in the sea the fermions are degenerate.

We can compute the particle number of the fermions as usual, from Eq. (4.101)

$$\begin{aligned} \langle N \rangle &= \sum_{\mathbf{n}} \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} + 1} \\ &= \int_0^{\infty} \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{1/2}}{e^{\beta(E_{\mathbf{n}} - \mu)} + 1} dE . \end{aligned} \quad (4.117)$$

Using the degenerate distribution Eq. (4.115) $\langle N_{\mathbf{n}} \rangle = 1$, this integral is easy

$$\langle N \rangle = \int_0^{E_F} \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{1/2} dE = \tilde{g} \frac{V}{(2\pi\hbar)^3} \left(\frac{4\pi}{3} p_F^3 \right) . \quad (4.118)$$

We have written Eq. (4.118) suggestively to show that the total number of fermions is just a “ball” in momentum space with radius given by p_F ,

$$\langle N \rangle = \tilde{g} \frac{V}{(2\pi\hbar)^3} \int_0^{p_F} 4\pi p^2 dp , \quad (4.119)$$

where each point inside this ball is an occupied principal quantum number \mathbf{n} . We can solve Eq. (4.118) for p_F ,

$$p_F = 2\pi\hbar \left(\frac{4\pi}{3} \right)^{-1/3} \left(\frac{N}{\tilde{g}V} \right)^{1/3} , \quad (4.120)$$

which allows us to relate the p_F to the Fermi energy

$$E_F = \frac{p_F^2}{2m} . \quad (4.121)$$

Now, how “low” is low temperature? The one obvious energy scale in the problem is the Fermi energy E_F , so we can use this to define a characteristic temperature called the **Fermi Temperature**

$$k_b T_F \equiv E_F \rightarrow \boxed{T_F \equiv \frac{E_F}{k_b}} . \quad (4.122)$$

You can convince yourself that at $T < T_F$, the distribution looks like a degenerate Fermi-Dirac distribution shown in Fig. 4.6. Using Eq. (4.120), we can see that the temperature scales like the density to the two-thirds

$$T_F = \frac{(2\pi\hbar)^2}{2mk_b} \left(\frac{4\pi}{3}\right)^{-2/3} \left(\frac{N}{\tilde{g}V}\right)^{2/3} \propto \left(\frac{N}{V}\right)^{2/3} . \quad (4.123)$$

So the denser the “gas”, the higher the Fermi temperature – a very dense object made out of fermions can have very high temperatures. One such object is the **neutron star**, which is the remnant of a supernova explosion of a massive star. The neutron star is made out of very tightly packed neutrons, supported by the fact that no two neutrons can occupy the same quantum state. Indeed, recently, the Laser Interferometer Gravitational Wave Observatory, LIGO, detected the collisions of two such neutron stars. Each neutron star is about 3 times the mass of the Sun, $M = 3M_\odot$ (where $M_\odot = 2 \times 10^{33}$ g), with the radius of about $R = 10$ km. The neutron mass is $m_{\text{neutron}} = 1.6750 \times 10^{-24}$ g and neutron is a spin-1/2 particle so $\tilde{g} = 2$. The total number of neutrons is

$$N = \frac{3M_\odot}{m_{\text{neutron}}} = 3.6 \times 10^{57} , \quad (4.124)$$

which gives us the number density of the neutron star

$$\frac{N}{V\tilde{g}} = 4.3 \times 10^{41} \text{ cm}^{-3} . \quad (4.125)$$

The Fermi temperature of the neutron star, using Eq. (4.123), is thus

$$T_F \approx 2 \times 10^{12} \text{ K} . \quad (4.126)$$

This incredibly high temperature is the temperature of a newly formed neutron star. Observed neutron stars are much lower in temperature, around $T \approx 10^6$ K, as neutrinos emitted from the neutron star will carry away the energy. These neutrinos are formed from the neutrons decaying into some other kind of exotic matter. Thus, “old” neutron stars are not really fully made out of neutrons. The structure of neutron stars is a subject of extremely active research at the moment.

Degeneracy pressure

For those who have studied the Astrophysics module, you learned that stars are supported by some kind of pressure to prevent it from collapsing due to gravity. For stars like our sun, this is the radiation pressure. Neutron stars support themselves with the pressure exerted by the fact that the fermions are degenerate and hence cannot occupy the same state. We can easily compute this pressure using the relationship Eq. (4.110), $PV = -\Psi = (2/3)\langle E \rangle$ which we have computed in the last section 4.3.2. To use this formula, we would need to know the energy, which can be easily computed using Eq. (4.102), and the Fermi-Dirac distribution Eq. (4.115),

$$\begin{aligned} \langle E \rangle &= \int_0^{E_F} \tilde{g} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{3/2} dE \\ &= \frac{3}{5} \langle N \rangle E_F . \end{aligned} \quad (4.127)$$

Notice that in this limit, the heat capacity $C_V = (\partial E / \partial T)_V = 0$ is zero. The pressure is then

$$P = \frac{(2\pi\hbar)^2}{5m} \left(\frac{4\pi}{3}\right)^{-2/3} \tilde{g}^{-2/3} \left(\frac{N}{V}\right)^{5/3} . \quad (4.128)$$

This pressure is called **degeneracy pressure**, and is what prevents neutron stars from collapsing. Another kind of astrophysical objects that is supported by degeneracy pressure are **white dwarfs**, which are supported by electron degeneracy pressure – as you will show in a homework problem.

Defining the mass density $\rho = (Nm/V)$, we can express the pressure as a function of density and *independent of temperature*

$$P = K\rho^{5/3} , \quad (4.129)$$

since K consists of just constants of nature. Such equations of state where the pressure is some power of the density $P \propto \rho^\gamma$ and independent of temperature are called **polytropic equations of state**. Such equations of state are very good models for many astrophysical objects such as stars and galaxies.

4.3.4 Slightly less degenerate fermion gas

Finally, for completeness, we describe the physics of a fermion gas that is not fully degenerate. The physics itself is not that difficult to understand, although the mathematics can be a bit tricky. From Fig. 4.6, we see that if $T \lesssim T_F$, the step function begins to deviate near the Fermi surface – as temperature increases from absolute zero towards T_F , the Fermi surface begins to “bubble up”. Nevertheless, in the deep depths of the sea, the fermions stay degenerate and couldn’t care less about the action on the surface.

As you have seen again and again, the integrals that we have to do often has the form

$$I = \int_0^\infty \frac{f(E)}{e^{\beta(E-\mu)} + 1} dE .$$

For example, for non-relativistic fermions, $f(E) \propto E^{3/2}$ for the energy integral (Eq. (4.102) and $f(E) \propto E^{1/2}$ for the particle number integral (Eq. (4.101)). We have seen in section 4.3.2 that in the high temperature limit $\beta\mu \ll 1$, we can use the small parameter $e^{\beta\mu}$ as an expansion parameter. In the low temperature limit, a possible “small parameter” we can use is the temperature ratio T/T_F . Indeed, this is exactly what we are going to use.

To save ink, we define

$$z \equiv \beta(E - \mu) \text{ such that } E = k_b T z + \mu . \quad (4.130)$$

The integral is then, converting the integral measure from $dE = k_b T dz$,

$$\begin{aligned} I &= k_b T \int_{-\mu/k_b T}^\infty \frac{f(\mu + k_b T z)}{e^z + 1} dz \\ &= k_b T \int_{-\mu/k_b T}^0 \frac{f(\mu + k_b T z)}{e^z + 1} dz + k_b T \int_0^\infty \frac{f(\mu + k_b T z)}{e^z + 1} dz \\ &= k_b T \int_0^{\mu/k_b T} \frac{f(\mu - k_b T z)}{e^{-z} + 1} dz + k_b T \int_0^\infty \frac{f(\mu + k_b T z)}{e^z + 1} dz \end{aligned} \quad (4.131)$$

where we have used the trick $z \rightarrow -z$ in the 2nd line on the first integral. The denominator of the first integrand can be factored

$$\frac{1}{e^{-z} + 1} = 1 - \frac{1}{e^z + 1} \quad (4.132)$$

so the integral is now split into three parts

$$I = \int_0^\mu f(E) dE - k_b T \int_0^{\mu/k_b T} \frac{f(\mu - k_b T z)}{e^z + 1} dz + k_b T \int_0^\infty \frac{f(\mu + k_b T z)}{e^z + 1} dz . \quad (4.133)$$

So far this is all exact – notice that the first integral is simply our degenerate limit. Now we use our approximation $T/T_F \ll 1$, and using $T_F = E_F/k_b = \mu/k_b$, this means that $\mu/k_b T \gg 1$, allowing us to take the upper limit of the 2nd integral to ∞ . We can do this because the denominator has a factor of e^z ,

so at large z the integrand is highly suppressed anyway. This lets us combine the 2nd and 3rd integrals into a single integral from 0 to ∞ ,

$$I = \int_0^\mu f(E)dE + k_bT \int_0^\infty \frac{f(\mu + k_bTz) - f(\mu - k_bTz)}{e^z + 1} dz . \quad (4.134)$$

Again using the approximation $\mu \gg k_bT$ we can Taylor expand

$$f(\mu \pm k_bTz) = f(\mu) \pm f'(\mu)k_bTz + \frac{1}{2!}f''(\mu)(k_bTz)^2 \pm \frac{1}{3!}f'''(\mu)(k_bTz)^3 + \dots \quad (4.135)$$

Summing the two terms, the even terms cancel, leaving us with the odd terms to obtain the following expansion of the integral

$$I = \int_0^\mu f(E)dE + 2(k_bT)^2 f'(\mu) \int_0^\infty \frac{z}{e^z + 1} dz + \frac{1}{3}(k_bT)^4 f'''(\mu) \int_0^\infty \frac{z^2}{e^z + 1} dz + \dots \quad (4.136)$$

The integrals are happily of the form Eq. (A.6) in Appendix A, so we finally obtain the following expansion in even powers of T ,

$$I = \int_0^\mu f(E)dE + \frac{\pi^2}{6}(k_bT)^2 f'(\mu) + \frac{7\pi^4}{360}(k_bT)^4 f'''(\mu) + \dots \quad (4.137)$$

We can now apply this formula to compute properties of slightly degenerate fermion gas. The first term in Eq. (4.137) is the fully degenerate case, so let's denote those quantities with the subscript 0. From Eq. (4.101) and Eq. (4.102)

$$\text{Particle number : } f(E) = E^{1/2} , \quad f'(E) = \frac{1}{2}E^{-1/2} . \quad (4.138)$$

and

$$\text{Energy : } f(E) = E^{3/2} , \quad f'(E) = \frac{3}{2}E^{1/2} . \quad (4.139)$$

We will leave the details of the algebra to a homework set (you should be used to the calculation methods by now). More importantly, you will show that

$$\langle E \rangle = \langle E_0 \rangle \left[1 + 0.27 \left(\frac{mk_bT}{\hbar^2} \right)^2 \left(\frac{V}{N} \right)^{4/3} + \mathcal{O}(T^4) \right] \quad (4.140)$$

Eq. (4.140) tells us that the correction to the slightly non-degenerate fermion gas scales as T^2 (recall that the degenerate term E_0 is independent of temperature), and inversely as the number density $(N/V)^{-4/3}$. The former means that the heat capacity is $C_V = (\partial E / \partial T)_V \propto T$. This tells us at very low temperature near degeneracy, the heat capacity of a fermion gas scales linearly with temperature T . How does this stack up with experiments?

Consider solids again. As we have seen in our study of phonons (section 4.2.2), solids can be modeled as a lattice of vibrating particles. In addition, this solid is also surrounded by a “gas” of free electrons. It turns out that this gas of electrons can be modeled as a non-interacting gas of almost degenerate electrons! This is not obvious – the electrons are negatively charged and so should repel each other. Furthermore, they are not moving in empty space, but in a lattice of positively charged nuclei! As it turns out, these two situations actually cancel each other – the lattice of positively charged nuclei “shields” the electrons from interacting with each other. We should think of the electrons as waves (using the wave-particle duality of quantum mechanics), so as in the phonons case (section 4.2.2), as long as the wavelength λ of the electrons is much longer than the separation a between the nuclei of the lattice $\lambda \gg a$, the electrons are insensitive to the structure of the lattice. You will learn more about this structure in next term's Solid State Physics module.

From our study of phonons, we learned that at low temperatures the sound waves contribute a heat capacity $C_V = \alpha T^3$. The presence of the free almost degenerate electron gas contribute an additional $C_V = \gamma T$ term, so the total heat capacity at low temperatures is

$$C_V = \alpha T^3 + \gamma T . \tag{4.141}$$

This is, as we have asserted in section 4.2.2, exactly as experiments observed in Fig. 4.4.

Chapter 5

Phase Equilibrium and Phase Transitions

In this final Chapter, we will take our first steps into the study of the singular success of statistical mechanics – its explanatory power to describe the physics of **phase transitions**. While you must be familiar with the phases of water, phase transitions occur in a wide variety of physical situations – from Metallurgy and ceramics (made since 8000 BC), to ferromagnets, superconductivity, superfluidity, the Higgs-Kibble mechanism of particle physics, black hole collapse, etc. Matter seems to possess certain tendency to spontaneously and rapidly rearrange themselves into states with more (or less) symmetry. Since the elements of any matter must interact with each other, this is plausible, but how did they interact *so quickly* suddenly at some thermodynamic state?

5.1 Bose-Einstein Condensates : your first phase transition

In the last Chapter, we saw that at very low temperatures, fermions become degenerate and its behaviour deviate radically from a classical ideal gas. In this section, we will study what happens to bosons away from the classical limit, and finally address our remiss of not considering non-relativistic bosons.

Consider the non-interacting Bose-Einstein distribution Eq. (4.31)

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} - 1} ,$$

with the total particle number

$$\langle N \rangle = \sum_{\mathbf{n}} \langle N_{\mathbf{n}} \rangle . \quad (5.1)$$

To convert the sum into an integral, we use the non-relativistic density of states Eq. (4.13),

$$g(E)dE = \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} E^{1/2} dE , \quad (5.2)$$

hence we get

$$\langle N \rangle = \int_0^\infty \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{1/2}}{e^{\beta(E - \mu)} - 1} dE . \quad (5.3)$$

This gives us a function of state $N(V, \mu, T)$, where $\mu < 0$ for bosons (section 4.2). So far, this is general. In the classical limit, you have shown in a homework problem that for high T and low density, turning the crank on these equations will lead us to the ideal gas law $PV = Nk_bT$. We want to now explore away from this limit.

In the fermion case, we have argued that taking the low temperature limit and high density limit are equivalent. Let's now take the high density limit. We can do this by fixing V and T , and then slowly increase N by adding bosons incrementally, such that the system remains in equilibrium throughout the process while we increase the density N/V . From Eq. (5.3), we see that if we slowly increase N , the RHS must also increase, and the only way we can do this is to increase μ (since everything else has been fixed). Since $\mu < 0$, this means $\mu \rightarrow 0$ as we increase N .

It turns out that we reached $\mu = 0$ at finite N_{crit} , which we can compute via

$$\langle N_{\text{crit}} \rangle = \int_0^\infty \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{1/2}}{e^{\beta E} - 1} dE . \quad (5.4)$$

This integral is of the form Eq. (A.7) which you have seen many times before, so we leave the details to you. The result is

$$\frac{N_{\text{crit}}}{V} = \frac{2.612}{\lambda^3} \quad (5.5)$$

where we have suggestively used the thermal de Broglie wavelength Eq. (3.12)

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}} . \quad (5.6)$$

Eq. (5.5) tells us that $\mu = 0$ is reached when the number density is very near the thermal de Broglie densities – in other words, when we expect quantum mechanics to play an important role.

Instead of adding N , we can equivalently keep N fixed and lower the temperature. The equivalent critical temperature T_{crit} is then just inverting Eq. (5.5), which gives us

$$T_{\text{crit}} = \frac{(2\pi\hbar)^2}{(2.31 \times 4\pi\sqrt{2})^{2/3} k_b m} \left(\frac{N}{V}\right)^{2/3} . \quad (5.7)$$

Let's plow ahead and *keep adding bosons*. What happens next? Suppose we do this experiment, and plot the gas pressure P as a function of N , while fixing T and V . At low densities, we have the usual classical ideal gas law

$$P = N \frac{k_b T}{V} \propto N , \quad (5.8)$$

so P scales linearly as N , and this is observed. As we increase N and approaches N_{crit} , instead of $P \propto N$, the pressure becomes a constant! This is depicted in Fig. 5.1. What's going on here? Now,

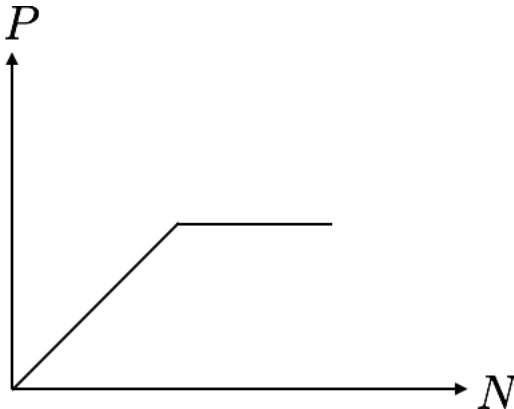


Figure 5.1: The P vs N plot of a Bose-Einstein gas, as we increase N while fixing V and T .

a non-interacting Bose-Einstein gas is an idealization, but this effect is seen in real gasses. Consider some quantity of oxygen gas in a piston. We increase the density by pushing the piston slowly inwards.

Initially, the density increases as P increases as an ideal gas. At some point however, instead of pressure increasing, *we begin to see droplets of liquid oxygen condensing inside the piston!* In other words, a **gas-liquid phase transition** has occurred. But if our whole statistical mechanics treatment is to be believed, we should see this mathematically too. Where are all the bosons hiding?

It turns out that we have already made a subtle, but incredibly important mistake! This occurs when we use the non-relativistic density of states Eq. (4.13), we have expressed

$$g(E)dE \propto E^{1/2}dE, \quad (5.9)$$

which implies that $g(0) = 0$, i.e. there are no bosons with the *ground state energy* $E = 0$. But this simply cannot be true – bosons can happily exist in their ground state! Consider the Bose-Einstein distribution of the ground state $E = 0$ at the limit when $\mu_- \rightarrow 0$ (the $-$ subscript means that we approach from the negative side),

$$\lim_{\mu_- \rightarrow 0} \langle N_0 \rangle = \lim_{\mu_- \rightarrow 0} \frac{1}{e^{-\beta\mu} - 1} \rightarrow -\frac{1}{\beta\mu}, \quad (5.10)$$

so as $\mu_- \rightarrow 0$, $\langle N_0 \rangle \rightarrow \infty$ starts to blow up – all the bosons want to go to the party at N_0 's house. As they are all in the same quantum state, they are *degenerate*. Unlike the fermions, there is no Pauli Exclusion Principle to prevent them from occupying the same state. This condensate of bosons at the ground state is known as a **Bose-Einstein condensate**, or **BEC** for short.

Let's now derive the equation of state for a BEC. In the limit of very low temperatures $T \lesssim T_{\text{crit}}$, we can split the total number of bosons N into the excited bosons N_* and the ground state bosons N_0 , such that

$$N = N_0 + N_*. \quad (5.11)$$

As previously covered, N_* is obtained by doing the integral Eq. (5.3) using the density of states Eq. (4.13) at $\mu \rightarrow 0$, which we have already computed previously in Eq. (5.4) that it is $N \propto T^{3/2}$, so

$$N_* = N \left(\frac{T}{T_{\text{crit}}} \right)^{3/2} \quad (5.12)$$

where we have used the definition of the critical temperature Eq. (5.7) to rescale the result such that

$$N_0 = N \left[1 - \left(\frac{T}{T_{\text{crit}}} \right)^{3/2} \right]. \quad (5.13)$$

In the limit when $T \rightarrow 0$, we expect all the bosons to be in the ground state – thus $N_0 \rightarrow N$ as desired. Conversely, at $T \rightarrow T_{\text{crit}}$, $N_0 \rightarrow 0$, so none¹ of the bosons are in the ground state.

Now, all the energy of the system are in the excited bosons,

$$\begin{aligned} \langle E \rangle &= \int_0^\infty g(E)E dE \\ &= \int_0^\infty \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{3/2}}{e^{\beta E} - 1} dE \\ &= 1.783 \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} (k_b T)^{5/2} \\ &= 0.77 k_b T N_*. \end{aligned} \quad (5.14)$$

Combining Eq. (5.14) with Eq. (4.110) $P = (2/3)E/V$, we get the equation of state for a BEC

$$PV = 0.513 N k_b T \left(\frac{T}{T_{\text{crit}}} \right)^{3/2} \propto T^{5/2}, \quad (5.15)$$

¹In reality, there is always a probability that some bosons are in the ground state, like party guests that never leave your home, but at this temperature they are negligible.

but now we can eliminate V using T_{crit} Eq. (5.7), we obtain

$$P = 1.2 \frac{k_b T}{\lambda^3}, \quad (5.16)$$

since $\lambda \propto T^{-1/2}$.

The equation of state is simply a function of temperature $T^{5/2}$, and independent of both V and N . This is a consequence of the fact that the bosons at the ground state possess no momentum, and hence don't contribute to the pressure – all the pressure here are due to the excited bosons. As we turned down the temperature, more and more of the bosons go into the ground state and hence pressure decreases. More surprisingly, this also imply that the *bosons at the ground state occupy zero volume!* A “real” condensate, like that of the liquid oxygen gas we described above, occupy a very small but finite amount of volume in comparison to the gaseous counterpart – one can see that at $N_0 = N$ occurs at $T_{\text{crit}} = \infty$, and since $T_{\text{crit}} \propto (N/V)^{2/3}$, $V = 0$ at this point. Our bosons have no “hard cores”.

5.1.1 BEC phase diagram

The behaviour of the BEC can be illustrated by plotting their phase diagrams Fig. 5.2. Recall that $T \lesssim T_{\text{crit}}$ is the onset of condensation, then using the equation of state, we can define a critical pressure $P_{\text{crit}} \propto (T_{\text{crit}})^{5/2}$, this allows us to plot the P - T phase diagram. Since $T_{\text{crit}} \propto (N/V)^{2/3}$, this curve is given by $P_{\text{crit}} \propto (N/V)^{5/3}$. Curves that partitions different phases are called **co-existence curves** – we will discuss more about the nomenclature of phase diagrams in the next section 5.2, but let's plow on. In

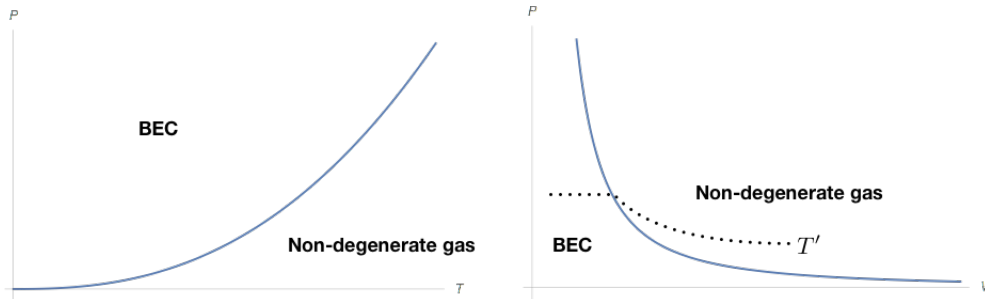


Figure 5.2: The P - T and P - V phase diagrams of a BEC, with the coexistence curves defined by P_{crit} . On the P - V diagram, the isotherm T' tracks the ideal gas case $P \propto 1/V$ in the non-degenerate phase, and is a constant in the BEC phase.

particular, on the P - V phase diagram, we can plot the lines of constant temperature, or **isotherm**, for some temperature T' . In the non-degenerate phase, the boson gas obeys the ideal gas law, so $P \propto 1/V$ as usual. In the BEC phase however, as we discussed P is independent of V , so the isotherm becomes constant. We can physically follow the isotherm as follows. We put some fixed N amount of boson particles into a piston, and immerse this piston into a heat bath of constant temperature T' . Then, we slowly push the piston, reducing V in a reversible way. Initially, at large V , the boson gas behaves like an ideal gas as usual with pressure increasing. But as we hit the existence curve, the bosons begin to occupy the ground state, “losing” their momentum and hence stop contributing pressure even as we reduce the volume. As we move deeper into the BEC region, the piston now contain a mixture of BEC condensate (ground state bosons) and excited boson gas – a two-phase mixture, with the fraction of excited bosons decreasing like $N_* \propto T_{\text{crit}}^{-3/2} \propto V$, reaching zero at $V = 0$. At this point, all the bosons are in the BEC phase.

5.1.2 Heat capacities of phase transitions

To dig deeper into the physics of the phase transition, we need to investigate the behaviour of the heat capacity C_V . The heat capacity of the non-degenerate boson gas is that of an ideal classical gas. Bosons have 3 translational d.o.f., so $C_V = 3/2Nk_b$ as usual. To calculate C_V in the BEC phase, we use Eq. (1.50) and the equation for the energy of the BEC Eq. (5.14)

$$\begin{aligned}
 C_V &= \left(\frac{\partial E}{\partial T} \right)_V \\
 &= \frac{\partial}{\partial T} (0.77k_bTN_*) \\
 &= \frac{\partial}{\partial T} \left(0.77k_bN \frac{T^{5/2}}{T_{\text{crit}}^{3/2}} \right) \\
 &= 1.93k_bN \left(\frac{T}{T_{\text{crit}}} \right)^{3/2}.
 \end{aligned} \tag{5.17}$$

Combining these two results, the C_V of boson gas then looks like Fig. 5.3. At $T = T_{\text{crit}}$, our calculation yields $C_V = 1.93Nk_b$, which indicates a *discontinuity* in C_V . But this is a mirage – we have carelessly assumed that the bosons behave like an ideal gas until the T_{crit} , which is not true. A more careful calculation, will show that the discontinuity is actually in the *first derivative*, $\partial C_V/\partial T$, i.e.

$$\Delta \left(\frac{\partial C_V}{\partial T} \right)_V \approx -3.66 \frac{N}{k_b T_{\text{crit}}}. \tag{5.18}$$

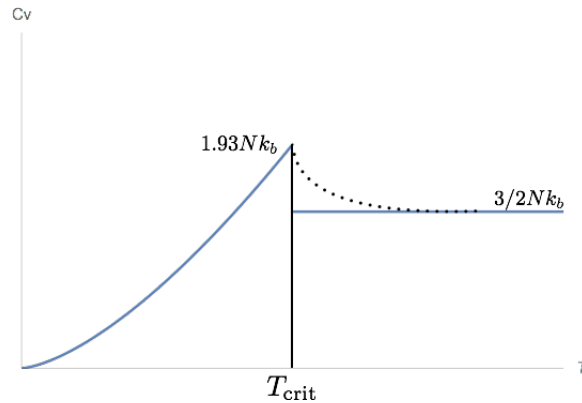


Figure 5.3: The thick light blue line is the C_V of our simple calculation, with a discontinuity in C_V at the critical temperature T_{crit} . A more careful calculation shows that this discontinuity is actually only present in the 1st derivative, $\partial C_V/\partial T$, as indicated in the dotted line.

The general lesson here is that a phase transition is often accompanied by discontinuities. Such transitions are called **first order**. This terminology originates from the old days (it is due to Ehrenfest), when scientists struggle to understand the physics behind these phenomena, phase transitions are classified according to the order of the discontinuities in the free energy F . So if F is discontinuous at first derivative of T , it is first order; if it is discontinuous at 2nd derivative of T , it is second order, and so on.

Nowadays, these definitions are no longer in vogue, and phase transitions are now categorized as whether during the phase transition, *latent heat is required*. If latent heat is required, then the phase transition is classified as a **first order phase transition**, which is a vestigial from the old terminology. Such phase transitions are common – processes such as the ice melting into water (solid water into liquid water) are first order phase transitions. On the other hand, if the transition does not require input of any latent heat, they are called **second order phase transitions**, or **continuous phase transitions**.

The “continuous” here means that latent heat is zero, so the phase changes continuously without needing to “pause” to take in heat.

Indeed, according to the old classification, since $C_V \propto T \frac{\partial S}{\partial T}$, and $S = -\frac{\partial F}{\partial T}$, since BEC’s C_V is only discontinuous in the derivative of C_V , it should be classified as 3rd order phase transition. However, since it has a latent heat, nowadays it is classified as first order.

We will spend the rest of the chapter discussing phase transitions.

5.1.3 Real BEC

BEC was predicted by Bose and Einstein way back in 1924, but was only finally created in the lab in 1995, by Eric Cornell and Carl Wieman by cooling a gas of Rubidium atoms to a temperature of 170 nK. Shortly afterwards, Wolfgang Ketterle performed similar experiments with Sodium atoms. The results

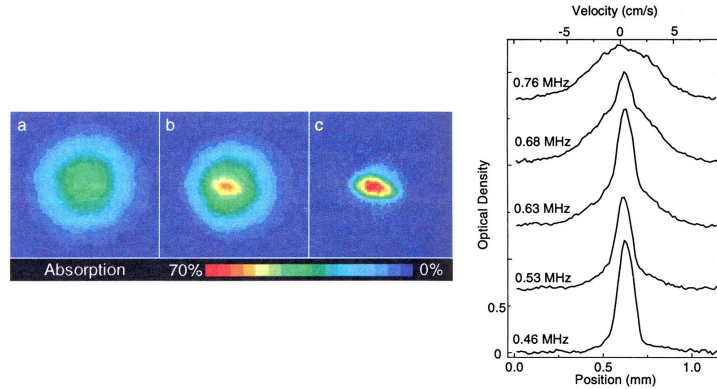


Figure 5.4: The results of the Ketterle experiment. The left figure shows the density of the Sodium atomic cloud. The temperature drops from left to right, showing first a thermal distribution, then the atoms condensing into a sharp peak surrounded by a thermal cloud, to finally complete condensation – the volume decreases as more and more of the bosons occupy the ground state. The right figure shows that velocity (and hence momentum) and position distribution of the atoms – as the temperature cools from top to bottom, the velocity of the bosons approaches zero and the location localizes. (Figure from the Physics Nobel Prize 2001 scientific background document.)

from the Ketterle experiment is shown in Fig. 5.4. For this achievement, the three were awarded the 2001 Nobel Prize in Physics.

One of the main technological breakthroughs which allowed the creation of such ultra-cold atoms is the invention of *laser cooling*. Atoms can absorb photons of certain frequencies (recall the spectrum of quantum mechanics), and the subsequent spontaneous emission in an arbitrary directions will slow down the atom. By using doppler shifting, one can make atoms absorb photons only in their forward direction, and hence selectively slow down the velocity in that particular direction. Thus all three translational d.o.f. can be cooled this way. Indeed, the invention of laser cooling itself was awarded its own Nobel Prize in 1997 (to Steven Chu, Claude Cohen-Tannoudji and William Phillips).

5.2 Overview of phases of matter

We now take a step back from the giddy frontiers of the exotic BEC, and come back to discussing the basics of phases in matter. An example of a typical phase diagram is shown in Fig. 5.5. Phase diagrams such as these are typically plotted for some fixed N , where at each point on the diagram is the matter in equilibrium. Let’s consider matter whose functions of state has only two independent parameters

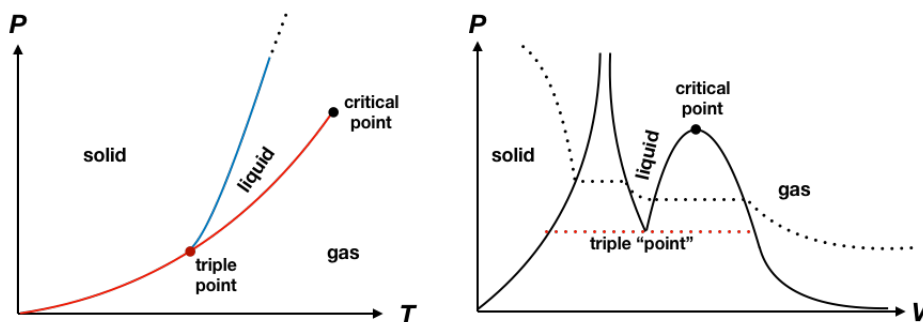


Figure 5.5: A phase diagram with 3 distinct phases. In the P - T diagram, showing the existence of the triple point (red dot) and the critical point (black dot). In the P - V diagram, all the points under the curve are when the matter is in a mixture, while all the points above the curve are when the matter has a distinct phase. Dotted curves on this diagram indicates trajectories of constant temperature, or *isotherms*. The triple “point” on this diagram corresponds to the horizontal red dotted line.

(for example, for the ideal gas P , V and T must be related to each other by some equation of state at equilibrium), so we can plot them either as a P - T diagram, as a P - V diagram, or as a T - V diagram. Here we plot the first two.

From the P - T diagram, we see that the phases are roughly divided into its solid, liquid and gas phases. The curves that separate these phases are called **co-existence curves**². At these curves, the phases can co-exist as a *mixture* – you see this every day when you boil water to make a cup of tea. At the co-existence curves, a single thermodynamic state variable P or T will suffice to describe the state. The point where the two curves meet is called the **triple point**, and at this point all three phases can co-exist.

Importantly, the liquid/gas co-existence curve terminates at some point, called the **critical point**. This means that at sufficiently high P and T , *there is no distinction between liquid and gas phases*. Such a “combined” phase is sometimes called *superheated* or *supercritical phase*, although the terminology is not really important. The really important bit is that, as far as we know, *there is no critical point for the liquid/gas-solid co-existence curve*. Why is this so? One way to understand is to recognize that particles in the solid phase are arranged in a *lattice* and thus possess a rigid discrete *symmetry*, while the liquid/gas phases, the particles are free to move around and hence has no such symmetry.

We can learn more about the phases when we look at the P - V phase diagram. Unlike the P - T diagram, since during a phase transition, the volume of the matter can change, states where the phases are in transition (say from liquid to solid) are no longer points, but regions. All the regions under the curve are where more than one phase can exist, while all the regions above the curve are where the phases are distinct. Curves of constant temperature can be plotted on this diagram, and are called **isotherms**. For example, in Fig. 5.5, the black dotted curve is an isotherm. Moving from right to left, the pressure increase as we decrease the volume, except when the moving through the phase transitions. As the mixture of the two phases changes from mostly gas to mostly liquid, the total volume also changes. *During this phase transition, the isotherm is a horizontal line*, i.e. the pressure is constant

$$\left(\frac{\partial P}{\partial V}\right)_T = 0. \quad (5.19)$$

²Sometimes the curves between solid/gas, solid/liquid, and liquid/gas curves are known as the *sublimation*, *melting* and *boiling* curves, although we won’t worry with these specifics.

To show this, we first argue that for all matter, the following thermodynamic inequality holds true

$$\boxed{\left(\frac{\partial P}{\partial V}\right)_T \leq 0} . \quad (5.20)$$

In words, this equation says that *isotherms cannot slope upwards*. You will derive this relationship in a homework set, but intuitively one can see it as follows. Put some gas into a piston, which is immersed in a heat bath of fixed temperature T . Now as we pull the piston out (increasing V), the pressure inside must *decrease* which gives us the inequality Eq. (5.20). What happens, instead, the pressure inside *increases*? This means that as we increase V , the pressure also increases, further pushing the piston out even more, and so on – thus the gas is *unstable*.

Returning to our argument, from the P - T diagram, lines of constant T (i.e. vertical lines) will intersect the co-existence curves at some fixed P , so this means that in the P - V diagram, the right “entry” P and the left “exit” P must be equal, and this fact combined with Eq. (5.20) implies the condition Eq. (5.19). Indeed, horizontal isotherms is characteristic of a phase transition (see the BEC phase diagram Fig. 5.2).

In particular, since the triple point contains all three phases, the isotherm corresponding to the triple point must make contact with all three phases in the P - V diagram. The only horizontal line which this occurs is the line making contact with the local minimum of P (red dotted line in Fig. 5.5).

Finally, notice that the the critical point on the P - T diagram is mapped to a local maximum of P in the P - V diagram, as P_c is maximum in the P - T diagram. Any isotherm that passes through this point then *must be an inflection point*, thus in addition to $(\partial P/\partial V)_T = 0$, the critical point has the condition

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 . \quad (5.21)$$

The transition through the phases (i.e. from “entry” to “exit”) is accompanied by the evolution or absorption of some heat ΔQ – some energy has to be exchanged since the volume is changing while P and T are fixed. Since the transition process occurs under constant P and constant T , the total heat exchanged throughout is the difference between the *enthalpies* of the two states, since (Eq. (1.37)) $dH = TdS + VdP \rightarrow TdS = dQ$, hence

$$\boxed{\Delta Q \equiv L = H_{\text{entry}} - H_{\text{exit}} = T(S_{\text{entry}} - S_{\text{exit}})} . \quad (5.22)$$

This quantity of heat, L , is called **the latent heat of transition**. For example, in your Thermal Physics module, you learned that to melt ice, you need to apply a quantity of heat to overcome its **latent heat of melting**, and to boil water you need to apply heat to overcome its **latent heat of boiling** etc. As we briefly discuss in section 5.1 when a **first order phase transition** is characterized by a non-zero latent heat during the transition.

5.2.1 Phase equilibrium

Let’s now study the mixture of a matter during a phase transition. Consider the same matter, but in two different phases in equilibrium, immersed in a heat bath of constant temperature T . Since the two phases are in equilibrium, we can follow the same arguments when we derive the equality of temperatures in the microcanonical ensemble (section 2.2.1). The statistical weight, and hence the entropy, here now depends on E , N and V , i.e. $S(E, V, N) = k_b \ln \Omega(E, V, N)$, where

$$E = E_A + E_B , \quad V = V_A + V_B , \quad N = N_A + N_B , \quad (5.23)$$

which implies that

$$\frac{\partial E_B}{\partial E_A} = -1 , \quad \frac{\partial V_B}{\partial V_A} = -1 , \quad \frac{\partial N_B}{\partial N_A} = -1 . \quad (5.24)$$

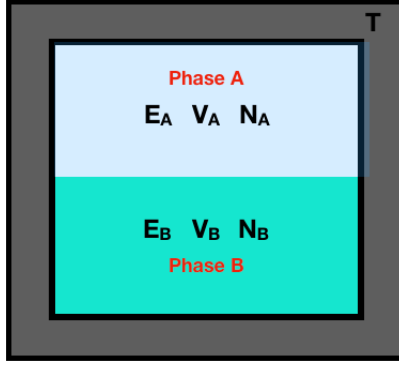


Figure 5.6: Equilibrium of two phases of a single-component system, in a heat bath with temperature T .

As usual, the total entropy is the sum of the two phases' entropies,

$$S(E, V, N) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B) , \quad (5.25)$$

which means that, combining with the partial derivative relations above Eq. (5.24),

$$\begin{aligned} dS &= \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \right] dE_A \\ &+ \left[\left(\frac{\partial S_A}{\partial N_A} \right)_{E_A, V_A} - \left(\frac{\partial S_B}{\partial N_B} \right)_{E_B, V_B} \right] dN_A \cdot \\ &+ \left[\left(\frac{\partial S_A}{\partial V_A} \right)_{E_A, N_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{E_B, N_B} \right] dV_A \end{aligned} \quad (5.26)$$

Since the system is in equilibrium, $dS = 0$ must vanish, thus all the three terms must vanish individually. The first term just the definition for the equality of temperature Eq. (2.16), while the 2nd term defines equality of the chemical potential Eq. (2.106). This leaves the final line to be the definition for the equality of pressure, which we can see as follows. From Eq. (1.32), Eq. (2.74) and Eq. (2.72)

$$\begin{aligned} P &= k_b T \left[\frac{1}{k_b} \left(\frac{\partial S}{\partial V} \right)_T + \frac{\partial}{\partial V} \left(\beta \frac{\partial \ln Z}{\partial \beta} \right)_T \right] \\ &= T \frac{\partial S}{\partial V} , \end{aligned} \quad (5.27)$$

where the second term vanishes since E is fixed. Hence pressure can be similarly define as

$$\boxed{P = T \left(\frac{\partial S}{\partial V} \right)_{E, N}} . \quad (5.28)$$

Thus phases in equilibrium must obey the following conditions

$$T_A = T_B , P_A = P_B , \mu_A = \mu_B . \quad (5.29)$$

This result confirms our assertion in the previous section that co-existence are curves in the P - T diagram, but not in the P - V diagram.

5.2.2 The Clausius-Clapyron equation

Taking the total derivative energy potential Eq. (1.71) $E = TS - PV + \mu N$, and subtracting it from Eq. (1.58), we get

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP , \quad (5.30)$$

where

$$\frac{\partial\mu}{\partial T} = -\frac{S}{N}, \quad \frac{\partial\mu}{\partial P} = \frac{V}{N}. \quad (5.31)$$

This tells us that we can express μ as a function of T and P , $\mu(P, T)$. However, on the co-existence curve, once we know P , we also know T , i.e. $P(T)_{\text{coex}}$ where “coex” indicates we are on the co-existence curve. Now while the *value* $\mu_A = \mu_B$ is the same at the co-existence curve, the *functional forms* of μ_A and μ_B as functions of T are *different!* Intuitively, μ_A is the chemical potential for one phase (say the liquid phase) and μ_B is the chemical potential for another phase (say the gas phase), and they must be different even though they are made out of the same matter. This is easy to see from the first equation of Eq. (5.31), $\partial\mu/\partial T = -S/N$. $S/N \equiv s$ measures the entropy per particle (or **specific molar entropy**), and since in general they are different for different phases³ the chemical potentials for different phases have different functional forms.

From the phase equilibrium conditions Eq. (5.29), we have $\mu_A(T, P) = \mu_B(T, P)$, then taking the derivative of both sides w.r.t. T

$$\frac{\partial\mu_A}{\partial T} + \frac{\partial\mu_A}{\partial P} \frac{dP}{dT} = \frac{\partial\mu_B}{\partial T} + \frac{\partial\mu_B}{\partial P} \frac{dP}{dT}, \quad (5.32)$$

and now using Eq. (5.31), and rearranging, we get

$$\frac{dP}{dT} = \frac{S_A - S_B}{V_A - V_B}. \quad (5.33)$$

Combining this with the definition for the latent heat L (Eq. (5.22)), we finally get the **Clausius-Clapyron equation**

$$\boxed{\frac{dP}{dT} = \frac{L}{T(V_A - V_B)}}. \quad (5.34)$$

We have derived this equation using nothing more than some basic classical thermodynamics – there is no input from statistical mechanics or any more “fundamental” microphysics. Thus it won’t help us in understanding the physics of phase transitions. On the other hand, this means that it is a very general relation – whatever theory of phase transitions we eventually come up with, must obey this relation.

Nevertheless, even in its current form, we can use it to derive some useful quantities. For example, we can derive the **vapour pressure** – the pressure of a gas that is in equilibrium with its liquid phase. Since $V_{\text{gas}} \gg V_{\text{liquid}}$, we can neglect it, then the Clausius-Clapyron equation becomes

$$\frac{dP}{dT} = \frac{L}{TV_{\text{gas}}}. \quad (5.35)$$

Assuming the ideal gas law so $V = Nk_bT/P$, we have

$$\frac{dP}{dT} = \frac{LP}{Nk_bT^2}, \quad (5.36)$$

which can be easily to solve to give us the **vapour pressure curve**

$$P = \text{const} \times e^{-L/Nk_bT}, \quad (5.37)$$

which is just the co-existence curve between the liquid and the gas phases in the P - T diagram. This is only approximate of course, since we have assumed that L is independent of T (it usually is not), and the vapour is an ideal gas (it usually is not).

³Roughly speaking, the more “space” the phase occupy per particle, the higher the specific molar entropy since the disorder is greater, so usually $s_{\text{gas}} > s_{\text{liquid}} > s_{\text{solid}}$. This is not always true – indeed, it is well known that ice occupies more space than water, so $s_{\text{ice}} > s_{\text{water}}$.

5.2.3 The Van der Waals model of phase transition

One of the earliest attempts to understand phase transitions come from the Van der Waals. In section 3.5.2, we showed that a low density interacting classical gas has the Van der Waals equation of state (with a slight rewriting from Eq. (3.79))

$$Nk_bT = \left(P + \frac{N^2}{V^2}a \right) (V - Nb) . \quad (5.38)$$

The derivation is actually a bit of a mis-representation of history. Van der Waals actually “derived” his equation⁴ with the hope of understanding the *liquid-gas phase transition*. Now you might correctly point out that the Van der Waals equation should only be valid for the gas phase, since we have assumed that the density is low in our derivation. While you would be right, we will see that the Van der Waals equation of state does represent a crude caricature of a liquid-gas phase transition – it predicts the wrong values when compared to experiments. However, it does reproduce the broad features of a phase transition, so we’ll study it as a way of introducing you to the lay of the land of phase transitions.

We begin by plotting the isotherms of the Van der Waals equation on a P - V phase diagram, Fig. 5.7. There is a lot to digest. Ignoring the different coloured lines for the moment, we see that at large

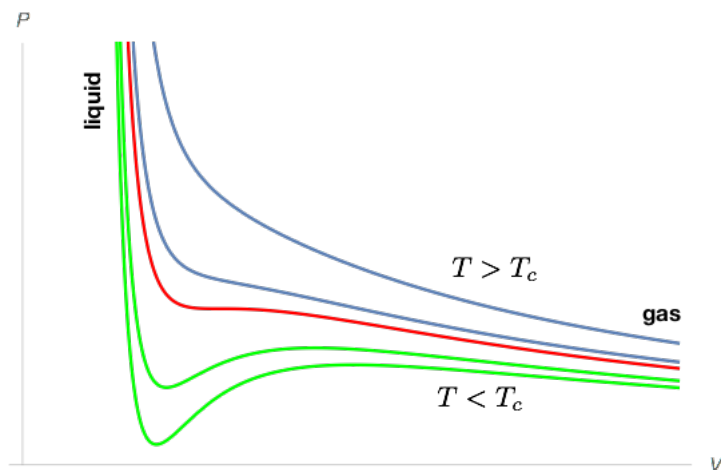


Figure 5.7: Isotherms of the Van der Waals equation of state. The red isotherm is the isotherm at the critical temperature T_c , while the blue isotherms are $T > T_c$ and the green isotherms are $T < T_c$.

V such that $N/V \gg r_0^{-3}$, we get the gas phase. In this region, the Van der Waals equation is valid, and as we increase V , all the isotherms $P \propto 1/V$ behave like the classical ideal gas. Conversely, at small $N/V \approx r_0^{-3}$, i.e. when the particles are touching each other, we see that P increases rapidly for very small changes in V . This means that the system is *highly incompressible*, though not infinitely so. This is how we expect a liquid to behave, so despite our protestations of the limits of the derivation, we got this for free.

The middle part between the liquid and the gas phase is where the interesting stuff lie. The red isotherm, T_c is the isotherm associated with the critical point, i.e. when the gas and liquid phase become “the same” – we can find it by imposing the constraints, $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$, (Eq. (5.19) and Eq. (5.21)) – note the presence of the inflection point.

Above the critical isotherm $T > T_c$, the gas and liquid phases are indiscernible, so the isotherm is monotonic. On the other hand, below the critical isotherm $T < T_c$, the isotherms are not monotonic. Indeed, it looks like an “S”, with a clear maximum and a clear minimum, see Fig. 5.8. The first thing to

⁴His derivation is a bit more heuristic, and does not follow our more modern method. Before you become snarky, *his* equation is the central result from his PhD thesis.

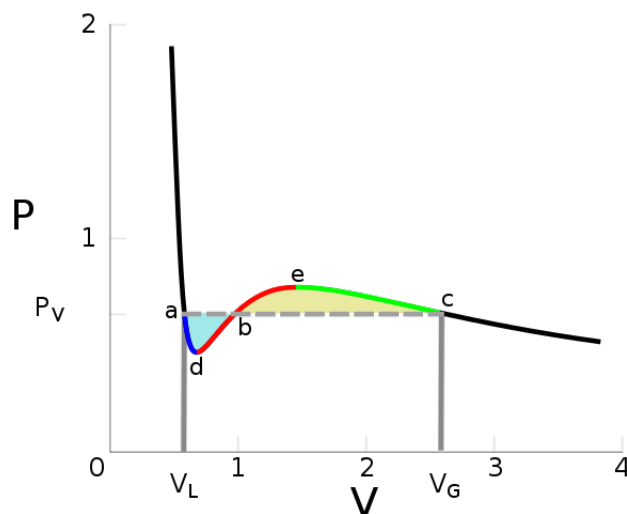


Figure 5.8: An isotherm where $T < T_c$. (Figure from Wikipedia, because I can't figure out how to fill a region with colour.)

notice is that the section $d-b-e$ has the behaviour $(\partial P/\partial V)_T > 0$, which violates the stability condition Eq. (5.20). This section is sometimes called *metastable* – in reality it is incredibly difficult to keep the system in this state, thus it is never achieved in real life.

Instead, as we reduce the volume of the system while keeping N and T fixed, the gas will increase its pressure until some point c with pressure P_V , and then it will begin to condense – undergo a phase transition. The actual physical isotherm is the horizontal dotted line $a-b-c$ – as we discussed in section 5.2, this is a key characteristic of a phase transition. To find P_V , we use the fact that during a phase-transition, P , T and μ are equal (Eq. (5.29)), thus

$$\begin{aligned}
 \mu_L - \mu_G &= \int_G^L d\mu \\
 &= - \int_G^L \frac{S}{N} dT + \int_G^L \frac{V}{N} dP \\
 &= \int_G^L \frac{V}{N} dP \\
 &= \int_G^b \frac{V}{N} dP + \int_b^L \frac{V}{N} dP ,
 \end{aligned} \tag{5.39}$$

where we have also used the fact that $d\mu$ is a total differential in the first line, Eq. (5.30) in the second line, and the fact that we are integrating along an isotherm to drop the dT integral in the third line. In the last line, we split the integral into the light green and dark green regions in Fig. 5.8.

Since N is just a constant, the integral is just the area under the curve. But these must sum to zero, so the dark green area must cancel the light green area, thus we can use this construction to find P_V . This method is called the **Maxwell construction**.

Finally, Van der Waals noticed something interesting at the critical point. If we fix N , then there are three state variables P , V and T , and the equation of state Eq. (3.79), and the critical conditions $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$ give us 3 equations, allowing us to completely solve it (homework) to get

$$P_c = \frac{a}{27b^2} , \quad k_b T_c = \frac{8a}{27b} , \quad V_c = 3Nb . \tag{5.40}$$

If we now introduced the “reduced” variables,

$$\bar{t} = \frac{T}{T_c} \quad \bar{v} = \frac{V}{V_c} \quad , \quad \bar{p} = \frac{P}{P_c} \quad , \quad (5.41)$$

then we can write the “reduced” Van der Waals equation

$$\left(\bar{p} + \frac{3}{\bar{v}^2} \right) (3\bar{v} - 1) = 8\bar{t} \quad . \quad (5.42)$$

Thus the space of all possible Van der Waals equations of state is parameterized by the coefficients (a, b) . For each (a, b) , we can compute its associated critical variables P_c, T_c and V_c . States of different theories with identical reduced variables \bar{p} , \bar{t} and \bar{v} are called **corresponding states** – this relation is sometimes called the **Law of Corresponding States**.

Van der Waals’ hope was nothing short of a unification of all possible liquids/gas systems – the reduced equation of state Eq. (5.42) would describe all liquids/gas and hence is universal. How close did he get? We notice that we can algebraically arrange the critical variables Eq. (5.40) such that the model parameters (a, b) cancel to get a universal constant

$$\frac{P_c V_c}{k_b T_c} = \frac{3}{8} = 0.375 \quad . \quad (5.43)$$

Since we can experimentally measure P_c , V_c and T_c of various matter, we can check if Eq. (5.43) actually holds. It turns out that this value varies between 0.23 and 0.3. Some common examples are water (0.23), hydrogen (0.3), argon (0.29) etc. Not bad, but not entirely correct.

5.2.4 Universality, order parameters and critical exponents

We will now discuss one of the most remarkable phenomenon in physics, which occurs near the critical point. We investigate the behaviour of thermodynamic variables as we approach the critical point along some curve, for example either along an isotherm or the co-existence term. Consider pressure, $P(\rho, T)$, where we will approach the critical point along an isotherm. Expanding this around the critical values ρ_c and T_c , we get

$$\begin{aligned} P(\rho_c + \Delta\rho, T_c) &= P(\rho_c, T_c) + \left(\frac{\partial P}{\partial \rho} \right)_{T_c} \Delta\rho + \frac{1}{2!} \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T_c} (\Delta\rho)^2 + \frac{1}{3!} \left(\frac{\partial^3 P}{\partial \rho^3} \right)_{T_c} (\Delta\rho)^3 + \dots \\ &= P(\rho_c, T_c) + \frac{\partial V}{\partial \rho} \left(\frac{\partial P}{\partial V} \right)_{T_c} \Delta\rho + \frac{1}{2!} \left(\frac{\partial^2 P}{\partial V^2} \left(\frac{\partial V}{\partial \rho} \right)^2 + \frac{\partial V}{\partial \rho} \frac{\partial P}{\partial V} \left(\frac{\partial}{\partial V} \frac{\partial V}{\partial \rho} \right) \right)_{T_c} (\Delta\rho)^2 \\ &\quad + \frac{1}{3!} \left(\frac{\partial^3 P}{\partial \rho^3} \right)_{T_c} (\Delta\rho)^3 + \dots \end{aligned} \quad (5.44)$$

where we have used the chain rule to convert derivatives w.r.t ρ to derivatives w.r.t. V . Using the criticality condition, the $\partial P / \partial V = 0$ and $\partial^2 P / \partial V^2 = 0$, so the 2nd and 3rd terms vanishes, and we can arrange

$$P - P_c \propto (\rho - \rho_c)^3 \quad , \quad (5.45)$$

since $\Delta\rho = \rho - \rho_c$. Experimentally, this is $(P - P_c) \propto (\rho - \rho_c)^\delta$, with $\delta \approx 4.8$, which is *independent of the atomic make-up of the gas*. For example, $\delta_{\text{Xe}} = 4.74$, $\delta_{\text{CO}_2} = 4.85$, and $\delta_{\text{SF}_6} = 4.99$.

Wait what? While it is not surprising that we didn’t get the exact value 3, why does it not depend on what atoms our gas are made out of? Maybe this is a co-incidence? Let’s look at other variables. What we want to do is to perform a general expansion of the reduced Van der Waal’s equation in terms of the small variables $\Delta V = V - V_c$ and $\Delta T = T - T_c$ around the critical point. Defining

$$\Delta T = T - T_c \rightarrow \tau \equiv \bar{t} - 1 \quad , \quad (5.46)$$

and

$$\Delta V = V - V_c \rightarrow \theta \equiv \bar{v} - 1, \quad (5.47)$$

and then plugging $\bar{t} = \tau + 1$ and $\bar{v} = \theta + 1$ into the reduced Van der Waals equation Eq. (5.42), we expand the series up to third order in small variables

$$\bar{p} = 1 + 4\tau - 6\tau\theta - \frac{3}{2}\theta^3 + 9\theta^2\tau + \mathcal{O}(4). \quad (5.48)$$

Below $T < T_c$, we can see from Fig. 5.8 that there are 3 solutions for \bar{v} for fixed \bar{t} – recall that each point on the co-existence curve corresponds to a horizontal isotherm in the P - V diagram. One of these solutions is the metastable (i.e. unstable) point, so that leaves two solutions. As we approach the critical point T_c along the co-existence curve from below $T < T_c$ (see Fig. 5.7), the three solutions begin to approach each other, and becoming the same solution at the inflection point of the critical isotherm T_c . We want to know the behaviour of the solutions slightly away from the critical point. Since we are on an isotherm, $\bar{p}_1 = \bar{p}_2$, the two solutions for \bar{v} are just a small deviation ϵ from the critical value of 1, i.e. $\bar{v}_1 = 1 - \epsilon$ and $\bar{v}_2 = 1 + \epsilon$, such that $\theta_1 = -\theta_2$. Plugging these back into the expansion Eq. (5.48), we get

$$\bar{p}_1 = \bar{p}_2 \rightarrow \theta_1^2 = -4\tau \quad (5.49)$$

or

$$(V - V_c) \propto (T - T_c)^{1/2}. \quad (5.50)$$

Experimentally, we find that for $(V - V_c) \propto (T - T_c)^\beta$, $\beta \approx 0.33$, which is not 0.5 as predicted by Van der Waals, but again broadly independent of the atomic make-up!

Indeed, when we look at other thermodynamic variables, they are indeed not coincidences. For example, the heat capacity shows similar independence of the gas type, with

$$C_V \propto (T - T_c)^{-\alpha} \quad (5.51)$$

where $\alpha \approx 0.33$ experimentally (you will show in a homework problem that Van der Waals theory predicts $\alpha = 0$), and the **isothermal compressibility** (homework)

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \propto (T - T_c)^{-\gamma}, \quad (5.52)$$

with $\gamma \approx 1.2$ experimentally. What is going on here?

This behaviour, where thermodynamic properties are independent of the type of gas/liquid we are considering, is called (doh) **universality**. To be specific, small deviations of the thermodynamic variables from the critical point, say $\rho - \rho_c$, $\tau = \bar{t} - 1$ (or $T - T_c$), $\theta = \bar{v} - 1$ (or $V - V_c$), $(\bar{p} - 1)$ etc are called **order parameters**. (We will explain why they are called “order” parameters in the next section.) The exponents δ , α , β , γ , etc are called **critical exponents**. Universality states that, near the critical point, the critical exponents are independent of the atomic make up of the system. Another way to put it, is that near the critical point, the system does not care about the details of the microphysics – information about the kind of atoms and interactions are lost at the critical point. Systems that possess the same critical indices (and hence the same critical behaviour) are said to belong to the same **universality class**. We will see in section 5.4 another member of this class.

The notion of universality is one of the most important concepts in modern theoretical physics. Understanding the nature of universality led to major advances in quantum field theory, especially the idea of the *renormalization group flow* which has far reaching impact on not just statistical physics, but also particle physics⁵. Unfortunately, we won't be going that direction. In the next section, we turn instead to try to understand the physics of phase transitions.

⁵Indeed, the solution was primarily the work of Leo Kadanoff, a condensed matter physicist, and Kenneth Wilson, a particle theorist. Wilson was awarded the Nobel Prize in 1982 for this work, and it was an enduring controversy that Kadanoff was not accorded the same honour. For an accessible account, see Wilson's essay *Problems in Physics with Many Scales of Length* which is available on the class website.

5.3 Phase transitions

By now, you will have had some amorphous sense that phase transition is associated with some form of discontinuity. Throughout the lectures, you have been told that all the information in any statistical system is contained in the partition function

$$Z = \sum_r e^{-E_r/k_b T} , \quad (5.53)$$

which is a sum of exponentials, over all possible microstates of the system. Given the partition function, we can compute the Helmholtz free energy

$$F = -k_B T \ln Z , \quad (5.54)$$

from which we can then compute all the other thermodynamic quantities such as pressure, specific heat etc, by taking the suitable derivatives. For example, we can compute the entropy by $S = -(\partial F/\partial T)_V$ and then the heat capacity with $C_V = T(\partial S/\partial T)_P$ etc.

During a phase transition, some of these quantities become discontinuous – recall that for the BEC, the first derivative of C_V becomes discontinuous at the phase transition. Since they are usually derivatives of F , then F must possess some derivative discontinuities. But F comes from a sum of exponentials – which are famously continuous and easy to take derivatives of. Discontinuities are singularities, or infinities (e.g. the derivative of the discontinuous Heaviside step function is a Dirac delta function, whose derivative is formally infinite). Where then, did all these infinities come from?

This question vexed physicists for many years, until in the 1960s Leo Kadanoff realizes that there *is* an infinity hidden in the partition function Eq. (5.53) – the number of microstates r is formally infinite in the thermodynamic limit (see section 2.3.1). In real physical systems, the number of degrees of freedom is so large that it is essentially infinite – Kadanoff called this the “extended singularity theorem”. This leads to the aforementioned revolution in the development of renormalization group flow.

5.3.1 Landau Theory

Sadly, instead of taking that brave new step forward, we will take a step back in our lectures, back to the time of Landau, in the 1940s. At that time, he was trying to understand the physics of superconductivity. He understood that it is the discontinuities in the partition function, and hence in F , that led to phase transitions. So what he wanted is some theory that is formulated around an “extension” F to incorporate the (at that time) unknown physics that led to the generation of these discontinuities.

What kind of extension then? For now, to illustrate the ideas, we will work with temperature T though the formalism is general. Landau’s idea is that, instead of considering the large number of degrees of freedom in system, if we can somehow find some way to aggregate the physics of the degrees of freedom into some smaller subset *which capture all the important features*, then things will be much easier. Let’s suppose that these super special amazing degrees of freedom are called $m(x)$, or the **order parameters** – $m(x)$ in general can be a function of space. Landau’s suggestion is then to formally replace the partition function with

$$Z = e^{-F/k_b T} \rightarrow e^{-F_0/k_b T} \int \mathcal{D}m e^{-F_L[T,m]/k_b T} , \quad (5.55)$$

where $F_0(T)$ is some smooth function of temperature. The modified $F = F_0 + F_L[T, m]$ is called the **Landau functional**, and is a *functional*⁶ of the order parameter $m(x)$. For some configuration of $m_0(x)$, there is a function $F_L[T, m_0]$. The functional integral $\int \mathcal{D}m$ is hence an integral over all the possible configurations – all the microstates – of this new degree of freedom m . This conversion of a system with a large number of degrees of freedom to a smaller subset of degrees of freedom is called **coarse-graining**.

⁶A functional is a function of a function – since $m(x)$ is in general a function.

But as we have learned in way back in section 1.3.1, the equilibrium states are where F is *minimum*. To find the minimum, we need to find a configuration of $m(x)$ which minimizes F , i.e.

$$\delta_m F = 0, \quad F = F_0 + F_L. \quad (5.56)$$

This is a usual variation principle problem – the same way you found the Euler-Lagrange equation. For simplicity, let’s consider the special case where m is just a parameter and does not depend on space – we simply take the derivative to find the minimum

$$\frac{\partial F}{\partial m} = 0, \quad (5.57)$$

and the solution to this equation will give us some configuration or value of m at which the system is in equilibrium. Now, since $F[T, m]$ itself is also a function of T , one can imagine that *different T might lead to different minimum points m for $F[T, m]$* . Indeed, this possibility is how Landau “sneak” in the physics of phase transitions – the fact that we need to *find* the equilibrium values for m is key to Landau’s construction, as we will soon see.

All this is very mysterious, and formal. What is m ? What is the form of F_L ? How do we even begin to construct such a thing?

The fact that we have called m the order parameter, something you have learned in the previous section 5.2.4 might have clued you in. Think of the phase transition of water into ice. In the water phase, the water molecules are *disordered*, freely floating around without any notion of symmetry. On the other hand, in the ice phase, water molecules are arranged in an *ordered* manner with some symmetry (e.g. hexagonal lattice for regular ice). *The order parameter must be zero when the phase is disordered, and non-zero in the ordered phase.* The order parameter is some quantity that will capture this sense of order/disorder. For example, in section 5.2.4, the (inverse) density ($V - V_c$) is an order parameter. This explains the nomenclature of the order parameter. Nevertheless, it is not always obvious what the correct order parameter is.

More difficult is the construction of F_L . This in general has to come from how the order parameter m is related to the true degrees of freedom (i.e. how we perform the coarse-graining). This is actually a very hard thing to calculate in general, but fortunately some tractable models exist. In section 5.4, we will discuss one of the canonical model – the **Ising Model**.

For now, we will let ourselves make up F_L in order to show how the Landau model can sneak in discontinuities into the free energy.

5.3.2 2nd order phase transition

Let’s look at 2nd order phase transitions first. We will consider a simple model, where the order parameter m is simply a variable (remember in general it can be some complicated function). Suppose the Landau functional is given by

$$F = F_0(T) + a(T)m^2 + b(T)m^4. \quad (5.58)$$

We note in passing for the moment that F is invariant under the interchange of $m \rightarrow -m$. To find the equilibrium value of m , we want to minimize F as usual, so we take the first derivative w.r.t m

$$\frac{\partial F}{\partial m} = \frac{\partial F_L}{\partial m} = 2a(T)m + 4b(T)m^3 = 0. \quad (5.59)$$

Notice that the “background” term F_0 has dropped out of the conversation altogether.

The solutions to Eq. (5.59) depends on the functions $a(T)$ and $b(T)$, in particular, their signs. Let’s assume that $b(T) > 0$ for the sake of illustration. We have cases

- Case $a(T) > 0$: There is only one possible solution to Eq. (5.59), which is $m = 0$. This solution is stable since it is a minima.

- Case $a(T) < 0$: There are three possible solutions to Eq. (5.59), which is $m = \pm\sqrt{-a/2b}$, and $m = 0$. The solution $m = 0$ is a maxima, so is unstable. The other two $m \neq 0$ solutions are stable minima.

We can visualize this by plotting the free energy, by fixing $b(T) > 0$ to be a constant (we can assume that it changes very slowly w.r.t. T), see Fig. 5.9. As $a(T)$ goes from + to -, we move from a single to

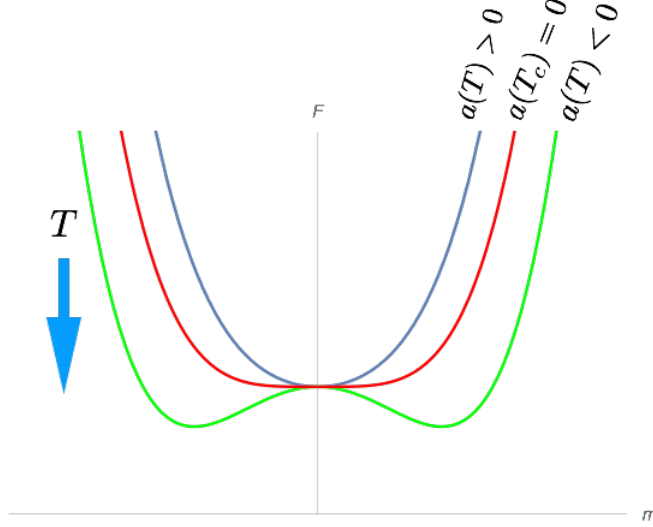


Figure 5.9: The Landau functional as a function of $a(T)$. At $a(T) > 0$, there is only one solution at $m = 0$. This solution is a minima, so is stable. At $a(T) < 0$, there are three solutions at $m = 0$ and $m = \pm\sqrt{-a/2b}$. The solution at $m = 0$ is unstable since it is a maxima, but the other two non-zero solutions are minima. The transition from one stable to two stable solutions occurs at $a(T_c) = 0$, which we identify as the critical temperature T_c .

two stable equilibrium solutions. Since we want $a(T)$ to be some monotonic function of T near T_c , we can define it as

$$a(T) \equiv \alpha(T - T_c) + \mathcal{O}(T - T_c)^2 + \dots, \quad (5.60)$$

where α is some positive definite constant. Near $T = T_c$, only the first term will matter. The Landau functional then has the solutions

$$F(T) = \begin{cases} F_0 & , T > T_c \\ F_0 - \frac{\alpha^2(T-T_c)^2}{2b} + \mathcal{O}(T - T_c)^3 & , T < T_c \end{cases} \quad (5.61)$$

To calculate the above equation, note that for the case $T > T_c$, we have substituted in the stable equilibrium solution $m = 0$ into Eq. (5.58), while for the case $T < T_c$ we substitute in the stable equilibrium solutions $m = \pm\sqrt{-a/2b}$. At T_c , the free energy is continuous at F_0 . The first derivative of F at T_c , approaching from both $T < T_c$ and $T > T_c$ is also continuous

$$\lim_{T \rightarrow T_c} \left. \frac{\partial F}{\partial T} \right|_{T_c} = \lim_{T \leftarrow T_c} \left. \frac{\partial F}{\partial T} \right|_{T_c} = \frac{\partial F_0}{\partial T}. \quad (5.62)$$

Hence the entropy $S = -(\partial F / \partial T)_V$ is also continuous. However, the 2nd derivative of F w.r.t to T

$$\lim_{T \rightarrow T_c} \left. \frac{\partial^2 F}{\partial T^2} \right|_{T_c} - \lim_{T \leftarrow T_c} \left. \frac{\partial^2 F}{\partial T^2} \right|_{T_c} = -\frac{\alpha^2}{b}, \quad (5.63)$$

which is clearly discontinuous at T_c . This means that the heat capacity $C_V = T(\partial S / \partial T)_V$ changes discontinuously at T_c .

Such a transition, where F is discontinuous only in the 2nd order derivative, was used to be defined as a **second order phase transition**. Although, as we mentioned in section 5.1.2, this is no longer quite in vogue (though still very useful, so you should learn it). For our model, notice that since S is continuous through T_c , the latent heat Eq. (5.22) is $L = T_c \Delta S = 0$, which is our “modern” definition of a 2nd order phase transition.

Notice that $F[T, m]$ is smooth and does not possess any discontinuities – Eq. (5.58) is smooth and continuous in both T and m . However, when we calculate quantities such as S and C_V , we must first substitute in the equilibrium values of m into $F[T, m]$. Since different m will lead to different functional forms of $F(T)$, and the minima of $F[T, m]$ are in general disconnected from one another, this leads to apparent discontinuities.

Finally, before we proceed to study 1st order phase transitions, we should address the question of “which” minima did the system choose? Is it m_+ or m_- ? The short uninteresting answer is that it doesn’t matter since they are both degenerate in the value of F . The more interesting point however, is to note that while the Landau functional Eq. (5.59) is invariant under $m \rightarrow -m$, the solutions m_{\pm} are not. What we mean is that solutions to an equation do not necessarily obey the symmetry of the equation – indeed, most solutions do not obey the original symmetry of the equation. So, as $T \rightarrow T_c$, the system has to make a choice – go + or go –, and once it made up its choice and made its bed, it will live in that minima. This kind of “breaking the symmetry of the equation by its solution” is called **spontaneous symmetry breaking**, and it is one of the great modern fundamental concepts of theoretical physics. For example, it is by this very mechanism that the Higgs particle was predicted and described accurately for the first time.

5.3.3 1st order phase transition

Let’s look at a model with a first order phase transition. This can be executed by a Landau functional

$$F = F_0(T) + a(T)m^2 + j(T)m^3 + b(T)m^4 . \quad (5.64)$$

Compared to Eq. (5.58), we have added the odd power term m^3 meaning that the functional is no longer invariant under $m \rightarrow -m$. To illustrate the physics, let’s set $b(T) > 0$ and $j(T) > 0$ as constants for simplicity. Again we want to consider the behaviour of the functional as T drops from $T > T_c$ to $T < T_c$, so we set $a(T)$ to be some monotonically decreasing function of $T - T_c$. The equilibrium points are given by

$$\frac{\partial F}{\partial m} = m(2a(T) + 3j(T)m + 4b(T)m^2) = 0 , \quad (5.65)$$

with solutions

$$m = 0 , \quad m_{\pm} = \frac{-3j \pm \sqrt{-32ab + 9j^2}}{8b} . \quad (5.66)$$

We can see that the number of real roots depend on whether the square root is real or imaginary. We define the critical temperature T_c to be such that the square root vanishes, i.e.

$$a(T_c) = \frac{9j^2}{32b} . \quad (5.67)$$

For $-32ab + 9j^2 < 0$, there is only one solution $m = 0$ (red curve in Fig. 5.10) – this corresponds to the phase above the critical temperature $T > T_c$. On the other hand, for $-32ab + 9j^2 > 0$, there are three solutions (yellow curve in Fig. 5.10). The two solutions m_{\pm} have different values for F such that (unlike the 2nd order case where $F(m_+) = F(m_-)$),

$$F(m_+) - F(m_-) = \frac{j(-32ab + j^2)^{3/2}}{256b^3} + \frac{3j^3 \sqrt{-32ab + j^2}}{64b^3} . \quad (5.68)$$

Since $F(m_+) > F(m_-)$ (remember that we have assumed $b > 0$ and $j > 0$), which means that $F(m_+)$ is not the true minimum – it is a **false minimum** – the system will eventually end up in the “true minima” $F(m_-)$. So we will only consider $F(m_-)$ in what follows. As T goes from $T > T_C$ through to $T < T_C$,

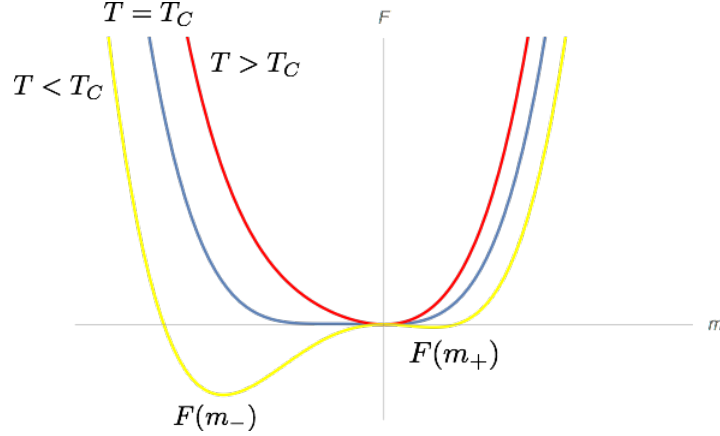


Figure 5.10: The Landau functional as $a(T)$ goes from $a(T) > 0$ to $a(T) < 0$. At high temperature (red), there is only one solution at $m = 0$ – this is the disordered phase. As the temperature drops below $T < T_C$ (yellow), additional solutions m_{\pm} begin to form. Since $F(m_-) < F(m_+)$ (for $j, b > 0$), $F(m_-)$ is the true minimum, so the system will eventually end up at that point.

we go from one solution $m = 0$ (minima) to three solutions, with $m = 0$ (maxima) and m_{\pm} (minima). The system then wants to go fall into one of the minimum – in general some part of the system will fall into m_- and some m_+ and for some time both phases can co-exists. This is a “mixture phase” (e.g. water/vapour) – i.e. the system is now in a phase transition. However, since m_+ is a false minimum, it is unstable, and eventually the system will fall into the m_- true minimum phase.

Thus the Landau model captures one of the essential features of a 1st order phase transition – that of the presence of metastable phase where the two phases are in equilibrium during the transition. The eagle-eyed amongst you will point out that phase transitions occur at fixed T , while in our model above, we seems to require T to change. The reason for this is because we have restricted our discussion to just considering changes in T . Nevertheless, it provides a good jumping off point – recall that we have fixed b and j as constants when they are actually also functions of T .

Finally, we can compute the entropy

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = \frac{\partial F_0}{\partial T} + \frac{\partial}{\partial T}(am^2) + \frac{\partial}{\partial T}(jm^3) + \frac{\partial}{\partial T}(bm^4), \quad (5.69)$$

where $m(T)$ is the minima which depends on $a(T)$ and hence implicitly depends on T . Again, *we need to substitute in the equilibrium values for m before taking the derivative w.r.t. T in Eq. (5.69)*. Since m depends on the a , which depends on T , S will have different functional forms for different equilibrium values of m .

Just like in the 2nd order case, we define the *critical temperature* T_c such that $a(T_c) \equiv 0$. Since we want $a(T)$ to be monotonic in T , and obey the condition Eq. (5.67) $a(T_c) = 9j^2/32b$, we can express it as

$$a(T) = \alpha(T - T_c) + \frac{9j^2}{32b}, \quad (5.70)$$

so $da/dT = \alpha$. At the beginning of the phase transition, $m = 0$, while at the end of the phase transition occurs when the system is at the true minimum m_- . Thus, keeping terms only to order $(T - T_c)$, we

have (considering only the $F(m_-)$ since it is the true minima)

$$F(T) = \begin{cases} F_0 & , \quad T > T_c \\ F_0 + \frac{27j^4}{4096b^3} + \frac{9j^2\alpha}{64b^2}(T - T_c) + \dots & , \quad T < T_c \end{cases} \quad (5.71)$$

This means that there is a *discontinuity in the order parameter*, which means that there is a discontinuity in S

$$\lim_{T \rightarrow T_c} \Delta S = \lim_{T \rightarrow T_c} (S(m=0) - S(m_-)) = \alpha \frac{9j^2}{64b^2} , \quad (5.72)$$

which justifies our assertion that this is a first order phase transition. As we discussed in section 5.2, first order phase transitions are accompanied by the release/addition of latent heat, which from Eq. (5.22) is, for a phase transition occurring at T (not necessarily T_c – as discussed in 5.2),

$$L \approx T \Delta S . \quad (5.73)$$

Finally, we should point out that one can also construct first order phase transitions with F that are symmetric under $m \rightarrow -m$ – you will do that in a homework set.

5.4 The Ising model

Our final mountain to climb in these lectures is to learn about the **Ising Model**. The Ising model was originally studied by Ernst Ising as part of his PhD thesis (who was given the problem by his advisor Wilhelm Lenz) in the 1920s. It was intended as a simple model to describe **Ferromagnetism** – the presence of permanent magnetic fields in some metals – but has since gained a life of its own as a particularly simple and illustrative model to study statistical mechanics models, finding applications in a wide range of fields such as gas mechanics, quantum field theory, string theory, condensed matter systems, and neuroscience.

One of the key features of a ferromagnet is that, in the absence of a magnetic field ($H = 0$), when you *cool it down past some critical temperature $T < T_c$ (called the **Curie temperature**), the magnetic dipoles suddenly, and spontaneously align itself to produce a net magnetization*. You must have played with plenty of permanent magnets in your life! This phenomenon is called **spontaneous magnetization**. But if you heat up the magnet to its Curie temperature T_c , it will suddenly lose all its magnetic properties. In other words, the ferromagnet undergoes a phase transition at temperature T_c . We want to study this phase transition using the Ising model.

As it turns out, you have already seen a baby version of the Ising model, way back in section 2.3.4, where we model a paramagnet with a lattice of dipoles which has two states – a spin-up state or a spin-down state. There, we have assumed that the dipoles do not interact (or only weakly interact) with each other. However, in the Ising model, we now allow them to interact with *their nearest neighbour*.

Suppose we label the spins s_i such that

$$s_i = \begin{cases} +1 & , \quad \text{for spin up } \uparrow \\ -1 & , \quad \text{for spin down } \downarrow \end{cases} \quad (5.74)$$

we can write the energy (or Hamiltonian) for a configuration or microstate of a lattice of dipoles as follows

$$E = -\mu H \sum_i s_i - \sum_{j, (n.n.)} J_{ij} s_i s_j . \quad (5.75)$$

The first term is the same as we have discussed in our discussion on paramagnetism (section 2.3.4) where $H > 0$ is the magnetic field (pointing in the same direction as \uparrow), and μ is the magnetic moment (again don't confused this with the chemical potential μ). The second term is the interaction term, where J_{ij}

is the *interaction matrix*. The additional energy for the interactions only come from interaction of each element with its nearest neighbour, so “n.n.” reminds us that we are only summing over the nearest neighbours of element i . So for 1D, 2D and 3D models, every element has 2, 4 and 6 neighbours – it is easy to show that for d dimension models, there are $2d$ neighbours per element. Recall from your classical

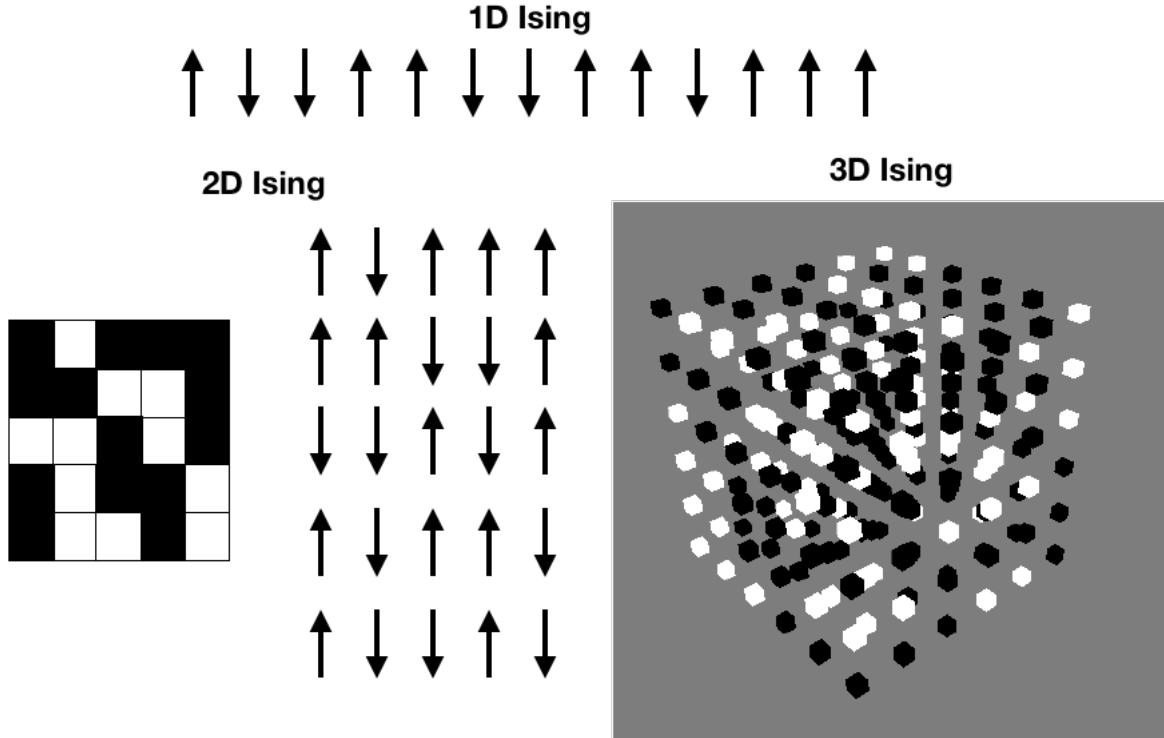


Figure 5.11: The Ising model for 1D, 2D and 3D. The Ising model can only be used to model a lattice gas – where the lattice is identified as a space where an \uparrow is occupied by a particle and \downarrow is empty – we show this equivalence in the 2D model example in this figure. (Source for 3D figure: McMullen et al (2012).)

mechanics module that the lower the energy E , the more stable the system (i.e. the more favoured the microstate), so the property of the model depends on the sign of J_{ij} . If $J_{ij} > 0$, this means that $\uparrow\uparrow$ or $\downarrow\downarrow$ configurations are more stable and hence more favoured – this is a **ferromagnet**. Conversely, if $J_{ij} < 0$, then $\downarrow\uparrow$ or $\uparrow\downarrow$ configurations are more stable – this is a **anti-ferromagnet**.

Following section 2.3.4, we want to calculate the partition function

$$Z = \sum_{\text{all microstates}} e^{-\beta E} , \quad (5.76)$$

where “all microstates” mean every single possible configuration of s_i (remember that the energy E is calculated for one single configuration). For N dipoles, this would be 2^N microstates, which is a mind boggling big number. Unlike the paramagnetic case however, where due to the lack of interactions we can calculate the partition function for a single dipole Z_1 , and then use the fact that partition functions factor $Z = \prod Z_1$, the presence of interactions rendered this trick unusable. Like in the paramagnet case, our goal is to derive the magnetization M of the system given by

$$M = \frac{N\bar{\mu}}{V} \quad (5.77)$$

where $\bar{\mu}$ is the mean magnetic moment given by (see Eq. (2.85))

$$\bar{\mu} \equiv \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} . \quad (5.78)$$

To solve this, we need to evaluate the partition function. This is a difficult problem.

Famously, Ising solved this problem analytically as his PhD thesis for a 1D model. You will retrace Ising's steps⁷ in a homework problem, to find that the partition function for the 1D model is given by

$$Z_{1D} = \lambda_+^N + \lambda_-^N \quad (5.79)$$

where

$$\lambda_{\pm} = e^{\beta J} \left[\cosh(\beta \mu H) \pm \sqrt{e^{-4\beta J} + \sinh^2(\beta \mu H)} \right] . \quad (5.80)$$

Now since N is a very big number, $\lambda_+ > \lambda_-$ meant that $\lambda_+^N \gg \lambda_-^N$, so we can drop λ_- , thus $\ln Z = N \ln \lambda_+$, and it is a matter of some algebra (homework) to show that

$$M = \frac{e^{\beta J}}{V \lambda_+ \beta} \left[\mu \beta \sinh(\beta \mu H) + \frac{\mu \beta \sinh(2\beta \mu H)}{2\sqrt{e^{-4\beta J} + \sinh^2(\beta \mu H)}} \right] . \quad (5.81)$$

As we dial down the magnetic field $H \rightarrow 0$, then both $\sinh(\beta \mu H) \rightarrow 0$ and $\sinh(2\beta \mu H) \rightarrow 0$, and thus the magnetization $M \rightarrow 0$, at any temperature T . The paramagnet case with no interactions give us the same limit at $H = 0$, so we conclude that there is no ferromagnetic effects in a 1D Ising model (recall that ferromagnets are materials which are magnetic in the absence of an external magnetic field).

What about the 2D and 3D cases? The 2D Ising model, as it turns out, is also solvable analytically. It was first solved by Lars Onsager in 1944. The solution is a wee bit more complicated than the 1D model you have (hopefully) diligently solved in the homework set, so we will leave it for the brave to check it out (see section 12.2 of Parthia's book in the Bibliography). The key result is the 2D Ising model indeed exhibits spontaneous magnetization, where at temperatures below a critical temperature

$$T_c = \frac{2.27J}{k_b} , \quad (5.82)$$

a non-zero M spontaneously appear in the absence of any external magnetic fields.

Finally, there is no analytic result for the 3D Ising model (a prize probably awaits the person solves it). Fortunately, the system itself is simple enough for physicists to attack it numerically with high performance computers. What do they get?

Recall from our discussion in section 2.3.4 that there is an equivalence between pressure and mean magnetic moment (Eq. (2.87))

$$P \leftrightarrow \bar{\mu} , \quad dV \leftrightarrow dH , \quad (5.83)$$

and from our discussion on critical exponents in section 5.2.4 that, experimentally,

$$P - P_c \sim (\rho - \rho_c)^\delta \quad (5.84)$$

where $\delta \approx 4.8$ experimentally. Now since $\rho \propto V^{-1}$, the equivalent critical relation for a ferromagnet is

$$\bar{\mu} \propto (H - H_c)^{1/\delta} . \quad (5.85)$$

Numerically, it has been shown that $\delta \approx 4.8$ (the additional inverse is a long story). Indeed, it has been shown that the 3D Ising model has the following critical components

$$\bar{\mu} \propto (T - T_c)^\beta , \quad \beta = 0.33 \quad (5.86)$$

and the magnetic susceptibility (see Eq. (2.93)) scales like

$$\chi \propto (T - T_c)^{-\gamma} , \quad \gamma = 1.2 . \quad (5.87)$$

⁷Actually, you will be guided through the calculation by Kramers and Wannier, who solved this problem in 1941 using a much more elegant trick.

This is almost exactly as the experimental values for a real atomic gas (the magnetic susceptibility is the equivalent of the compressibility κ)! This is another manifestation of the physics of universality that we discussed in section 5.2.4 – the Ising model in 3D is in the same universality class as atomic gas. This is one reason why it is such a useful model, and have been extensively studied.

5.4.1 Mean field theory

We will now study an approximate solution to the d -dimensional Ising model (we keep dimensionality general), using a method called the **mean field theory**. The idea is to that, instead of keeping individual track of spins (\uparrow or \downarrow) of all the dipoles, we define an averaged (“mean”) spin value (“field”), which encodes in some rough way the state of the system. We want this mean field to be large when a lot of the spins are correlated (say a lot of the pointing \uparrow), and the mean field to be small when the spins are uncorrelated (i.e. random). Recall our discussion of the order parameter in Landau theory – highly correlated means that the system is *ordered* while random means that the system is *disordered*. Hence, the mean field is an order parameter.

A reasonable choice for such a mean field is the *average spin*

$$m \equiv \frac{1}{N} \sum_i s_i , \quad (5.88)$$

so $-1 \leq m \leq 1$. Indeed, this is directly related to the total mean magnetic moment

$$\bar{\mu}_N = \mu \sum_i s_i = Nm\mu . \quad (5.89)$$

We can now rewrite the interaction (2nd) term of the Ising model Eq. (5.75) as

$$\begin{aligned} \sum_{j,(\text{n.n.})} J_{ij} s_i s_j &\rightarrow \sum_{j,(\text{n.n.})} J_{ij} [(s_i - m) + m][(s_j - m) + m] \\ &= \sum_{j,(\text{n.n.})} J_{ij} [(s_i - m)(s_j - m) + m(s_i - m) + (s_j - m) + m^2] . \end{aligned} \quad (5.90)$$

If we now assume that the averaged *difference* $\sum_i (s_i - m)$ is small, then the above equation can be categorized as $\mathcal{O}(s - m)^2$, $\mathcal{O}(s - m)$ and $\mathcal{O}(1)$ terms. This means that we can neglect the first term, and assuming for simplicity that J_{ij} to have constant J values for all (i.e. $J_{ij} \equiv J\delta_{ij}$), the new mean field energy is now

$$E \approx -\mu H \sum_i s_i - \sum_{j,(\text{n.n.})} J [m(s_i + s_j) - m^2] . \quad (5.91)$$

The last term is

$$\sum_{\text{n.n.}} m^2 = \frac{1}{2} 2dNm^2 = Ndm^2 . \quad (5.92)$$

A few words here : we are summing over *pairs of nearest neighbours*, so for every element, we have to multiply by $2d$ neighbours. Meanwhile, we are summing over pairs, we don't want to double count, so we multiply by $1/2$. Finally there are N elements, hence the final answer.

Similarly, the first term is

$$\sum_{\text{n.n.}} m(s_i + s_j) = \sum_i 2dms_i , \quad (5.93)$$

where for each element, again there are $2d$ neighbours. Putting everything together, we have

$$E = -(2dJm + \mu H) \sum_i s_i + NJdm^2 . \quad (5.94)$$

The sum over neighbours are gone, and now we only have a sum over elements – each spin now effectively acts independently of each other – plus a constant term. Comparing this result to the non-interacting case, we see that, if we define an “effective magnetic field”

$$H_{\text{eff}} = H + \frac{2dJm}{\mu} , \quad (5.95)$$

the partition function for each dipole is then

$$Z_1 = (e^{-\beta\mu H_{\text{eff}}} + e^{\beta\mu H_{\text{eff}}}) . \quad (5.96)$$

The total partition function is then a product of all dipoles, plus the constant factor from the $NJdm^2$ term,

$$Z = e^{-\beta NJdm^2} \prod_i Z_1 = e^{-\beta NJdm^2} 2^N \cosh(\beta\mu H_{\text{eff}})^N . \quad (5.97)$$

Taking stock, we have expressed the Ising model partition function as a function of m and $H_{\text{eff}}(m)$, the latter which itself depends on m . All the difficult mutual interactions have been aggregated into a single parameter. Indeed, this is an excellent example of the *coarse-graining* that we have discussed when we talked about the Landau theory in section 5.3.1 – m is an order parameter. If the spins are correlated (e.g. aligned), then they are ordered and m is large, and *vice versa*. We will come back to discuss its connection to the Landau theory in the next section 5.4.2.

With the partition function in hand, we can find the mean magnetic moment (Eq. (2.85))

$$\bar{\mu}_N = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} = N\mu \tanh(\beta H_{\text{eff}}\mu) \quad (5.98)$$

but $\bar{\mu}_N/\mu N = m$ from Eq. (5.88) and Eq. (5.89), and thus we obtain the following implicit equation for m

$$m = \tanh(\beta H\mu + 2\beta dJm) . \quad (5.99)$$

We now want to find the solutions for m as a function of H , d , J and $\beta = (k_b T)^{-1}$. Notice that N has dropped out of the story altogether. This doesn’t mean that the size of the system is not important – indeed we have used the fact that N is large to construct a “mean” field m .

There is no analytic solutions for implicit equations like Eq. (5.99), so we will use a graphical method to find the solutions – plot LHS and RHS as a function of m and the intersections of these two graphs will be the solution(s). Let’s consider the solutions depending on whether $H = 0$ or $H \neq 0$ separately – we will see that they have drastically different kind of solutions.

- $H = 0$: For notational wieldiness, we define

$$q \equiv 2\beta dJ \quad (5.100)$$

such that the equation becomes

$$m = \tanh(qm) . \quad (5.101)$$

The number of solutions to this equation now depends on whether $q < 1$ or $q > 1$ – see Fig. 5.12.

For $q < 1$, or $k_b T > 2dJ$, i.e. the *high temperature limit*, there is only one solution at $m = 0$ – there is no magnetization. This makes sense, since at high temperature, the dipoles are energetic so we expect them to fluctuate rapidly and the self-interactions of the dipoles are too weak to keep them aligned.

For $q > 1$, or $k_b T < 2dJ$, i.e. the *low temperature limit*, we have three solutions at $m = 0$ and $m = m_0^\pm$. The $m = 0$ solution is actually unstable – we will show this in the next section 5.4.2. The two non-zero solutions m_0^\pm are stable – the interactions of the dipoles are strong enough to

keep them aligned due to the low temperature. In the limit of $T \rightarrow 0$, or $\beta \rightarrow \infty$, $m_0^\pm \rightarrow \pm 1$. At absolute zero temperature, all the spins are pointing in the same direction!

This is exactly what we expect from a ferromagnet, as we describe in the beginning of this section. The critical temperature

$$T_c = \frac{2dJ}{k_b} \quad (5.102)$$

is then the Curie temperature.

Notice that the two solutions are equal except in signs, i.e. $m_0^+ = -m_0^-$. This means that if we cool down a ferromagnet to T_c , it has a 50% chance of aligning in the + or - direction respectively. The initial symmetry (no alignment, or preferred direction, $m = 0$) has been broken and a preferred direction m_0^+ or m_0^- has been chosen. This is exactly the situation we described when we discussed 2nd order phase transition in section 5.3.2. We will see how this connects, again in the next section 5.4.2.

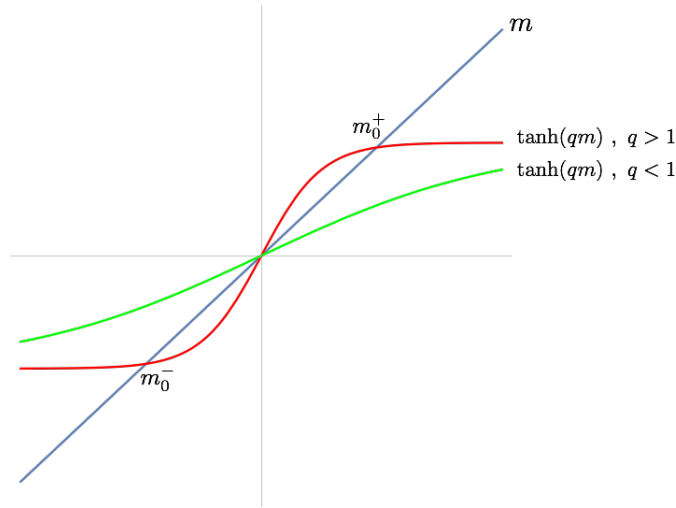


Figure 5.12: For $H = 0$, with $q \equiv 2\beta dJ$. The cyan line is the linear m . When $q < 1$ (green line), there is only one solution at $m = 0$. On the other hand, when $q > 1$ (red line), there are three solutions: $m = 0$ (unstable) and m_0^\pm (stable).

- $H \neq 0$: The analysis again depends on whether or not $q < 1$ or $q > 1$.

For $q < 1$, or $k_b T > 2dJ$, i.e. the *high temperature limit*, there is only one solution at m_0 , although in general this solution is not at $m_0 = 0$. If $H > 0$ then $m_0 > 0$ and *vice versa*. This makes sense – the presence of an external magnetic field induces a small magnetization on the ferromagnet.

For $q > 1$, or $k_b T < 2dJ$, i.e. the *low temperature limit*, there can be one, or three solutions depending on T . At high temperature, we have one solution which coincides with the $q < 1$ solution above – this is not surprising. More interestingly, as we decrease the temperature, the additional solutions m_0^\pm begin to appear. As we approach $T \rightarrow 0$, these new solutions asymptote to a fixed point. Unlike the $H = 0$ case however, the direction of H breaks the symmetry of the system, and the system will settle on the equilibrium (either of the m_0^\pm) with the sign identical to the sign of H . E.g. if $H < 0$ then, then the equilibrium state is m_0^- and *vice versa*. To show this we need to calculate the free energy F and look for the true minimum – we will discuss this in the next section. Importantly, this process is *continuous and smooth* – the equilibrium point move smoothly from m_0 to m_0^\pm without any discontinuities.

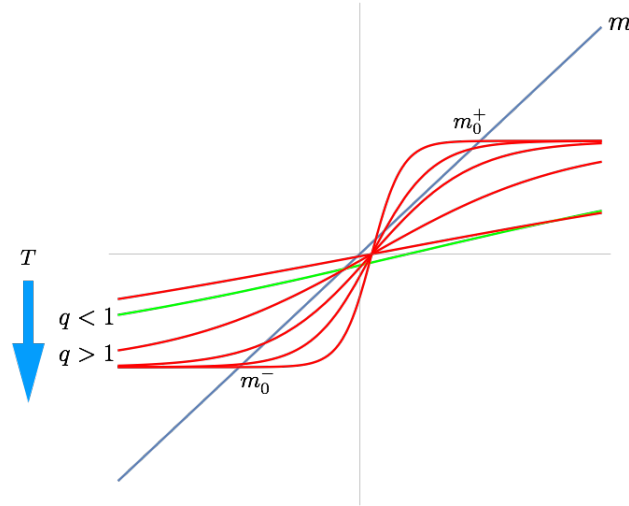


Figure 5.13: For $H \neq 0$, with $q \equiv 2\beta dJ$. We plot the case where $H < 0$. The cyan line is the linear m . When $q < 1$ (green line), there is only one solution m_0 , although this solution is generally not at $m = 0$. On the other hand, when $q > 1$ (red lines), there may be one, two or three solutions, depending on the temperature T . As we reduce $T \rightarrow 0$, the solution tends to m_0^- for $H < 0$ (shown in this figure), while as we increase $T \rightarrow \infty$, we again approach the same single solution of the $q < 1$ case.

In summary the behavior of m as a function of T is plotted in Fig. 5.14. In the case of $H = 0$, there is a phase transition at T_c as we lower the temperature. For the case $H \neq 0$, there is no phase transition if we fix H , and then lower the temperature – the equilibrium points goes smoothly to $m \rightarrow \text{sgn}(m)$. However, if we fix $T < T_c$, and then vary H from positive to negative (or negative to positive), there will be a phase transition – m flips sign spontaneously as H crosses the zero line.

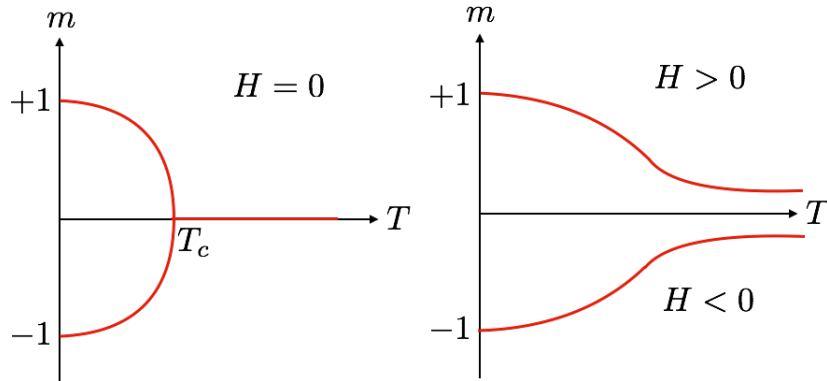


Figure 5.14: The left plot is the case $H = 0$, while the right plot is for the case $H \neq 0$.

5.4.2 Connection to Landau Theory

We will now discuss the mean field Ising model in context of the Landau theory. To begin let's calculate the Helmholtz free energy with the mean field partition function Eq. (5.97)

$$\begin{aligned}
 F &= -k_b T \ln Z \\
 &= \frac{N}{\beta} [\beta J d m^2 - \ln 2 - \ln \cosh(\beta H \mu + 2\beta d J m)] .
 \end{aligned}
 \tag{5.103}$$

In Landau theory (section 5.3.1), it was argued that we can express a coarse-grained version of the

original partition function (and hence Helmholtz free energy via $F = -k_b T \ln Z$) by expressing it as a function of some order parameter m which encodes how ordered/disordered the system is. As we have seen, the mean field of the Ising model, the average spin m , is an order parameter in the context of Landau theory – the fact that we have used m for both is a convenient coincidence.

Indeed, we can view Eq. (5.103) as a Landau functional, with m as its order parameter. To find the equilibrium points, we can then take derivative w.r.t. m ,

$$\frac{\partial F}{\partial m} = 0 \quad (5.104)$$

which gives us the solution

$$m = \tanh(\beta H \mu + 2\beta d J m) , \quad (5.105)$$

which is exactly as what we found previously in Eq. (5.99)! This is not a coincidence of course – the mean field theory is a direct application of the Landau theory in action. We have coarse-grained the interactions of the system into a mean field, the average spin m . Note that not all values of m are minima of F , and hence they are not equilibrium solutions.

We can make further connections. Using the expansion $\ln \cosh x = x^2/2 - x^4/12 + \dots$ (notice that it is an expansion in *even* powers of the argument), the free energy becomes

$$F = N \left[J d m^2 - \frac{1}{\beta} \ln 2 - \frac{1}{\beta} \left(\frac{1}{2} (\beta H_{\text{eff}} \mu)^2 - \frac{1}{12} (\beta H_{\text{eff}} \mu)^4 + \dots \right) \right] . \quad (5.106)$$

Now the series in general does not necessarily converge, so it's debatable whether we can Taylor expand F . For this module, let's run with it, and see what it tells us.

- $H = 0$: For $H = 0$, $H_{\text{eff}} = 2dJm/\mu$, so the evenness of the $\ln \cosh x$ expansion is maintained as a function of m , we can express F as

$$F = -\frac{N \ln 2}{\beta} + N d J (1 - 2dJ\beta) m^2 + \frac{4}{3} N (dJ)^4 \beta^3 m^4 + \dots \quad (5.107)$$

Comparing this equation to the *even* order Landau model, Eq. (5.58), we see that

$$F_0(T) = -\frac{N \ln 2}{\beta} , \quad a(T) = N d J (1 - 2dJ\beta) , \quad b(T) = \frac{4}{3} N (dJ)^4 \beta^3 . \quad (5.108)$$

Recalling from our discussion in section 5.3.2 that a 2nd order phase transition occurs when $a(T) = 0$, or

$$1 - 2dJ\beta = 0 \rightarrow k_b T = 2dJ \quad (5.109)$$

which again is exactly as we computed using our graphical method in the previous section 5.4.1. Indeed, you will show in a homework set that the transition is indeed 2nd order by calculating the derivatives of F w.r.t T .

- $H \neq 0$: On the other hand, since the argument of the expansion $\beta H_{\text{eff}} \mu = \beta H \mu + 2\beta d J m$ under an even power will lead to cross terms between m and H , this means that the expansion no longer leads to only even powers of m , but also odd powers of m . In words, the presence of the H field has broken the symmetry $m \rightarrow -m$ – eminently reasonable since H picks out a particular direction, so the expansion will look like

$$F = F_0(T) + a(T)m + b(T)m^2 + c(T)m^3 + d(T)m^4 + \dots \quad (5.110)$$

We won't do the (rather messy algebra) here to compute the coefficients. Instead we will elaborate on our discussion in section 5.4.1 that as we dial H from negative to positive, there will be a phase transition as m will flip from $-$ to $+$. Fixing $T < T_c$, we plot $F(m)$ for $H < 0$, $H = 0$ and $H > 0$,

see Fig. 5.15. We draw your attention to the minima of the various curves for F . Recall that the equilibrium point is the true minimum (not the false minimum), as we dial H from negative to positive, we see that the minimum point skips from $m < 0$ to $m > 0$, with a discontinuous jump occurring at $T = T_c$ (the blue line). This is a first order phase transition.

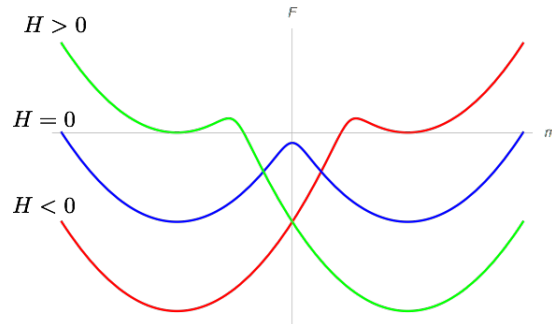


Figure 5.15: The Helmholtz free energy for the mean field Ising model, for $T < T_c$, for $H < 0$, $H = 0$ and $H > 0$. As we dial from H negative to positive, the minimum point of F jumps from $-m$ to $+m$ – this is a 1st order phase transition.

5.4.3 The missing physics of fluctuations

Finally, let's calculate how m behave near the critical temperature T . In particular, we want to know what are the critical exponent of this theory, for the case when $H = 0$. Let's make our life easier by using the series expansion in m for F , Eq. (5.107). The minimum for F occurs for $\partial F/\partial m = 0$, or

$$m_0^\pm = \pm \sqrt{6 \left(\frac{T_c}{T} \right)^3 \left(\frac{T}{T_c} - 1 \right)} \quad (5.111)$$

but now as $T \rightarrow T_c$, $(T_c/T)^3 \rightarrow 1$, and we are left with the critical behaviour

$$m_0^\pm \propto |T - T_c|^{1/2}. \quad (5.112)$$

But since $\bar{\mu} = m_0 \mu$, this means that

$$\bar{\mu} \propto |T - T_c|^\beta, \quad \beta = \frac{1}{2}. \quad (5.113)$$

Comparing this with the exact 3D Ising model Eq. (5.86) and real gasses, which has $\beta = 0.33$, we see that we are not quite correct. Indeed, you can calculate in the privacy and comfort of your own home(work set) that for the mean field Ising model, the other critical exponents are

$$\chi \propto (T - T_c)^{-\gamma}, \quad \gamma = 1 \quad (5.114)$$

and

$$\bar{\mu} \propto (H - H_c)^\delta, \quad \delta = 3. \quad (5.115)$$

Compared to the exact 3D Ising model and real gas $\gamma = 1.2$ and $\delta = 4.8$, the mean field Ising model gets it wrong by a bit.

So what went wrong? It turns out, that the mean field theory gets it wrong immediately by its name “mean”. By executing the averaging $m = (1/N) \sum s_i$ and then throwing away $(s - m)^2$ terms, we threw away the information of the *fluctuations* of the system.

As our time is almost up, let's briefly discuss this issue, and leave the hard details for when you take a more advanced course. Let's consider an order parameter $m(x)$, which now we allow it to vary over the

space – you can think that it is the spin of an Ising lattice if that helps in your visualiation. Suppose the system is in equilibrium m_0 . Now we know from our studies of statistical ensemble that, in reality, even a system in equilibrium will undergo fluctuations, $\delta m(x)$, such that

$$m(x) = m_0 + \delta m(x) . \quad (5.116)$$

Now these fluctuations do not live forever – the system *wants* to be in its equilibrium state, so fluctuations once formed, wants to return to its home base of equilibria. Fluctuations then only “know about each other”, or correlated, over some distance scale, called its **correlation length**⁸ ξ – they usually don’t live long enough to find all their friends (no social media for them). ξ can be shown to behave like

$$\xi = \sqrt{\frac{\gamma}{2a(T)}} \quad (5.117)$$

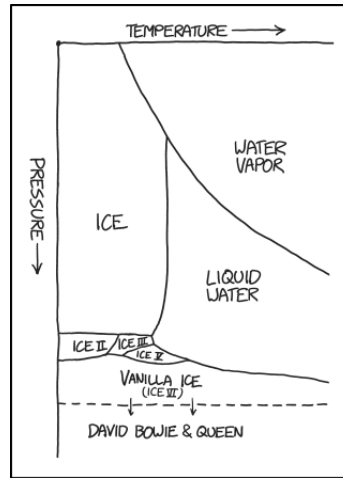
where γ is some function of temperature T . More importantly $a(T)$ is the coefficient in front of the m^2 term of the Landau functional Eq. (5.58), such that as $a(T \rightarrow T_c) \rightarrow 0$. In other words, $\xi \rightarrow \infty$ – the system becomes *infinitely correlated*. In other words, at the critical temperature, *all the fluctuations know about each other*. This is why, at the phase transition, the entire system seems to change instantaneously – the average spin of the Ising model m flips sign or changes discontinuously, water freezes and organizes itself into a symmetric lattice etc.

But, alas, we are out of time.

⁸This is called the Ornstein-Zernike correlation length.

Epilogue

I don't really have any inspirational things to say. I hope you have had fun learning statistical mechanics! Relevant XKCD (credit Randall Munroe <http://www.xkcd.com/>).



Appendix A

Some Mathematical Formulas

A.1 Stirling's Approximation

We will show that the oft-seen $\ln N!$ is given by the approximation

$$\boxed{\ln N! \approx N \ln N - N}, \quad (\text{A.1})$$

for very large $N \gg 1$. To prove this, we first note that

$$\begin{aligned} \ln N! &= \ln [N \times (N-1) \times (N-2) \times \cdots \times 1] \\ &= \ln N + \ln(N-1) + \cdots + \ln 1 \\ &= \sum_{m=1}^{m=N} \ln m. \end{aligned} \quad (\text{A.2})$$

For sufficiently large N , we can approximate the sum as an integral

$$\begin{aligned} \sum_{m=1}^{m=N} \ln m &= \int_1^N dm \ln m \\ &= [m \ln m - m]_{m=1}^{m=N} \\ &= N \ln N - (N-1) \\ &\approx N \ln N - N, \end{aligned} \quad (\text{A.3})$$

which proves our assertion. More precisely, one can show that

$$\ln N! = N \ln N - N + \ln(2\pi N) + \mathcal{O}(1/N). \quad (\text{A.4})$$

which as $N \gg 1$ becomes very large, allows us to drop the last two terms to get Eq. (A.1).

A.2 Some useful integrals

Integrals of the type

$$I = \int_0^\infty \frac{x^{n-1}}{e^x \pm 1} dx, \quad (\text{A.5})$$

appear frequently in statistical mechanics. They have the solutions

$$\int_0^\infty \frac{x^{n-1}}{e^x + 1} dx = (1 - 2^{1-n})\Gamma(n)\zeta(n), \quad (n > 0), \quad (\text{A.6})$$

and

$$\int_0^{\infty} \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n)\zeta(n), \quad (n > 1), \quad (\text{A.7})$$

where $\zeta(n)$ is the **Riemann Zeta function**

$$\zeta(p) \equiv \sum_{n=1}^{\infty} \frac{1}{n^p} \quad (\text{A.8})$$

and $\Gamma(n)$ is the **Gamma function**

$$\Gamma(n) \equiv \int_0^{\infty} x^{n-1} e^{-x} dx. \quad (\text{A.9})$$

The Gamma function for $n > 0$ integers is just the factorial

$$\Gamma(n) = (n-1)!, \quad n \in \mathcal{N} - \{0\}. \quad (\text{A.10})$$

A very common type of integral that you will encounter is the so-called **Gaussian integral**

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}. \quad (\text{A.11})$$

Proof: Since the integrand is invariant under $x \rightarrow -x$, we can also write it as

$$J = \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \int_{-\infty}^{\infty} e^{-ax^2} dx. \quad (\text{A.12})$$

Now take the square of J ,

$$\begin{aligned} J^2 &= \int_0^{\infty} e^{-ax^2} dx \int_0^{\infty} e^{-ay^2} dy \\ &= \int_0^{\infty} \int_0^{\infty} e^{-a(x^2+y^2)} dx dy. \end{aligned} \quad (\text{A.13})$$

Switching to polar coordinates (r, θ) such that $r = \sqrt{x^2 + y^2}$, $x = r \sin \theta$, $y = r \cos \theta$, the integral measure is then $r dr d\theta$, with the domain changing from $0 < r < \infty$ and $0 < \theta < \pi/4$. (Notice that we only integrate the first quadrant of θ .) Thus,

$$\begin{aligned} J^2 &= \int_0^{\pi/2} \int_0^{\infty} e^{-ar^2} r dr d\theta \\ &= \frac{\pi}{2} \cdot \left(-\frac{1}{2a} e^{-ar^2} \right)_0^{\infty} \\ &= \frac{\pi}{4a}. \end{aligned} \quad (\text{A.14})$$

Since $J^2 = (1/4)I^2$, then $I = \sqrt{\pi/a}$ and our proof is complete.

Higher order even integrals can be easily extracted from this result, viz.

$$\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = (-1)^n \frac{\partial^n}{\partial a^n} \left(\int_{-\infty}^{\infty} e^{-ax^2} dx \right) = (-1)^n \frac{\partial^n}{\partial a^n} \sqrt{\frac{\pi}{a}} = \sqrt{\frac{\pi}{a}} \frac{(2n-1)!!}{(2a)^n}. \quad (\text{A.15})$$