Statistical Physics

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Chapter 1

Basics of Thermodynamics

1.1 Introduction

There are two general approaches into teaching statistical physics. The first possibility is to start directly with the statistical description of many-particle systems and then, based on the obtained results, introduce the concept of thermodynamics. The second approach is reverse, i.e., one starts with some basic principles of thermodynamics and then builds the statistical physics based on those. Even though the first approach is logically more consistent, from the pedagogical point of view, I prefer the second one, and that's why the first chapter of these lecture notes is devoted to the introduction to thermodynamics.

Thermodynamics is one of the most fascinating fields of physics, primarily due to the reason that it is extremely general. I believe that one of the first examples of a physical system most of us would imagine in this context is probably something like an ideal gas, or a hot cup of coffee, etc. But thermodynamics can be equally as good applied to, e.g., the electrons inside a conductor, radiation emitted by the Sun, or even to the whole universe we live in right now. (I am trying to come up with examples that would otherwise appear as completely unrelated.) And, at least to me, this truly is fascinating. At the same time, thermodynamics is one of the hardest subjects to understand properly. It is by no means hard mathematically. We just need some basic knowledge of the multi-variable calculus. But it introduces some new concepts such as, e.g., the *entropy*, which is arguably the most mysterious quantity in the world of physics. And I can guarantee you (this is also a little warning) that you might spend many long hours trying to decipher even the absolute basics. My personal experience is that when you study thermodynamics for the first time, it seems relatively easy. But once you start digging a bit deeper, all you have learned so far starts to fall apart up to the point you admit that you actually do not understand anything. But don't worry, since once you reach that point, you are finally ready to make some real progress!

As the primary goal of this course is the statistical description of many-particle systems, we will discuss only the very basics of thermodynamics that are necessary for the proper understanding of the upcoming topics. The modern way of doing so is by formulating the *three laws of thermodynamics*, mostly because it is physically more intuitive and simpler to get a grasp on. Nevertheless, we are going to choose a different approach, based primarily on the exceptional book *Thermodynamics and an Introduction to Thermostatistics* by H.B. Callen, where thermodynamics is built upon a priori given postulates, similarly as, e.g., the quantum mechanics. And even though the physical interpretation can be a bit more tricky here, it will provide us with the cleanest correspondence to the the statistical mechanics, which is what we are aiming at.

1.2 Many-Particle Systems

I do not think that there is an universally accepted definition of what exactly is thermodynamics. Many times, people tend to include terms like *temperature* and *heat* in the definition, and it is logical, as these are exactly the words that come up to mind first in this context. The problem is that, even though the meaning of such words is intuitive to us (each one of us understood the concept of temperature the first time we touched a hot pan just taken out of the oven), we are lacking a proper definition, and hence, it is not a good idea to base the sought definition on terms that are, at this point, rather abstract. My personal attempt to formulate a sensible definition would be:

Thermodynamics studies macroscopic properties of many-particle systems.

What do we mean by a many-particle system? The simplest example would be a flask filled with a gas containing roughly $N \sim 10^{23}$ particles. Now let's discuss why this is problematic. From the classical point of view, if we have N particles in our system, then we can construct the Hamilton function

$$H = H(x, p)\,, \tag{1.1}$$

where

$$x = \{x_i\}_{i=1}^{3N}\,, \quad p = \{p_i\}_{i=1}^{3N} \tag{1.2}$$

represent the generalized coordinates and the corresponding conjugate momenta of each constituent particle, respectively. Further, the time evolution of such system is governed by the system of equations

$$\dot{x}_i = \frac{\partial H}{\partial p_i}\,, \quad \dot{p}_i = -\frac{\partial H}{\partial x_i}\,. \tag{1.3}$$

That is, we would need to:

1. formulate $6N$ initial conditions as $x_i(t_0) = x_{i,0}$, $p_i(t_0) = p_{i,0}$,
2. solve a (generally coupled) system of $6N$ first-order (generally non-linear) differential equations.

I hope that you get the feeling of how totally absurd both of these sound considering $N \sim 10^{23}$. Theoretically speaking, nothing prohibits such a calculation, but realistically, it cannot be done. And this is not "cannot" as "it would be really hard", this is "cannot" as "simply impossible".

We can also sketch a similar idea but now treating the system quantum mechanically. In that case, we would introduce the linear hermitian operators

$$\hat{\mathbf{x}} = \{\hat{\mathbf{x}}_i\}_{i=1}^{3N}\,, \quad \hat{\mathbf{p}} = \{\hat{\mathbf{p}}_i\}_{i=1}^{3N} \tag{1.4}$$

with the property

$$[\hat{\mathbf{x}}_i, \hat{\mathbf{p}}_j] = \mathrm{i}\hbar\delta_{ij}\,, \tag{1.5}$$

while the time evolution of the system $|\psi\rangle$ is then given by the Schrödinger equation

$$\mathrm{i}\hbar\frac{\mathrm{d}\,|\psi\rangle}{\mathrm{d}t} = H(\hat{\mathbf{x}}, \hat{\mathbf{p}})\,|\psi\rangle\ . \tag{1.6}$$

In the standardly used x-representation

$$\hat{\mathbf{x}}_i \to x_i\,, \quad \hat{\mathbf{p}}_i \to -\mathrm{i}\hbar\frac{\partial}{\partial x_i}\,, \quad |\psi\rangle \to \psi(t,x)\,, \tag{1.7}$$

this becomes

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\sum_{i=1}^{3N}\frac{\partial^2\psi}{\partial {x_i}^2} + V(x)\psi(t,x)\,, \tag{1.8}$$

and so we are required to:

1. formulate the initial condition $\psi(t_0, x) = \psi_0(x)$,
2. solve a partial differential equation of $3N + 1$ (the $+1$ is for the time) variables.

An equally absurd task as in the classical case.

Clearly, even though a nice try, this is not the way to go.

1.3 Equilibrium

Recall from your previous courses on theoretical physics that at a given time t, either the combination $x(t), p(t)$ (classically) or $|\psi(t)\rangle$ (quantum mechanically) is referred to as the *state* of the (many-particle) system. Since the word "state" is usually used in the context of thermodynamics with quite a different meaning, to avoid further confusions, we are going to relabel the states to *microstates*, hereinafter. If we know the exact microstate, then

1. we know how will the system evolve in time,

2. we can determine the value of any other physical quantity.

Based on the previous discussion, it is impossible to know the exact microstate of, e.g., a gas enclosed in a flask. But at the same time, whatever we plan to use the gas for, it is highly probable that we are actually not interested in the microstate itself, but instead, we would like to know the macroscopic quantities of the system, whereas in the context of a gas, that could be, e.g., the temperature, pressure, etc. If we are somehow able to determine those, the knowledge of the specific microstate is not (that much) important, which is basically what we meant by the definition of thermodynamics mentioned at the beginning. However, there is one crucial problem. A system is always in some definite microstate, as, e.g., in the classical case, the particles always have some positions and momenta. So no matter what we do with our system, in principle, a corresponding microstate always exists at any time. But what about the macroscopic quantities?

Imagine we have two flasks connected by a closed valve, the first one of them being filled with gas of given initial pressure and the second one empty. We then open the valve and let the gas freely expand into the second flask. Clearly, during this process, there is no way to properly define the pressure of the gas as a whole, as, e.g., the concentration of molecules would be higher in the first flask when compared to the second one. However, if we wait long enough time, the flow of particles will eventually stop, the inhomogeneities will smooth out and, at that point, there is nothing preventing us from defining the total final pressure of the fully expanded gas inside the combined volume of both the flasks, see Fig. 1.1.

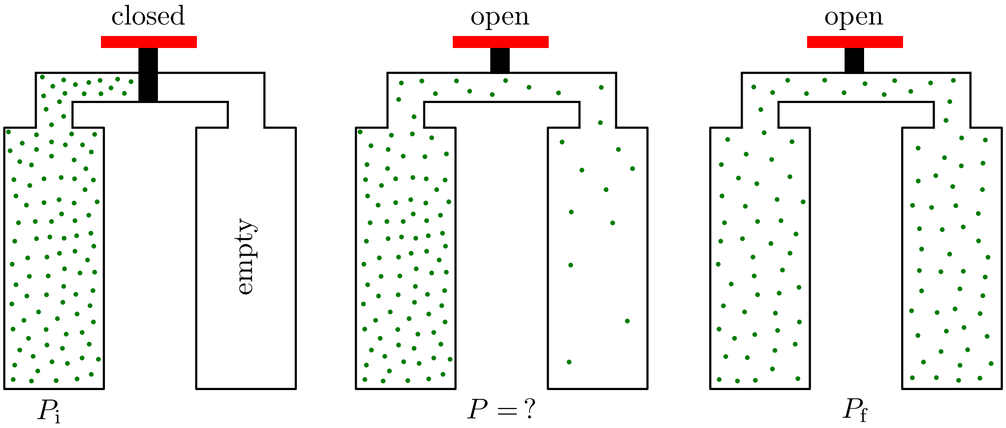

Figure 1.1: Two connected flasks.

The key observation here is that – in contrast to the microstate – the macroscopic quantities (i.e., in this case, the pressure) can be defined only in specific situations where the studied system is in the so called *equilibrium*.

We define the *equilibrium* of a system by:

1. all macroscopic quantities remain constant in time,
2. no macroscopic flows (of energy, particles, etc.) exist.

Note that the equilibrium is sometimes in the literature referred to as the *equilibrium state*, which is basically the reason why we renamed the many-particle system states to microstates at the beginning of this section to avoid confusions. For the purpose of this course, we further introduce two types of systems that we are going to encounter.

1. A *simple system* in equilibrium is homogeneous,
2. A *composite system* in equilibrium consists of two or more simple systems, hereinafter referred to as the *subsystems*, all of them being individually in equilibrium.

A typical example of a simple system is a (generally multi-component) gas. An example of the composite system could then be a cube of ice submerged into water. Such a composite system in equilibrium is not globally homogeneous, as, e.g., the water has different density than the ice. Note that some authors also add to the definition of a simple system the statement that it is single-phase, but I think this is already covered by the term homogeneous.

Now we are ready for the first postulate.

1.4 Postulate I. - Reaching Equilibrium

An isolated system eventually reaches equilibrium.

A few comments here. First, we are talking about a general system, so this holds regardless of it being simple or composite. I mention this because some of the postulates will be relevant only to one of those types, so we should always read carefully. Second, we require the system to be isolated to avoid any possible external agents acting on our system and possibly preventing it from reaching equilibrium. But it is important to note that this does not mean that we cannot have a system in equilibrium that is not isolated! The direct counterexample of this is simply the composite system, where we have several subsystems, each one of them being in equilibrium, but at the same time not isolated from the other ones (at least not generally). Third, we stated that the system will reach equilibrium, but we did not specify how long is that going to take. In this regard, we define the *relaxation time* τ as the time needed for a system to reach equilibrium after being disturbed. Last but not least, this postulate is rather a formal statement that won't be of much of a practical use, it's purpose is mostly for the complete set of the postulates to be logically consistent.

Now that we know that each isolated system will eventually reach equilibrium, we can move on to the next postulate.

1.5 Postulate II. - Equilibrium Parameters

The equilibrium of a simple system is fully determined by the internal energy U, the volume V and the number of particles N.

Just to clarify, regarding the number of particles N, we are simplifying things here a bit, as generally, a simple system does not necessarily have to be constituent of just one type of particles. E.g., the air consists of molecules of oxygen, nitrogen and a few others. In such case, we shall replace N by the numbers of particles of each constituent particle type, i.e., $N_1, N_2, N_3, \ldots$ But since in the majority of the examples that we are going to encounter in this course we will be considering just one type of particles, we can keep the postulate in this simplified form.

Further, since the equilibrium state is fully determined by U, V, N, then any other macroscopic quantity A of a simple system must also be able to be expressed by those, i.e.,

$$\boxed{A = A(U, V, N)}\,. \tag{1.9}$$

This should be taken as the analogy with the Hamiltonian mechanics, where we have a set of generalized coordinates (q, p) and any other dynamical quantity dependent on those, i.e., $A = A(q, p)$. In this sense, (U, V, N) are sometimes denoted as the *thermodynamical coordinates* of a simple system.

Now there is one important property that the parameters U, V and N have in common – they are all *extensive.*

1.6 Extensive Quantities

The best way to explain the term *extensive* is by an example. Assume we have a (simple) system in equilibrium determined by (U, V, N) and a general quantity

$$A = A(U, V, N)\,. \tag{1.10}$$

We then take the system and double it, which essentially means taking two identical copies of it and joining them together. It should be evident that, in such case,

$$U \to 2U\,, \quad V \to 2V\,, \quad N \to 2N\,. \tag{1.11}$$

The equilibrium of the doubled system is therefore determined by $(2U, 2V, 2N)$ with the corresponding value of A being

$$A(2U, 2V, 2N) \tag{1.12}$$

If A is an extensive, then it scales in exactly the same way as (1.11), i.e.,

$$A \to 2A\,, \tag{1.13}$$

and hence,

$$A(2U, 2V, 2N) = 2A(U, V, N)\,, \tag{1.14}$$

see Fig. 1.2.

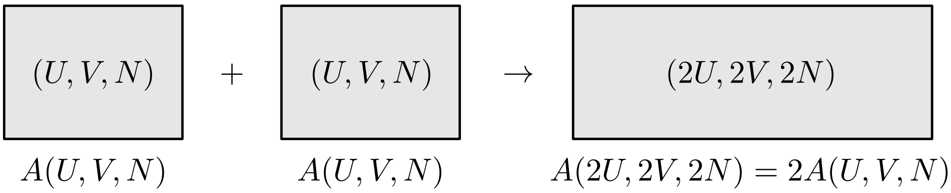

Figure 1.2: Extensive quantity.

To generalize this, we then simply replace the factor of 2 with an arbitrary scaling coefficient λ, that is

$$U \to \lambda U\,, \quad V \to \lambda V\,, \quad N \to \lambda N\,, \tag{1.15}$$

with the defining condition of an extensive quantity becoming

$$\boxed{A(\lambda U, \lambda V, \lambda N) = \lambda A(U, V, N)}\,. \tag{1.16}$$

And of course, as all the U, V, N obey the above simply based on what do we mean by scaling the system (Eq. (1.15)), they must be extensive by themselves. Note that in the language of mathematics, a multi-variable function with the property (1.16) is called a homogeneous function of the first order.

1.7 An Aside: Perfect and Imperfect Differentials

For the sake of the upcoming section, there is one mathematical concept that we need to properly understand, being the difference between perfect and imperfect differentials. Note that some authors prefer the term differential forms, but in the modern view, this typically refers to a bit more abstract objects studied in the field of differential geometry, which is out of the scope of this course, so we will better stick just with the term differentials.

For a single-variable function $f(x)$, we define the differential $\mathrm{d}f$ as

$$\mathrm{d}f = \frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x\,, \tag{1.17}$$

with the interpretation of how does the value of f change if we shift the variable by an infinitesimal amount $x \to x + \mathrm{d}x$ as illustrated in Fig. 1.3.

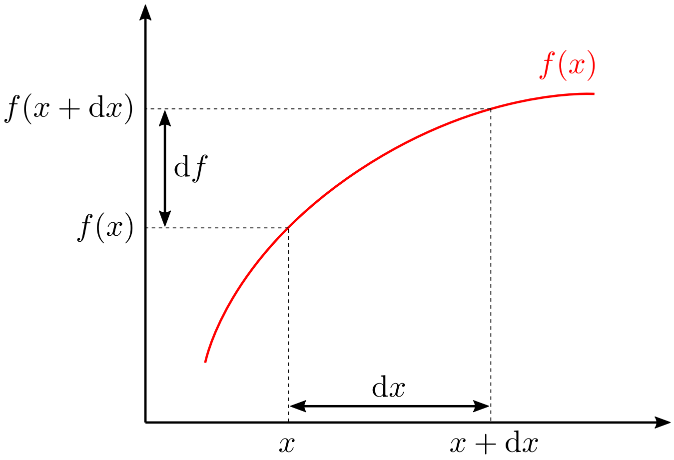

Figure 1.3: Illustration of a differential of a single-variable function.

Then, for a multi-variable function $f(x_1, \ldots, x_N)$, (1.17) generalizes into

$$\mathrm{d}f = \frac{\partial f}{\partial x_1}\mathrm{d}x_1 + \cdots + \frac{\partial f}{\partial x_N}\mathrm{d}x_N = \sum_k \frac{\partial f}{\partial x_k}\mathrm{d}x_k\,. \tag{1.18}$$

E.g., for

$$f(x_1, x_2) = x_1^2 + x_2^2\,, \tag{1.19}$$

we get

$$\mathrm{d}f = 2x_1\mathrm{d}x_1 + 2x_2\mathrm{d}x_2\,. \tag{1.20}$$

So for any (differentiable) function $f(x_1, \ldots, x_N)$, we can always construct the corresponding differential. But now let us now ask a somewhat reverse question. Assume that we are a priori given an expression of the form

$$\mathrm{d}\omega = a_1(x_1, ..., x_N)\mathrm{d}x_1 + \cdots + a_N(x_1, ..., x_N)\mathrm{d}x_N = \sum_k a_k(x_1, ..., x_N)\mathrm{d}x_k\,, \tag{1.21}$$

which we will hereinafter refer to as a differential (or differential expression). The question then is, if there exists a function $f(x_1, \ldots, x_N)$ such that

$$\mathrm{d}\omega \overset{?}{=} \mathrm{d}f\,. \tag{1.22}$$

The answer is provided by the following theorem.

Theorem 1: Assume a differential of the form

$$\mathrm{d}\omega = \sum_k a_k(x_1, ..., x_N)\mathrm{d}x_k\,. \tag{1.23}$$

Then, the following properties are equivalent:

1. There exists a function $f(x_1, \ldots, x_N)$ such that $\mathrm{d}\omega = \mathrm{d}f$, i.e.,
$$a_k = \frac{\partial f}{\partial x_k} \,.$$
2. There exists a function $\varphi(x_1, \ldots, x_N)$ such that for a curve integral from A to B we get
$$\int\limits_A^B \mathrm{d}\omega = \varphi(B) - \varphi(A) \,.$$
3. The curve integral of $\mathrm{d}\omega$ between A and B is independent of the curve γ, i.e.,
$$\int\limits_\gamma \mathrm{d}\omega \quad \text{is independent on } \gamma \,.$$
4. The curve integral of $\mathrm{d}\omega$ is zero over any closed curve γ, i.e.,
$$\oint \mathrm{d}\omega = 0 \,.$$
5. The coefficients a_k fulfill
$$\frac{\partial a_k}{\partial x_\ell} = \frac{\partial a_\ell}{\partial x_k} \,, \quad \forall k, \ell \,.$$

Our task now is to prove this. As all of those shall be mutually equivalent, then technically, there are 20 implications to prove. But we can simplify our life by proving just $1 \to 2 \to 3 \to 4 \to 5 \to 1$, as this is sufficient to get from any of those properties to another one. So let's do this.

Proof:

$1 \to 2)$ Assuming $\mathrm{d}\omega = \mathrm{d}f$,
$$\int\limits_A^B \mathrm{d}\omega = \int\limits_A^B \mathrm{d}f = f(B) - f(A) \,.$$

So the function f itself plays the role of the sought function φ. Generally then,
$$\varphi = f + C \,,$$
as
$$\mathrm{d}\varphi = \mathrm{d}(f + C) = \mathrm{d}f \,,$$
and so
$$\int\limits_A^B \mathrm{d}\omega = \varphi(B) - \varphi(A) \,.$$

$2 \to 3)$ Assuming

$$\int_A^B \mathrm{d}\omega = \varphi(B) - \varphi(A)\,,$$

then for any (continuous) curve $\gamma_{A\to B}$ we must have

$$\int_\gamma \mathrm{d}\omega = \int_A^B \mathrm{d}\omega = \varphi(B) - \varphi(A)\,,$$

and since the result depends only on A and B, the integral cannot depend on the specific choice of the curve.

$3 \to 4)$ Assuming

$$\int_\gamma \mathrm{d}\omega \quad \text{is independent on } \gamma\,,$$

lets take any closed curve $\gamma_{A\to A}$, meaning that it ends at the same point as it started. Further, we take an arbitrary point $B \in \gamma_{A\to A}$ such that $B \neq A$ and decompose the curve into

$$\gamma_{A\to A} = \gamma^{(1)}_{A\to B} + \gamma^{(2)}_{B\to A}\,,$$

see Fig. 1.4.

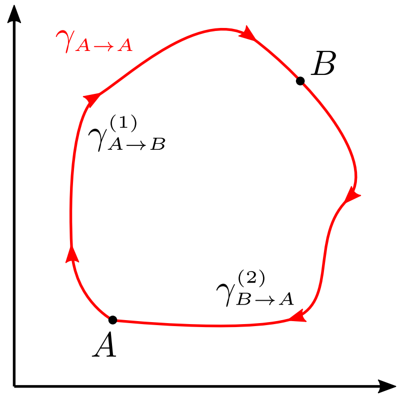

Figure 1.4: Closed curve decomposed.

Then,

$$\oint \mathrm{d}\omega = \int_\gamma \mathrm{d}\omega = \int_{\gamma^{(1)}} \mathrm{d}\omega + \int_{\gamma^{(2)}} \mathrm{d}\omega = \int_{\gamma^{(1)}} \mathrm{d}\omega - \int_{-\gamma^{(2)}} \mathrm{d}\omega\,.$$

But since both $\gamma^{(1)}_{A\to B}$ and $-\gamma^{(2)}_{B\to A}$ start at A and end at B, and at the same time we assume that the curve integral does not depend on the curve, we must have

$$\oint \mathrm{d}\omega = 0\,.$$

4 → 5) This is the hardest proof if one wants to be general, and in such case I suggest consulting any book on differential geometry. Here we only show this for the case of two variables x_1, x_2. So assume

$$\oint \mathrm{d}\omega = 0$$

over a closed curve γ with

$$\mathrm{d}\omega = a_1 \mathrm{d}x_1 + a_2 \mathrm{d}x_2 \,.$$

Then, we can make use of the Green's theorem to write

$$0 = \oint \mathrm{d}\omega = \int\limits_{\gamma} \mathrm{d}\omega = \int\limits_{\partial S} a_1 \mathrm{d}x_1 + a_2 \mathrm{d}x_2 = \int\limits_{S} \left(\frac{\partial a_2}{\partial x_1} - \frac{\partial a_1}{\partial x_2} \right) \mathrm{d}S \,,$$

where S represents the surface area bounded by γ, see Fig. 1.5.

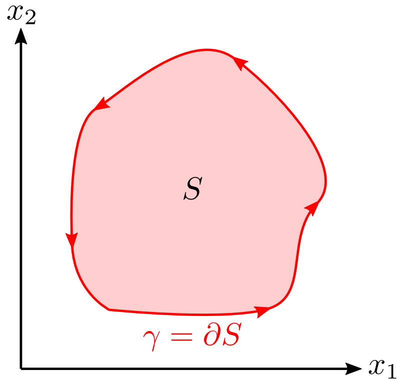

Figure 1.5: Surface S bounded by the curve $\gamma = \partial S$.

But since γ is chosen arbitrarily, then the only way this can hold true is by having

$$\frac{\partial a_2}{\partial x_1} = \frac{\partial a_1}{\partial x_2} \,.$$

5 → 1) This part is a bit cumbersome but nevertheless doable. So assume

$$\frac{\partial a_k}{\partial x_\ell} = \frac{\partial a_\ell}{\partial x_k} \,, \quad \forall k, \ell \,.$$

We then define

$$f(x_1, \ldots, x_N) = \int\limits_0^1 \sum_k a_k(tx_1, \ldots, tx_n) x_k \, \mathrm{d}t$$

and differentiate by x_ℓ:

$$\frac{\partial f}{\partial x_\ell} = \int\limits_0^1 \left[\sum_k \left(\frac{\partial a_k}{\partial t x_\ell} t x_k \right) + a_\ell(tx_1, \ldots, tx_N) \right] \mathrm{d}t \,.$$

Now we make use of the assumption to interchange the indices in the partial derivative term inside the round brackets as

$$\frac{\partial f}{\partial x_\ell} = \int\limits_0^1 \left[\sum_k \left(\frac{\partial a_\ell}{\partial t x_k} t x_k \right) + a_\ell(tx_1, \ldots, tx_N) \right] \mathrm{d}t \,.$$

By separating the above integral into

$$\frac{\partial f}{\partial x_\ell} = \int\limits_0^1 \sum_k \frac{\partial a_\ell}{\partial t x_k} x_k t \,\mathrm{d}t + \int\limits_0^1 a_\ell(tx_1, \ldots, tx_N) \,\mathrm{d}t$$

and further denoting

$$\frac{\mathrm{d}u}{\mathrm{d}t} = \sum_k \frac{\partial a_\ell}{\partial t x_k} x_k \,, \quad v = t \,,$$

the first one can be integrated by parts as

$$\int\limits_0^1 \frac{\mathrm{d}u}{\mathrm{d}t} v \,\mathrm{d}t = \big[uv\big]_0^1 - \int\limits_0^1 u \frac{\mathrm{d}v}{\mathrm{d}t} \,\mathrm{d}t \,,$$

while

$$\begin{aligned} u &= \int \sum_k \frac{\partial a_\ell}{\partial t x_k} x_k \,\mathrm{d}t = \sum_k \frac{\partial a_\ell}{\partial t x_k} \,\mathrm{d}(t x_k) \\ &= \int \mathrm{d}a_\ell(tx_1, \ldots, tx_N) = a_\ell(tx_1, \ldots, tx_N) + C \,, \end{aligned}$$

where in the second equality we used the fact that x_k is considered constant within the integral. We get

$$\frac{\partial f}{\partial x_\ell} = \big[t a_\ell(tx_1, \ldots, tx_N) + tC\big]_0^1 - \int\limits_0^1 \big[a_\ell(tx_1, \ldots, tx_N) + C\big] \mathrm{d}t + \int\limits_0^1 a_\ell(tx_1, \ldots, tx_N) \,\mathrm{d}t \,.$$

Finally, after canceling out most of the right hand side, we arrive at

$$a_\ell(x_1, \ldots, x_N) = \frac{\partial f}{\partial x_\ell} \,,$$

which is what we wanted to proof.

Just to comment on the last property, if we have

$$a_k = \frac{\partial f}{\partial x_k} \,, \quad a_l = \frac{\partial f}{\partial x_l} \,, \tag{1.24}$$

for some $k \neq l$, then differentiating the first one by x_l and vice versa yields

$$\frac{\partial a_k}{\partial x_l} = \frac{\partial^2 f}{\partial x_l \partial x_k} \,, \quad \frac{\partial a_l}{\partial x_k} = \frac{\partial^2 f}{\partial x_k \partial x_l} \,. \tag{1.25}$$

But as we know, for well behaved functions, the order of the second derivatives must be interchangeable, and that is why it must hold that

$$\frac{\partial a_k}{\partial x_l} = \frac{\partial a_l}{\partial x_k}\,. \tag{1.26}$$

(This would actually be the proof of the implication 1 → 5).

Well, that was quite a ride, but we have done it! Accordingly, we adopt the following terminology.

Any differential that

1. fulfills the properties of the Theorem 1 will be denoted as $\mathrm{d}\omega$ and hereinafter referred to as a *perfect differential.*
2. does not fulfill the properties of the Theorem 1 will be denoted as $\text{đ}\omega$ and hereinafter referred to as an *imperfect differential.*

Let us now demonstrate this on two specifically chosen examples.

1. We are given

   $$\mathrm{d}\omega = 2xy\,\mathrm{d}x + x^2\mathrm{d}y$$

   and are asked to decide, whether it is a perfect or an imperfect differential, and in case of the perfect one, to find the corresponding function f such that $\mathrm{d}\omega = \mathrm{d}f$. The simplest way to do this is to denote

   $$a_x(x,y) = 2xy\,, \quad a_y(x,y) = x^2\,,$$

   and further make use of the property 5, i.e., to check whether

   $$\frac{\partial a_x}{\partial y} \overset{?}{=} \frac{\partial a_y}{\partial x}\,.$$

   We get

   $$\frac{\partial}{\partial y}(2xy) = 2x = \frac{\partial}{\partial x}\left(x^2\right)\,.$$

   Hence, $\mathrm{d}\omega$ is a perfect differential. To find the corresponding function f, we can, e.g., integrate $a_x(x,y)$ w.r.t. x, resulting in

   $$f(x,y) = \int a_x(x,y)\,\mathrm{d}x = \int 2xy\,\mathrm{d}x = x^2y + C\,.$$

   To validate the result, we further differentiate f w.r.t. y, obtaining

   $$\frac{\partial f}{\partial y} = \frac{\partial}{\partial y}\left(x^2y + C\right) = x^2 = a_y(x,y)\,.$$

   Everything works as it should and we are happy.

2. We are given
$$\mathrm{d}\omega = 2xy\,\mathrm{d}x + \frac{x^2}{2}\,\mathrm{d}y$$
and are asked the same question as with the first example. Hence, we check
$$\frac{\partial}{\partial y}(2xy) = 2x \neq x = \frac{\partial}{\partial x}\left(\frac{x^2}{2}\right) .$$
Hence, $\mathrm{d}\omega$ is an imperfect differential and the corresponding function $f(x, y)$ does not exist, which makes us unhappy.

Now we are ready to move on with our study of thermodynamics.

1.8 Work, Heat

The Postulates I. and II. describe a system in equilibrium, i.e., a state that is macroscopically static. But if we want our system to actually do something, we cannot let it remain in equilibrium forever. Instead, we would like to be able to analyze some macroscopically dynamical processes. In this regard, we understand the *thermodynamical process* to be a physical process in which the studied system starts in a defined initial equilibrium state and transitions into a generally different final equilibrium state. In this section, we introduce the two important quantities related to thermodynamical processes: *work* and *heat*.

The concept of work should be well known to us from any introductory course on classical mechanics, so let us directly demonstrate this on a thought experiment representing a simple example of a thermodynamical process. We start by assuming a container of a given fixed volume V with a small propeller inside connected to the outside. The walls of the container are constructed such that the only way to exchange energy between the inside and the outside is in form of a mechanical work realized by twisting the propeller, see Fig. 1.6.

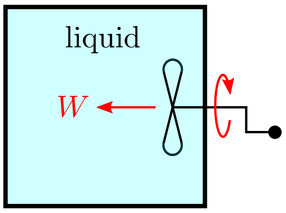

Figure 1.6: Container with a propeller.

Next, we fill up the container with a liquid, close the lid, and wait until the liquid reaches equilibrium determined by (U_i, V, N). This now represents the initial state of the upcoming process. We then start twisting the propeller until we have performed the total amount of work W on the liquid (theoretically, this can be measured). After that, we once again let the liquid reach equilibrium, this time being the final state of the process determined by (U_f, V, N). Clearly, it must hold that

$$\Delta U = U_\mathrm{f} - U_\mathrm{i} = W\,. \tag{1.27}$$

Hence, we performed a process resulting in a raise of the total internal energy of the liquid.

Now we make a slight adjustment to our experiment by relieving some of the constraints on the walls of the container such that they only keep V and N fixed. By performing exactly the same amount of work W onto the liquid as before, we find that, generally,

$$\Delta U \neq W\,. \tag{1.28}$$

Hence, there must exist another form of energy passing through the walls (one way or another) of our container, which is called the *heat.* The definition is then simply

$$Q = \Delta U - W\,. \tag{1.29}$$

And this is truly to be taken as the definition of heat in the context of thermodynamics, since we are studying only the macroscopic behavior of many-particle systems and so we should not be interested in what exactly happens on the microscopic level.

Moving on, rearranging Eq. (1.29) gives

$$\boxed{\Delta U = Q + W}\,, \tag{1.30}$$

which is usually referred to as the *first law of thermodynamics* and it is simply the law of energy conservation. An important note – in this convention, we understand the work term to be the work done onto the studied system and not the work done by it, so do not get confused if you open another textbook where the sign accompanying W would be opposite.

1.9 State and Process Quantities

As we now possess the proper definition of heat, there is an important distinction that we must understand. Generally, there are two types of quantities that appear in the context of thermodynamics, being

1. *State quantities* – characterize a system in equilibrium (e.g., U, V, N),
2. *Process quantities* – characterize thermodynamical processes (e.g., Q, W).

To demonstrate that neither Q nor W cannot characterize an equilibrium state, we propose the following counterexample. First, assume that there exist two functions

$$\mathscr{Q} = \mathscr{Q}(U, V, N)\,, \quad \mathscr{W} = \mathscr{W}(U, V, N)\,, \tag{1.31}$$

such that, for a general process with $N = const.$, we can write

$$\begin{aligned} Q &= \mathscr{Q}(U_\mathrm{f}, V_\mathrm{f}, N) - \mathscr{Q}(U_\mathrm{i}, V_\mathrm{i}, N)\,, \\ W &= \mathscr{W}(U_\mathrm{f}, V_\mathrm{f}, N) - \mathscr{W}(U_\mathrm{i}, V_\mathrm{i}, N)\,. \end{aligned} \tag{1.32}$$

Going back to our previous thought experiment where $V = const.$ also holds, assume we are given the initial (U_i, V, N) and final (U_f, V, N) states of the liquid. At this point, it should be clear that there are infinitely many possibilities of how to reach the final state with the only condition on Q and W being that together they must add up to the total difference in the internal energy ΔU as dictated by the first law (1.30), i.e.,

$$\Delta U = Q + W\,. \tag{1.33}$$

So without the loss of generality, let us consider two different processes which we label as 1 and 2, while

$$\Delta U = Q_1 + W_1 = Q_2 + W_2\,, \tag{1.34}$$

with

$$Q_1 \neq Q_2\,, \quad W_1 \neq W_2\,. \tag{1.35}$$

But this is strictly incompatible with (1.32), as we would have

$$\begin{aligned} \mathscr{Q}(U_\mathrm{f}, V, N) - \mathscr{Q}(U_\mathrm{i}, V, N) = Q_1 \neq Q_2 = \mathscr{Q}(U_\mathrm{f}, V, N) - \mathscr{Q}(U_\mathrm{i}, V, N)\,, \\ \mathscr{W}(U_\mathrm{f}, V, N) - \mathscr{W}(U_\mathrm{i}, V, N) = W_1 \neq W_2 = \mathscr{W}(U_\mathrm{f}, V, N) - \mathscr{W}(U_\mathrm{i}, V, N)\,, \end{aligned} \tag{1.36}$$

or simply

$$\begin{aligned} \mathscr{Q}(U_\mathrm{f}, V, N) \neq \mathscr{Q}(U_\mathrm{f}, V, N)\,, \\ \mathscr{W}(U_\mathrm{f}, V, N) \neq \mathscr{W}(U_\mathrm{f}, V, N)\,. \end{aligned} \tag{1.37}$$

And as we know, since no function can possess two distinct values at the same point, then such functions $\mathscr{W}, \mathscr{Q}$ cannot exist, meaning that Q and W must be strictly process quantities. Note that regardless of our assumptions not being fully general ($V = const.$), one counterexample is enough to disprove the otherwise general statement of Q, W being able to characterize an equilibrium state. But at the same time, do not get confused if you discover a singular case where you actually are able to find functions such that Eqs. (1.32) hold true. We will see this, e.g., in context of an isobaric ($P = const.$) process with $N = const.$, where the appropriate state quantity whose difference gives the total amount of the absorbed heat is the enthalpy.

In a similar manner, the state quantities have a proper meaning only in the equilibrium states, that is in the initial and the final state of a process. And we have already seen this in the previously mentioned example with the two flasks connected through a valve (Fig. 1.1). For simplicity, assume both the flasks to be perfectly isolated from the surroundings and of the same volumes V. In the initial state, all the gas was concentrated purely within the first flask with the corresponding parameters (U, V, N). After opening the valve, a process started, terminating in the final state represented by $(U, 2V, N)$. Clearly, during the process, the gas is not in equilibrium, and hence, we are not able to properly determine the corresponding state quantities such as the pressure, etc.

1.10 Quasi-static Processes

In the preceding sections, we defined the work and heat in context of a general thermodynamical process. Now there exists a special category of thermodynamical processes which – while being only an idealization that basically does not occur in nature – provides a useful approximation of real processes, allowing us to conduct various types of analytical calculations that otherwise would not be possible. These are called *quasi-static* processes and can be defined as follows:

During a *quasi-static* process, the system is always in some equilibrium state.

So if the process starts a t_{i} and ends at t_{f}, then $\forall t \in [t_{\mathrm{i}}, t_{\mathrm{f}}]$ the system is in equilibrium determined by the corresponding $\big(U(t), V(t), N(t)\big)$. Mathematically, this means that we can always represent a quasi-static process by a curve in the (U, V, N) space, see Fig. 1.7.

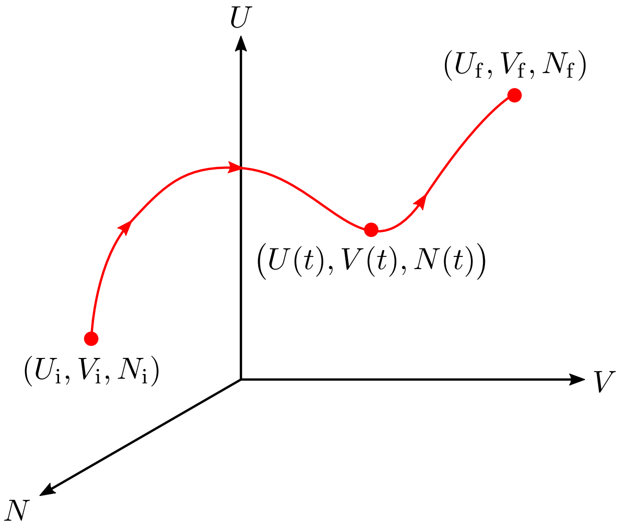

Figure 1.7: Quasi-static process.

In contrast, in a general process, the system is considered in equilibrium only at t_{i} and t_{f}, but not in between the two. (Note that in case of a composite system, the curve would need to be drawn in a $3\mathcal{N}$ dimensional space, $\mathcal{N}$ being the number of the constituent subsystems.) Typically, a process can be approximated by a quasi-static process if it runs slow enough compared to the relaxation time. As an example, consider a cylinder separated internally by a piston into two parts and a gas enclosed in one of them with the initial volume V_{i}. If we then move the piston slowly, gradually increasing the volume of the gas from V_{i} to V_{f}, then intuitively, such a process can be considered quasi-static, and, e.g., the pressure shall be well defined at any time, see Fig. 1.8.

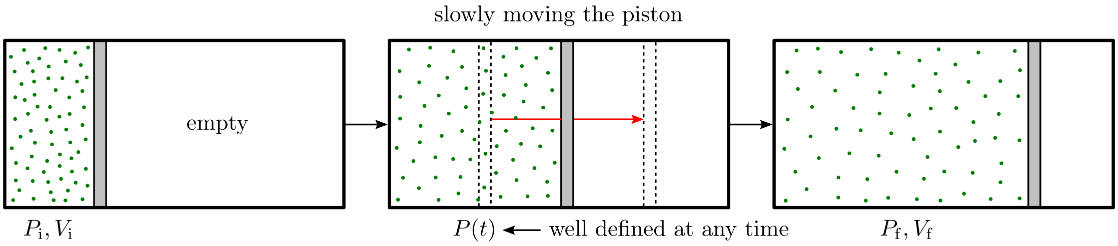

Figure 1.8: Quasi static expansion of a gas.

Let us now consider a general quasi-static process with $N = \mathit{const.}$ represented by a curve γ in the U-V plane and take two neighbouring equilibrium points infinitesimally close together, see Fig. 1.9.

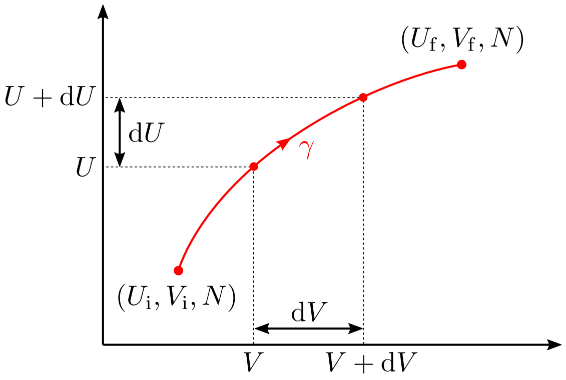

Figure 1.9: Quasi-static process with $N = \mathit{const.}$

We would now like to make use of the first law to express something like

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W\,, \tag{1.38}$$

where $\mathrm{d}Q$ and $\mathrm{d}W$ stand for the infinitesimal amount of heat absorbed by and the infinitesimal amount of work done onto our system during the transition

$$(U, V, N) \to (U + \mathrm{d}U, V + \mathrm{d}V, N)\,, \tag{1.39}$$

respectively. Clearly, for the whole process, it must hold that

$$\int\limits_\gamma \mathrm{d}U = U_\mathrm{f} - U_\mathrm{i} = \Delta U \tag{1.40}$$

Hence, we must also have

$$\Delta U = \int\limits_\gamma \mathrm{d}Q + \int\limits_\gamma \mathrm{d}W = Q + W\,, \tag{1.41}$$

where

$$Q = \int\limits_{\gamma} \mathrm{d}Q\,, \quad W = \int\limits_{\gamma} \mathrm{d}W \tag{1.42}$$

stand for the total amounts of heat and work absorbed by and done onto the system. But we have already shown that, generally, there do not exist functions $\mathscr{Q}, \mathscr{W}$ such that

$$W = \mathscr{W}_{\mathrm{f}} - \mathscr{W}_{\mathrm{i}}\,, \quad Q = \mathscr{Q}_{\mathrm{f}} - \mathscr{Q}_{\mathrm{i}}\,, \tag{1.43}$$

i.e.,

$$\int\limits_{\gamma} \mathrm{d}W \neq \mathscr{W}_{\mathrm{f}} - \mathscr{W}_{\mathrm{i}}\,, \quad \int\limits_{\gamma} \mathrm{d}Q \neq \mathscr{Q}_{\mathrm{f}} - \mathscr{Q}_{\mathrm{i}}\,. \tag{1.44}$$

According to the second property of the Theorem 1, this is just another way of saying that both $\mathrm{d}W$ and $\mathrm{d}Q$ are imperfect differentials, and therefore, we relabel

$$\mathrm{d}W \to đW\,, \quad \mathrm{d}Q \to đQ\,. \tag{1.45}$$

The only correct way to formulate the differential form of the first law for a quasi-static process is then

$$\boxed{\mathrm{d}U = đQ + đW}\,, \tag{1.46}$$

which we shall use henceforth. Nevertheless, none of this should be surprising to us as the work being generally path-dependent is a well known fact from the classical mechanics.

Now since the system we are going to spend the most time with is a gas, let us derive the corresponding formula of the quasi-static work term. Assume a gas with pressure P enclosed in a cylinder of the total volume V with a piston on one of it's sides, see Fig. 1.10.

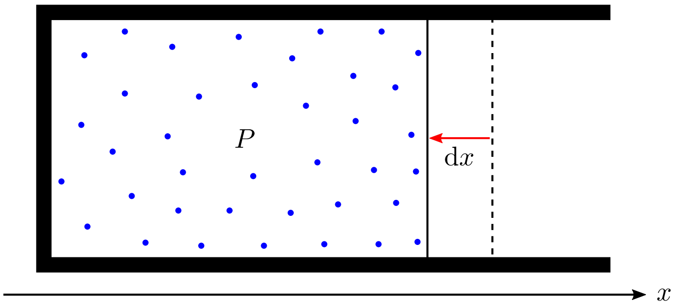

Figure 1.10: Gas in a cylinder with a piston.

The force exerted by the gas onto the piston in the x direction is

$$F_{\text{piston}} = P\mathcal{S}\,, \tag{1.47}$$

with $\mathcal{S}$ being the surface of the piston. According to the Newton's third law, that means that the piston exerts back the force

$$F_{\text{gas}} = -P\mathcal{S} \tag{1.48}$$

onto the gas. If we now compress the gas infinitesimally by $\mathrm{d}x$, the work done by the piston onto the gas is

$$đW = -P\mathcal{S}\mathrm{d}x = -P\mathrm{d}V\,. \tag{1.49}$$

Due to the importance of this formula, we put it in a box

$$\boxed{đW = -P\mathrm{d}V}\,. \tag{1.50}$$

Note that in case of the compression, $\mathrm{d}V < 0$, and hence, $đW$ is positive, which is what we would expect in this sign convention.

1.11 Walls, Constraints

As we now possess all the required definitions, here we provide a list of various types of walls that we are going to encounter in our study of thermodynamics and statistical physics, being:

- **Rigid wall** does not allow volume to change
- **Movable wall** or simply **piston** allows volume to change
- **Adiabatic wall** does not allow heat to flow
- **Diathermal wall** allows heat to flow
- **Impermeable wall** does not allow particles to pass
- **Permeable wall** allows particles to pass

Using this terminology, a system is then being *isolated* if it is enclosed by walls that are simultaneously rigid, adiabatic and impermeable.

Now if there are some walls present within the studied system (which will mostly be the case), we would say that the system is *constrained.* In that case, we distinguish two types of constraints:

1. *external constraints* are induced by walls that separate the system from the surroundings,
2. *internal constraints* are induced by walls that separate individual subsystems of a composite system.

E.g., a gas (simple system) enclosed by a rigid, adiabatic and impermeable wall is externally isolated, while a cylinder separated inside by a piston (composite system) is internally constrained by

$$V^{(1)} + V^{(2)} = V = \mathit{const.}\,, \tag{1.51}$$

with V being the total volume of the cylinder, see Fig. 1.11.

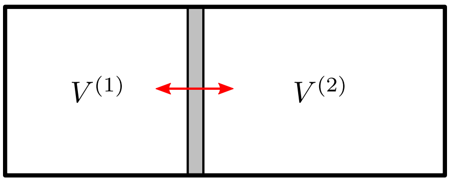

Figure 1.11: Internally constrained cylinder.

1.12 Postulate III. - Entropy

> There exists a function S called the *entropy* defined for each equilibrium state of a general system. The entropy is continuous, differentiable, and a monotonically increasing function of the internal energy.

As you have probably anticipated, the entropy is the central quantity in both thermodynamics and statistical physics. In my opinion, it is also one of the hardest quantities to understand properly. During this course, we will proceed slowly with building our intuition, and hopefully, in the end, you – the reader – will become somewhat proficient with it.

This postulate basically tells us two things. The first part guarantees the existence of entropy for each equilibrium state of any (not just simple) system. The purpose of the second part is as follows. For a simple system, the entropy is given as

$$S = S(U, V, N)\,. \tag{1.52}$$

The stated properties say that

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0\,. \tag{1.53}$$

We will see later that this is closely related to the definition of the temperature, which we require to be non-negative. Further, the above allows us to invert the relation (1.53) into

$$U = U(S, V, N)\,, \tag{1.54}$$

where the internal energy is also continuous, differentiable, and a monotonically increasing function of the entropy. Now once again, any macroscopic quantity of a simple system is expressible as

$$A = A(U, V, N)\,. \tag{1.55}$$

But if we combine this with (1.54), we get

$$A = A\left[U(S,V,N),V,N\right] \,, \tag{1.56}$$

and hence,

$$\boxed{A = A(S,V,N)}\,. \tag{1.57}$$

This means that the set of parameters (S,V,N) can be used equally as good as the (U,V,N) to determine the equilibrium of a simple system. For the purpose of this course, we will adopt the following nomenclature based on the choice of one of the respective sets:

1. $(U,V,N) \rightarrow$ *entropy representation*, since $S = S(U,V,N)$,
2. $(S,V,N) \rightarrow$ *energy representation*, since $U = U(S,V,N)$.

1.13 Postulate IV. - Additivity of Entropy

> The entropy of a composite system in equilibrium is additive over the constituent subsystems.

Based on our definition of a composite system, for each subsystem, we can write

$$S^{(i)} = S^{(i)}\left(U^{(i)},V^{(i)},N^{(i)}\right) \,. \tag{1.58}$$

This postulate then tells us that

$$S = \sum_i S^{(i)} \,, \tag{1.59}$$

where S stands for the total entropy of the composite system. Let's now conduct a similar analysis as presented in the section regarding the extensive quantities. We assume a simple system in equilibrium determined by (U,V,N) that we virtually separate into $\mathcal{N}$ identical subsystems. For each one of those, we must have

$$U^{(i)} = \frac{U}{\mathcal{N}}\,, \quad V^{(i)} = \frac{V}{\mathcal{N}}\,, \quad N^{(i)} = \frac{N}{\mathcal{N}}\,, \tag{1.60}$$

and as such,

$$S^{(i)} = S\left(\frac{U}{\mathcal{N}},\frac{V}{\mathcal{N}},\frac{N}{\mathcal{N}}\right) \,. \tag{1.61}$$

By using the additive property of the entropy (1.59), we can further write

$$S = \sum_i S^{(i)} = \mathcal{N} S\left(\frac{U}{\mathcal{N}},\frac{V}{\mathcal{N}},\frac{N}{\mathcal{N}}\right) \,, \tag{1.62}$$

rearranging of which gives

$$S\left(\frac{U}{\mathcal{N}},\frac{V}{\mathcal{N}},\frac{N}{\mathcal{N}}\right) = \frac{1}{\mathcal{N}}\,S\,. \tag{1.63}$$

By replacing $1/\mathcal{N}$ by a general scaling coefficient λ, we then get

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)\,, \tag{1.64}$$

and hence, the entropy is also an extensive quantity. It might be insightful at this point to note that while the additivity of a general quantity typically relates to a composite system, the extensivity truly makes sense only within a simple system.

1.14 Postulate V. - Entropy Maximum Principle

> In a general externally isolated system in equilibrium, the values taken by the extensive parameters are those that maximize the total entropy under the internal constraints.

Whenever a theory is based on a set of postulates, then it does not make much sense to say that one of them is more important than the others. The theory can only work with all of them together. Nevertheless, I am tempted to make an exception here as within the Postulate V. hides the answer to the vast majority of the problems we are going to encounter. Moreover, it also provides us with the thermodynamical interpretation of what the entropy actually is. The best way to show this is (once again) by an analogy with the analytical mechanics, where we postulated the existence of a functional called the *action* (incidentally also denoted as S), whereas the physical trajectory of a particle (or a system of particles) is that one that maximizes the action. See the similarity here? Whenever we have an isolated system in equilibrium – and it does not matter if we talk about a simple or a composite one – it chooses the values of the extensive parameters such that the total entropy is maximized. And that's it. I can imagine that you probably anticipated a bit more physically intuitive interpretation, but at this point, we simply cannot do any better. Most of you have probably heard something like: "entropy is the measure of a disorder in a system". But those kind of statements have nothing to do with thermodynamics. So until we get to the statistical part where such meaning actually starts to make some sense, I recommend you to forget all of this and just reconcile with the fact that entropy – in the context of thermodynamics – is a purely abstract quantity with no sensible physical interpretation.

Now there is a subtle part of the postulate that we should highlight as it is a common source of many misunderstandings. For the postulate to hold true, the system must be externally isolated. Otherwise, it simply won't work. The best way to demonstrate this is by a specific example. Imagine a gas enclosed by rigid, impermeable but not adiabatic walls. Now we try to use the Postulate V. to find the values of the extensive parameters corresponding to the equilibrium. The rigidity and impermeability of the walls imply:

$$V = const.\,, \quad N = const. \tag{1.65}$$

So considering the total entropy of the gas

$$S = S(U, V, N)\,, \tag{1.66}$$

there is only one parameter left that can be varied, being the internal energy U. But since there is no further constraint on U and the Postulate III. tells us that the entropy is a monotonically increasing function of the internal energy, to maximize the entropy would then require $U \to \infty$, which is simply wrong. The resolution to this issue lies in considering the externally isolated composite system consisting of the gas together with it's surroundings and only then applying the Postulate V. to get the correct answer. So please just keep in mind that for the Postulate V. to hold true, we need the total values of internal energy, volume and the number of particles to be fixed.

1.15 The Second Law

Let us now try to understand properly how do the thermodynamical processes fit within our framework of the postulates of thermodynamics. Assume we have an externally isolated composite system in equilibrium with internal constraints imposed by various types of walls separating the individual subsystems, determining the set Ω of allowed values of the extensive parameters (here denoted as $X^{(i)}$ for simplicity), see Fig. 1.12.

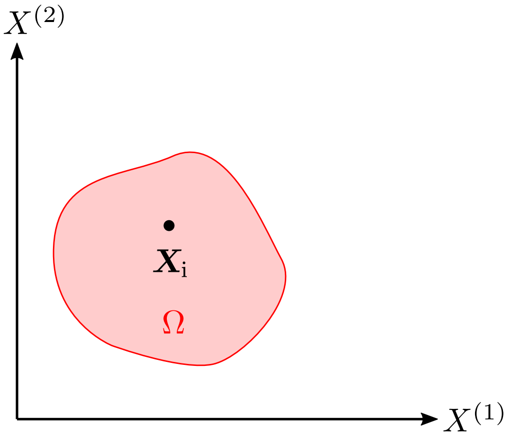

Figure 1.12: Initial equilibrium state of internally constrained system.

According to the Postulate V., the system chooses an equilibrium state

$$\mathbf{X}_{\mathrm{i}} = \left(X_{\mathrm{i}}^{(1)}, X_{\mathrm{i}}^{(2)}, \dots\right) \in \Omega \tag{1.67}$$

such that the total entropy

$$S = \sum_k S^{(k)}, \tag{1.68}$$

is maximized on Ω, i.e.,

$$S_{\mathrm{i}} = S\left(\mathbf{X}_{\mathrm{i}}\right) = \max_{\mathbf{X} \in \Omega} S(\mathbf{X}). \tag{1.69}$$

This is the initial state. Since equilibrium states are macroscopically static, then in order for a hypothetical process to happen, we further need to relax one or more of the internal constraints. By doing so, we thereby extend the original Ω into a new set $\Omega' \supseteq \Omega$ containing some new possible values of $X^{(i)}$ that were inaccessible before. The Postulate I. tells us that the system will sought a new equilibrium state, while the Postulate V. further specifies that the extensive parameters must adjust such that the total entropy is maximum but now on the whole Ω' instead of just Ω. (Note that for both of these we need the requirement of the system being externally isolated.) There are now two possible outcomes.

1. None of the newly accessible combinations of values of the extensive parameters gives the value of the total entropy greater then the initial one, i.e.,

$$\forall \boldsymbol{X} \in \Omega' \setminus \Omega \,, \quad S(\boldsymbol{X}) < S_{\mathrm{i}} \,, \tag{1.70}$$

   and hence, nothing happens. (The final state is the same as the initial one, see Fig. 1.13 (a).)

2. Within the newly accessible combinations of values of the extensive parameters exists exactly one with the highest possible value of the total entropy that is greater then the initial one, i.e.,

$$\exists! \, \boldsymbol{X}_{\mathrm{f}} \in \Omega' \setminus \Omega \,, \quad S_{\mathrm{f}} = S\left(\boldsymbol{X}_{\mathrm{f}}\right) = \max_{\boldsymbol{X} \in \Omega'} S(\boldsymbol{X}) > S_{\mathrm{i}} \,. \tag{1.71}$$

   A process will occur, terminating at the corresponding equilibrium state, being the final state, see Fig. 1.13 (b). (The black dashed line represents the fact that the process does not need to be quasi-static, i.e., representable by a curve.)

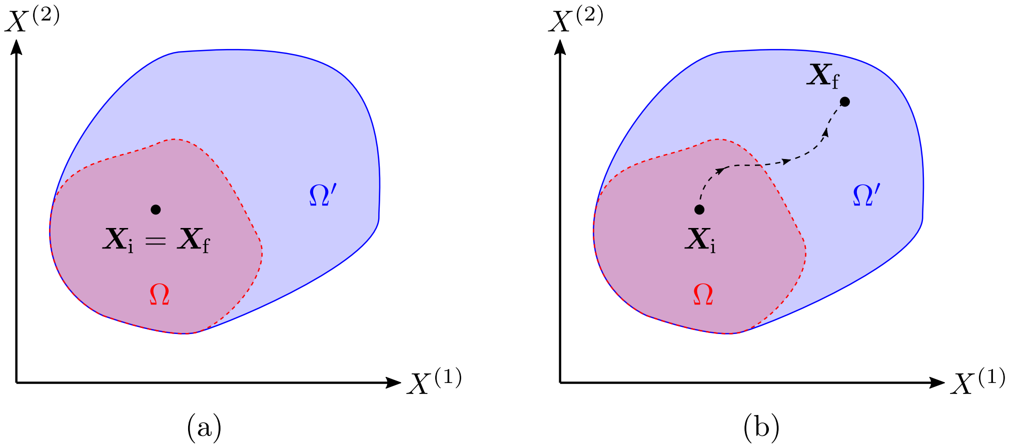

Figure 1.13: Two possible outcomes when relaxing one or more of the internal constraints of an externally isolated composite system.

This is the physical reality. Now theoretically speaking, there is a third option. Regardless of whether we do or do not relax the internal constraint(s) in the first place (for simplicity assume that we do not, keeping us restricted to just Ω), the Postulate V. technically states nothing about the point corresponding to the maximum of the total entropy being unique. So let's define the set of all such points

$$\Gamma = \arg\max_{\boldsymbol{X}\in\Omega} S(\boldsymbol{X})\,. \tag{1.72}$$

If Γ is continuous, then the system is allowed to evolve quasi-statically along an arbitrary curve $\gamma \in \Gamma$, as that is not in violation with any of the postulates, see Fig. 1.14.

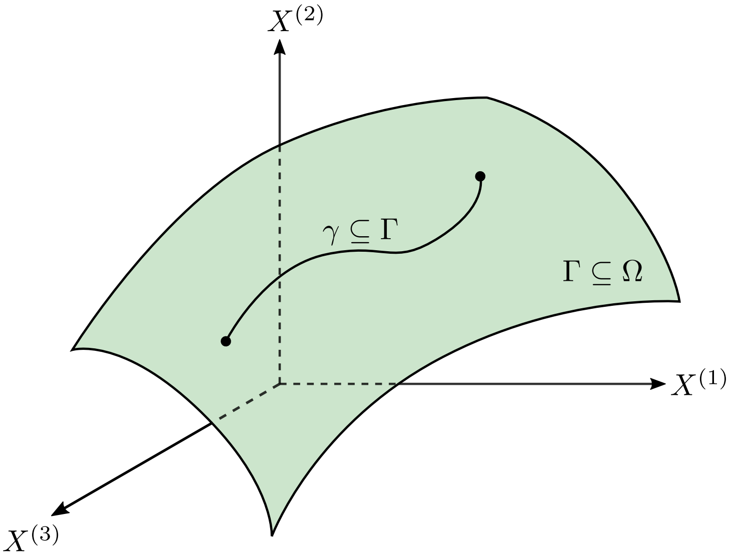

Figure 1.14: Reversible process.

Accordingly, we propose the following definition.

A *reversible process* is a quasi-static process defined by $S = const.$

But at the same time, if the system already is in equilibrium corresponding to one of the points of Γ, then there is no reason of why it should transition into another one. And so in reality, this would never happen. Nevertheless, reversible processes are often used in theoretical calculations as some sort of limiting cases, providing us with various useful results.

The important conclusion of all of this is that, for an externally isolated system,

$$\boxed{\Delta S \geq 0}\,, \tag{1.73}$$

which is the *second law of thermodynamics*. And to be honest, this is probably one of the most (if not the most) important laws in the whole physics, so please keep that in mind.

1.16 Intensive Parameters

Up to this point, we have used the terms temperature and pressure many times, but lacking the proper thermodynamical definition. Now is the time to fix that. For a simple system in equilibrium in the energy representation

$$U = U(S, V, N)\,, \tag{1.74}$$

we define the *temperature*

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_{V,N}}\,, \tag{1.75}$$

the *pressure*

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}}\,, \tag{1.76}$$

and further (possibly a not so well recognized quantity) the *chemical potential*

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}}\,. \tag{1.77}$$

First, it is easy to show that these all are the so called *intensive parameters* that do not scale with the system. Let's show this, e.g., for the temperature. Scaling the system by λ results in

$$U \to \lambda U\,, \quad S \to \lambda S\,. \tag{1.78}$$

However,

$$T \to \left(\frac{\partial \lambda U}{\partial \lambda S}\right)_{V,N} = \left(\frac{\partial U}{\partial S}\right)_{V,N} = T\,. \tag{1.79}$$

The same can be further done with the pressure and the chemical potential. A general intensive parameter A then obeys

$$\boxed{A(\lambda U, \lambda V, \lambda N) = A(U, V, N)}\,. \tag{1.80}$$

Our next task is to justify the newly introduced definitions. We start with the pressure. Assuming a quasi-static process with $N = const.$, we can express the infinitesimal change in the internal energy as

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,N} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \mathrm{d}V\,. \tag{1.81}$$

It it insightful to note here that while the above can always be expressed mathematically, the relevance to the physical process truly makes sense only in the quasi-static case. Employing (1.75) and (1.76), this can be further rewritten as

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V\,. \tag{1.82}$$

According to the first law of thermodynamics, it must simultaneously hold that

$$\mathrm{d}U = đQ + đW\,. \tag{1.83}$$

We already derived the formula for the quasi-static work in Eq. (1.50), using which the above becomes

$$\mathrm{d}U = đQ - P\mathrm{d}V\,. \tag{1.84}$$

Comparing (1.82) with (1.84), there are now two important observations. First, our formal definition of the pressure exactly reproduces the quasi-static work term and is hereby justified. Second, we can identify the *quasi-static heat* as

$$\boxed{đQ = T\mathrm{d}S}\,. \tag{1.85}$$

Before moving on to the justification of the definition of the temperature, we show how do the intensive parameters arise in the entropy representation. We start by expressing the total differential of the internal energy (1.74) as

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N\,, \tag{1.86}$$

rearranging of which gives

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N\,. \tag{1.87}$$

In the entropy representation, we have

$$S = S(U, V, N)\,, \tag{1.88}$$

whose total differential is

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N}\mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N}\mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,V}\mathrm{d}N\,. \tag{1.89}$$

By comparing the latter with (1.87), we can immediately identify

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}}\,, \tag{1.90}$$

$$\boxed{\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}}\,, \tag{1.91}$$

$$\boxed{\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}}\,. \tag{1.92}$$

Those relations will prove useful in the upcoming calculations.

1.17 Temperature

To justify the definition of the temperature is a bit more complicated. We do so by demonstrating three important properties it possesses that are in accordance with our intuitive concept of this phenomenon.

1.17.1 Temperature is Positive

This is actually trivial as it follows directly from the Postulate III. Recall that

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0\,. \tag{1.93}$$

But according to (1.90) ,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} > 0\,, \tag{1.94}$$

and so

$$\boxed{T > 0}\,. \tag{1.95}$$

This is our first clue.

1.17.2 Thermal Equilibrium

Next, assume a composite system in equilibrium consisting of two simple systems in thermal contact, meaning they are separated by rigid, impermeable and diathermal wall, see Fig. 1.15. In such case, we would say that the two systems are in *thermal equilibrium*.

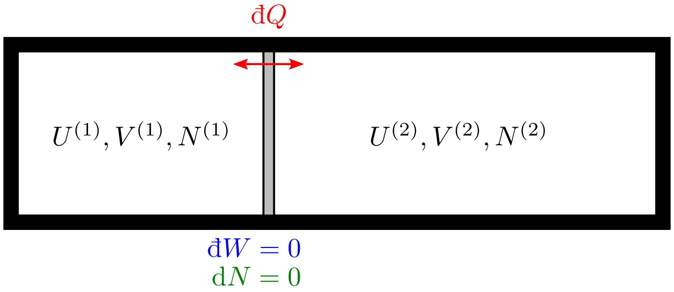

Figure 1.15: Thermal equilibrium.

First, since the system must be externally isolated, we have

$$U^{(1)} + U^{(2)} = const.\,, \tag{1.96}$$

i.e.,

$$\mathrm{d}U^{(1)} + \mathrm{d}U^{(2)} = 0\,. \tag{1.97}$$

The equilibrium further implies that the total entropy

$$S = S^{(1)} + S^{(2)} \tag{1.98}$$

is maximum, the necessary condition of which is

$$\mathrm{d}S = \mathrm{d}S^{(1)} + \mathrm{d}S^{(2)} = 0\,. \tag{1.99}$$

Since the volumes and the numbers of particles of both the subsystems are fixed, we can express the respective entropy differentials as

$$\left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)},N^{(1)}} \mathrm{d}U^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V^{(2)},N^{(2)}} \mathrm{d}U^{(2)} = 0\,, \tag{1.100}$$

which can be rewritten by employing the relation (1.90) as

$$\frac{1}{T^{(1)}}\mathrm{d}U^{(1)} + \frac{1}{T^{(2)}}\mathrm{d}U^{(2)} = 0\,, \tag{1.101}$$

Finally, combining the above with (1.97) gives

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{d}U^{(1)} = 0\,, \tag{1.102}$$

resulting in

$$\boxed{T^{(1)} = T^{(2)}}\,. \tag{1.103}$$

This is the condition for the two simple systems being in thermal equilibrium. Further, it should also be taken as our second clue, as this is exactly the physical behavior that we would intuitively expect.

1.17.3 Clausius Statement of The Second Law

Let's now modify the preceding calculation a bit. Assume the two subsystems being initially isolated with temperatures

$$T^{(1)} > T^{(2)}\,. \tag{1.104}$$

We then relax the internal constraint by turning the originally isolating wall into diathermal, allowing heat to pass. We already know that, in such case, a process will happen, terminating at the state of thermal equilibrium, i.e., both subsystems having the same temperature. Further, we assume the process to be sufficiently slow such that it can be considered quasistatic. As the system is externally isolated as a whole, it must still hold that

$$\mathrm{d}U^{(1)} + \mathrm{d}U^{(2)} = 0\,. \tag{1.105}$$

Since the only allowed exchange of energy between the two subsystems is in the form of a heat, then according to the first law (1.30),

$$\mathrm{d}U^{(1)} = đQ^{(1)}\,, \quad \mathrm{d}U^{(2)} = đQ^{(2)}\,, \tag{1.106}$$

while the combination of the above two results gives

$$đQ^{(1)} = -đQ^{(2)} . \tag{1.107}$$

The infinitesimal change in the total entropy can be written as

$$\mathrm{d}S = \mathrm{d}S^{(1)} + \mathrm{d}S^{(2)} . \tag{1.108}$$

Due to the process being quasistatic, we make use of the formula (1.85) for the quasi static heat, obtaining

$$\mathrm{d}S = \frac{1}{T^{(1)}} đQ^{(1)} + \frac{1}{T^{(2)}} đQ^{(2)} . \tag{1.109}$$

Together with (1.107), this becomes

$$\mathrm{d}S = \left(\frac{1}{T^{(2)}} - \frac{1}{T^{(1)}} \right) đQ^{(2)} . \tag{1.110}$$

Now the crucial step. The second law dictates

$$\mathrm{d}S \geq 0 . \tag{1.111}$$

But until $T^{(1)} = T^{(2)}$,

$$\frac{1}{T^{(2)}} - \frac{1}{T^{(1)}} > 0 , \tag{1.112}$$

and therefore,

$$đQ^{(2)} > 0 . \tag{1.113}$$

This means that the heat can flow only from the hotter subsystem into the colder one, which is the Clausius statement of the second law of thermodynamics. This is our last clue.

To sum up, we have demonstrated that

1. the temperature is always positive,
2. in thermal equilibrium, the temperatures of the constituent subsystems are equal,
3. heat always flows from the hotter subsystem into the colder one.

These observations together should justify that our definition of the temperature is sensible.

1.18 Postulate VI. - Absolute Zero

Entropy of a simple system approaches zero as

$$\left(\frac{\partial U}{\partial S} \right)_{V,N} \to 0 .$$

In other words, $S \to 0$ as $T \to 0$. This postulate won't be of much use to us and we primarily state it here for completeness. Nevertheless, the important part is that this is true regardless of the values of V, N, and so, in this sense, the entropy has a well defined minimum value. This is the last one of the postulates.

1.19 Mechanical Equilibrium

Next, we are going to derive the necessary conditions on two systems to be in a *mechanical equilibrium*. Same as in the case of thermal equilibrium, we assume an externally isolated cylinder separated inside into two parts, but now instead of a rigid wall we use a piston (impermeable). This means that the two subsystems are able to exchange energy in form of a mechanical work. Regarding the exchange of heat, we further distinguish two cases.

1.19.1 Diathermal Piston

In this case, as the title suggests, the piston is diathermal, so the heat is allowed to flow from one subsystem into another and vice versa. The situation is depicted in Fig. 1.16.

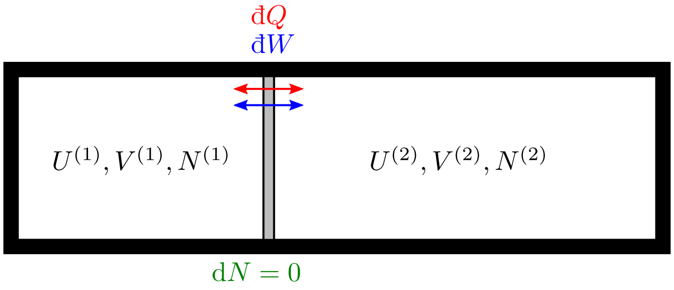

Figure 1.16: Mechanical equilibrium with diathermal piston.

In the upcoming calculation we will follow exactly the same steps as in the case of the thermal equilibrium. The system being externally isolated implies

$$U^{(1)} + U^{(2)} = const. \quad \to \quad dU^{(1)} + dU^{(2)} = 0\,, \tag{1.114}$$

and

$$V^{(1)} + V^{(2)} = const. \quad \to \quad dV^{(1)} + dV^{(2)} = 0\,. \tag{1.115}$$

In the equilibrium state, the total entropy

$$S = S^{(1)} + S^{(2)} \tag{1.116}$$

must reach it's maximum value, i.e.,

$$dS^{(1)} + dS^{(2)} = 0\,. \tag{1.117}$$

Now we make use of the expressions (1.90), (1.91) together with the constraints (1.114), (1.115) to rewrite the above as

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \mathrm{d}U^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) \mathrm{d}V^{(1)} = 0\,. \tag{1.118}$$

Finally, the resulting equilibrium conditions are

$$\boxed{T^{(1)} = T^{(2)}\,, \quad P^{(1)} = P^{(2)}}\,. \tag{1.119}$$

Exactly what we would have anticipated – the piston stabilizes at a position corresponding to the equal pressures on both the sides (i.e., no net force being exerted on the piston), while the diathermal property of the piston further ensures the temperatures of the both the subsystems to equalize.

1.19.2 Adiabatic Piston

The second possibility is to have the piston adiabatic instead of diathermal. Hence, we disallow the exchange of heat between the two subsystems, see Fig. 1.17.

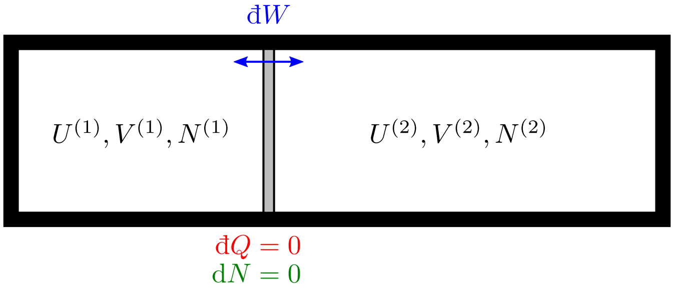

Figure 1.17: Caption

There is no need to repeat the process from the beginning, so we get right away to the entropy maximum condition (1.118)

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) \mathrm{d}U^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) \mathrm{d}V^{(1)} = 0\,. \tag{1.120}$$

Now you might ask: This seems exactly the same as before, so where is the difference? The subtlety lies in the fact that, at this point, $\mathrm{d}U^{(1)}$ and $\mathrm{d}V^{(1)}$ are actually not linearly independent, as we are going to show. Assume the two subsystems were to exchange an infinitesimal amount of energy. Due to the piston being adiabatic, the first law (1.30) applied to subsystem (1) dictates

$$\mathrm{d}U^{(1)} = đW^{(1)}\,. \tag{1.121}$$

We can then use the formula for the quasi-static work

$$đW^{(1)} = -P^{(1)}\mathrm{d}V^{(1)}\,, \tag{1.122}$$

while the combination of the two yields

$$\mathrm{d}U^{(1)} = -P^{(1)}\mathrm{d}V^{(1)}\,, \tag{1.123}$$

which is what we wanted to show. Now by inserting this into (1.120), we get

$$\frac{P^{(1)} - P^{(2)}}{T^{(2)}}\mathrm{d}V^{(1)} = 0\,. \tag{1.124}$$

This finally results in the condition

$$\boxed{P^{(1)} = P^{(2)}}\,. \tag{1.125}$$

So in contrast to the previous case, we no longer have the condition on the temperatures being equal, but that perfectly makes sense as the subsystems are no longer allowed to exchange heat.

1.20 Chemical Equilibrium

Last but not least, we focus here on demystifying a little bit the chemical potential. First, let us assume a quasistatic process but at this point allowing N to change as well. In such case, we can write the total differential of U as

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N\,. \tag{1.126}$$

We already know that $đQ = T\mathrm{d}S$ is the quasistatic heat and $đW = -P\mathrm{d}V$ the quasistatic work. Analogically, we define

$$\boxed{đW_{\mathrm{c}} = \mu\mathrm{d}N} \tag{1.127}$$

as the *quasistatic chemical work*. This term then describes the energy added to the system associated with the inflow of particles. Now let's move on to the derivation of the conditions of the so-called chemical equilibrium. Here we assume a cylinder separated inside by a rigid, diathermal and permeable wall. (It wouldn't be much physical to have a wall that is permeable but at the same time adiabatic.) The situation is depicted in Fig. 1.18.

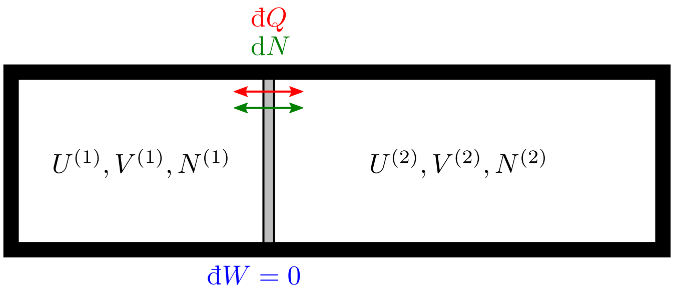

Figure 1.18: Chemical equilibrium.

The external isolation ensures

$$U^{(1)} + U^{(2)} = const. \quad \rightarrow \quad \mathrm{d}U^{(1)} + \mathrm{d}U^{(2)} = 0\,, \tag{1.128}$$

and

$$N^{(1)} + N^{(2)} = const. \quad \rightarrow \quad \mathrm{d}N^{(1)} + \mathrm{d}N^{(2)} = 0\,. \tag{1.129}$$

The entropy maximum further requires

$$\mathrm{d}S^{(1)} + \mathrm{d}S^{(2)} = 0\,, \tag{1.130}$$

which we can express as

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{d}U^{(1)} - \left(\frac{\mu^{(1)}}{T^{(1)}} - \frac{\mu^{(2)}}{T^{(2)}}\right)\mathrm{d}N^{(1)} = 0\,, \tag{1.131}$$

with the resulting equilibrium conditions being

$$\boxed{T^{(1)} = T^{(2)}\,, \quad \mu^{(1)} = \mu^{(2)}}\,. \tag{1.132}$$

For our purposes, this is probably the best way to understand the chemical potential. That is, if two systems are in chemical equilibrium, then their respective values of the chemical potential must be equal.

1.21 Maximum Work Theorem

In this section, we conduct a very general analysis of cyclic thermal engines. And even though this topic is not very relevant to our specific course, the resulting theorem will be extremely important in context of our definition of the temperature. We start by some definitions.

1. *Thermal reservoir* is a system of constant temperature externally constrained by impermeable rigid walls within which each process is quasi-static.

2. *Work source* is a system externally constrained by impermeable adiabatic walls within which each process is quasi-static.

As both of those operate quasi-statically, we can always employ the quasi-static heat formula to express

$$đQ = T\mathrm{d}S\,. \tag{1.133}$$

Moreover, due to the work source being adiabatically isolated, i.e.,

$$đQ^{(\mathrm{WS})} = 0 \tag{1.134}$$

then

$$\mathrm{d}S^{(\mathrm{WS})} = \frac{đQ^{(\mathrm{WS})}}{T} = 0\,, \tag{1.135}$$

so the entropy of a work source does not change.

Now we propose the simplest possible configuration of a thermal engine consisting of two thermal reservoirs of different temperatures $T^{(1)} > T^{(2)}$, hereinafter referred to as the "hot" and "cold", respectively; a work source and an arbitrary system denoted as "TS", see Fig. 1.19.

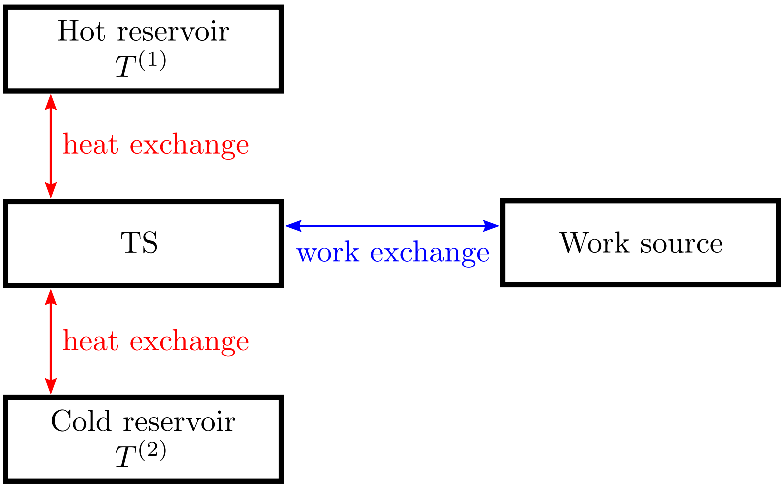

Figure 1.19: Thermal engine.

The colored arrows indicate the possible form of energy exchange between the constituent subsystem restricted by the internal constraints imposed by the respective types of walls. Further, by saying that such an engine is cyclic we mean that after a full cycle the system (not the whole engine) returns to the initial equilibrium state. But other then that, the process within the system generally does not have to be quasi-static. To determine the maximum possible work delivered to the work source during one cycle, we start by assuming the whole engine to be externally isolated, imposing the constraint

$$U^{(\mathrm{TS})} + U^{(\mathrm{H})} + U^{(\mathrm{C})} + U^{(\mathrm{WS})} = const. \tag{1.136}$$

After a full cycle, we must then have

$$\Delta U^{(\mathrm{H})} + \Delta U^{(\mathrm{C})} + \Delta U^{(\mathrm{WS})} = 0\,, \tag{1.137}$$

where $\Delta U^{(\mathrm{TS})} = 0$ due to the system returning to the initial state. The above can be expressed by means of the first law as

$$Q^{(\mathrm{H})} + Q^{(\mathrm{C})} + W^{(\mathrm{WS})} = 0\,. \tag{1.138}$$

(There is no work done onto the reservoirs and no heat input into the work source.) Now since the reservoirs operate quasi-statically and at constant temperature, the total heat input into the hot one can be expressed as

$$Q^{(\mathrm{H})} = \oint đQ^{(\mathrm{H})} = T^{(1)} \oint \mathrm{d}S^{(\mathrm{H})} = T^{(1)} \Delta S^{(H)}\,; \tag{1.139}$$

and similarly

$$Q^{(\mathrm{C})} = \oint \text{đ}Q^{(\mathrm{C})} = T^{(2)} \oint \mathrm{d}S^{(\mathrm{C})} = T^{(2)} \Delta S^{(C)} \tag{1.140}$$

for the cold one, where the circle over the integral suggests that we are integrating over one cycle of the engine. Eq. (1.138) now becomes

$$T^{(1)} \Delta S^{(\mathrm{H})} + T^{(2)} \Delta S^{(\mathrm{C})} + W^{(\mathrm{WS})} = 0\,. \tag{1.141}$$

From there, we can express

$$\Delta S^{(\mathrm{C})} = -\frac{T^{(1)}}{T^{(2)}} \Delta S^{(\mathrm{H})} - \frac{1}{T^{(2)}} W^{(\mathrm{WS})}\,. \tag{1.142}$$

The second law then dictates that, after one cycle,

$$\Delta S = \Delta S^{(\mathrm{H})} + \Delta S^{(\mathrm{C})} \geq 0\,, \tag{1.143}$$

whereas we have already shown at the beginning that $\Delta S^{(\mathrm{WS})} = 0$, and further

$$\Delta S^{(\mathrm{TS})} = 0 \tag{1.144}$$

due to the system returning to the initial state. By combining (1.142) and (1.143), we get

$$W^{(\mathrm{WS})} \leq \left(1 - \frac{T^{(2)}}{T^{(1)}}\right) Q_1\,, \tag{1.145}$$

where we have substituted

$$Q_1 \equiv -T^{(1)} \Delta S^{(\mathrm{H})} = -Q^{(\mathrm{H})} \tag{1.146}$$

for the heat withdrawn from the hot reservoir during one cycle. The maximum is then reached for a reversible process, i.e., $\Delta S = 0$, in which case the inequality sign becomes equality, resulting in

$$\boxed{W_{\max} = \left(1 - \frac{T^{(2)}}{T^{(1)}}\right) Q_1}\,, \tag{1.147}$$

where $W_{\max}$ is the maximum possible work delivered to the work source during one cycle. This is the *maximum work theorem.* The term in the parentheses is usually denoted as

$$\boxed{\eta_{\max} = 1 - \frac{T^{(2)}}{T^{(1)}}} \tag{1.148}$$

and called the *maximum thermal efficiency.* Note that for a realistic engine, we will always have $\Delta S > 0$, and hence,

$$\eta_{\mathrm{real}} < \eta_{\max}\,, \tag{1.149}$$

which is called the *Carnot theorem.* The key observation here is that the maximum efficiency is a function of the temperatures of the thermal reservoirs solely.

1.22 Carnot Cycle

We have shown that the maximum work delivered by our system to the work source is reached by a reversible process characterized by

$$\Delta S = 0\,. \tag{1.150}$$

Building on that, let us now try to put together the simplest possible cycle that does not increase the total entropy of the engine and, hence, reaches the maximum efficiency given by Eq. (1.148). And there is basically just one possibility called the *Carnot cycle*, consisting of four quasi-static (recall that a reversible process is quasi-static by definition) sub-processes. We assume the system to start in the equilibrium state (U_1, V_1) with the temperature $T^{(\mathrm{TS})} = T^{(1)}$ corresponding to that one of the hot reservoir. Then, the following happens:

$1 \to 2$) The system is placed in thermal contact with the hot reservoir, withdrawing the heat $Q_1 = -Q^{(\mathrm{H})}$ at constant temperature

$$T^{(\mathrm{TS})} = T^{(1)}\,,$$

while

$$\Delta S^{(\mathrm{TS})} = \frac{Q_1}{T^{(\mathrm{TS})}} = -\frac{Q^{(\mathrm{H})}}{T^{(1)}} = -\Delta S^{(\mathrm{H})}\,.$$

This means that the increase of the entropy of the system is compensated by exactly the same amount of decrease of the entropy of the hot reservoir, i.e.,

$$\Delta S_{1\to 2} = \Delta S^{(\mathrm{TS})} + \Delta S^{(\mathrm{H})} = 0\,,$$

and as such, the total entropy of the engine does not change. During this step, the system expands from V_1 to V_2, performing the amount of work

$$W_{1\to 2} = U_1 - U_2 + Q_1$$

onto the work source in accordance with the first law. Such a process at constant temperature is called *isothermal*.

$2 \to 3$) The system is removed from the thermal contact with the hot reservoir and further expands adiabatically from V_2 to V_3, performing an additional amount of work

$$W_{2\to 3} = U_2 - U_3$$

onto the work source, while the total entropy of the engine does not change due to the adiabatic constraint, i.e.,

$$\Delta S_{2\to 3} = 0\,.$$

During this step, the system cools down from the temperature of the hot reservoir $T^{(1)}$ to the temperature of the cold reservoir $T^{(2)}$.

$3 \to 4$) The system is placed in thermal contact with the cold reservoir, delivering the heat $Q_2 = Q^{(\mathrm{C})}$ at constant temperature

$$T^{(\mathrm{TS})} = T^{(2)} .$$

The total entropy of the engine does not change, as

$$\Delta S^{(\mathrm{TS})} = \frac{-Q_2}{T^{(\mathrm{TS})}} = -\frac{Q^{(\mathrm{C})}}{T^{(2)}} = -\Delta S^{(\mathrm{C})} ,$$

so the decrease of the entropy of the system is compensated by exactly the same amount of increase of the entropy of the cold reservoir, i.e.,

$$\Delta S_{3\to 4} = \Delta S^{(\mathrm{TS})} + \Delta S^{(\mathrm{C})} = 0 .$$

During this step, the system is compressed from V_3 to V_4, while the work source performs the amount of work

$$W_{3\to 4} = U_3 - U_4 - Q_2 \tag{1.151}$$

onto the system.

$4 \to 1$) The system is removed from the thermal contact with the cold reservoir and is further compressed adiabatically from V_4 back to V_1, while the work source performs an additional amount of work

$$W_{4\to 1} = U_4 - U_1$$

onto the system. The total entropy of the engine does not change due to the adiabatic constraint, i.e.,

$$\Delta S_{4\to 3} = 0 ,$$

and, during this step, the system heats up from the temperature of the cold reservoir $T^{(2)}$ back to the temperature of the hot reservoir $T^{(1)}$.

The system has now returned to the original equilibrium state (U_1, V_1) and the cycle is completed. As this might be quite overwhelming at first, I tried to summarize everything in Fig. 1.20, where the red and blue colors represent the heat delivered to and withdrawn from our system, respectively; and the green and purple the work performed by and done onto our system, respectively.

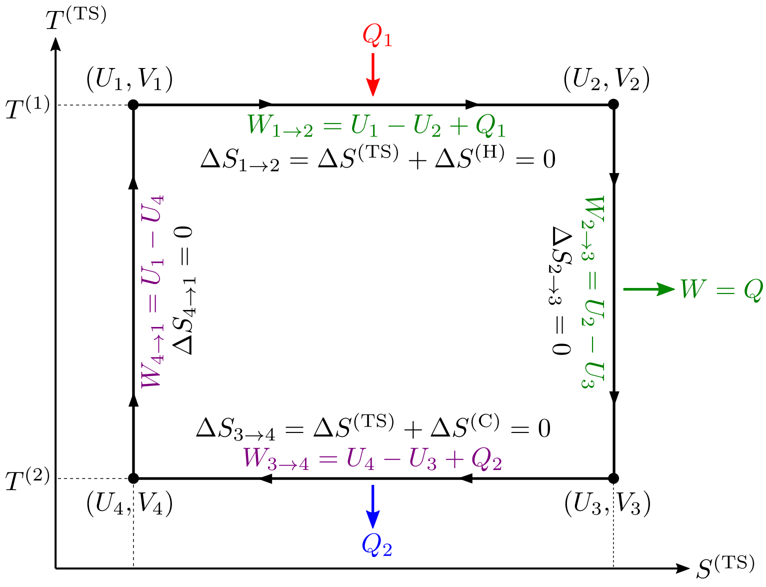

Figure 1.20: Carnot cycle.

By a simple calculation, we can show that the total amount of work done by our system is equal to

$$W = W_{1\to 2} + W_{2\to 3} - W_{3\to 4} - W_{4\to 1} = Q_1 - Q_2\,, \tag{1.152}$$

which is just the first law as stated for the complete cycle, see Eq. (1.138). Note that in case of the system being an ideal gas, the Carnot cycle is typically represented in the P-V diagram instead of the T-S one, but this is more general.

Based on the above walk through the individual steps of the Carnot cycle, it should be evident that the isothermal and adiabatic sub-processes are the only candidates that do not increase the total entropy of the engine, and as such, this is truly the simplest possible closed cycle. Any other more complex reversible cycle must then always be able to be decomposed into partial Carnot cycles, but we will not prove this statement.

We are not going to study the thermal engines any further as they are not of much relevance to this course. However, there is one extremely important conclusion of the maximum work theorem that will finally allow us to answer one of the questions that we have tactfully conceived up to this point.

1.23 Units of Temperature and Entropy

It might seem a bit weird, but the maximum work theorem derived in context of cyclic thermal engines is actually what allows us to properly define the units of temperature. So here it is.

To the triple point of water, we assign the temperature 273.16 K.

("K" stands for Kelvin, but you all know that.) The triple point of water is an equilibrium state between ice, water and the saturated water steam. To assign the value to any other temperature T, we conduct the following thought experiment. We build a reversible cyclic thermal engine with one of the reservoirs having temperature 273.16 K and the other one T. There are now two possibilities.

1. Assuming $T < 273.16$ K, i.e., T corresponding to the cold reservoir, we measure the thermal effectivity η of such engine. According to the maximum work theorem, then,
$$T = (1-\eta) \times 273.16\,\mathrm{K}\,. \tag{1.153}$$
Note that the temperature 0 K, or the so called *absolute zero*, corresponds to the thermal engine with the efficiency of 100 %, regardless of the temperature of the hot reservoir.

2. Otherwise, if $T > 273.16$ K, i.e., T corresponding to the hot reservoir, we get
$$T = \frac{1}{1-\eta} \times 273.16\,\mathrm{K}\,. \tag{1.154}$$

And this is truly the correct way to introduce the units of Kelvin in context of thermodynamics.

Having the units of temperature finally defined, it then follows directly what the units of the entropy are. By looking at the formula for the quasi-static heat
$$đQ = T\mathrm{d}S\,, \tag{1.155}$$
we immediately get
$$\boxed{[S] = \mathrm{J}\,\mathrm{K}^{-1}}\,. \tag{1.156}$$

1.24 An Aside: Legendre Transformation

To be able to proceed to the upcoming section, we need to introduce a mathematical concept that you might be already familiar with from the course of Hamiltonian mechanics, being the *Legendre transformation*. Nevertheless, repetition is the key to proper understanding, so even if you already know it, I still recommend reading through this section carefully.

Assume we have a function
$$f = f(x) \tag{1.157}$$
that contains all the information about the studied system regardless of what it is (it might not even be a physical system). Note that, for simplicity, we are considering having

only one independent variable x. (The generalization to the multi-variable case will be conducted later.) First, we define

$$p = \frac{\mathrm{d}f}{\mathrm{d}x}\,. \tag{1.158}$$

(The x and p used here have nothing to do with the position and momentum.) Now imagine that – for whatever reason – we do not want our system to be described by x but rather by p. How can we do this? The first idea might be as follows. From (1.158) we get $p = p(x)$, so we invert this (silently assuming it can be done) into $x = x(p)$ and further substitute into the original function $f(x)$ (1.157) as

$$f = f[x(p)]\,. \tag{1.159}$$

And even though a nice try, this necessarily leads to the loss of information, which is best demonstrated by a specific example. Take

$$f(x) = \mathrm{e}^x\,. \tag{1.160}$$

Then,

$$p(x) = \frac{\mathrm{d}f}{\mathrm{d}x} = \mathrm{e}^x\,. \tag{1.161}$$

By inverting the above, we get

$$x(p) = \ln(p)\,. \tag{1.162}$$

Finally, substituting into (1.160) yields

$$f(p) = p\,. \tag{1.163}$$

Up to this point, everything seems natural. But consider the opposite case, where you are given $f(p) = p$ (knowing that $p = \mathrm{d}f/\mathrm{d}x$) and are asked to reconstruct back the original function $f(x)$. In such case, we take Eq. (1.163) and substitute (1.158) for p as

$$f = \frac{\mathrm{d}f}{\mathrm{d}x}\,. \tag{1.164}$$

This is a first-order linear differential equation with the solution

$$f(x) = C\,\mathrm{e}^x\,, \tag{1.165}$$

where C stands for the integration constant. As you can see, we did not obtain the original expression for $f(x)$ and this is the loss of information mentioned above as we possess no further information to uniquely determine the respective value of C. Fortunately, there is another way to interchange $x \leftrightarrow p$ without losing any information. Instead of thinking of $f(x)$ as a function, think of it as a set of points $[x, f(x)]$. It can be shown (the proof is behind the scope of this text) that we can equally good describe the function by a different set of points $[p, g(p)]$, where p (according to the definition) stands for the derivative of f w.r.t. x at a given point and $g(p)$ is the y-component of the intersection between the corresponding tangent line and the y-axis, see Fig. 1.21.

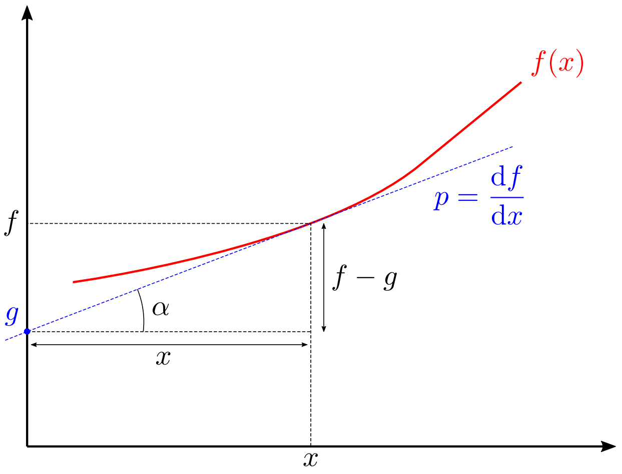

Figure 1.21: Legendre Transformation.

By providing a complete list of such points, we essentially define the set of all the tangent lines to the function and it can then be uniquely reconstructed back. Based on the figure, we can now express p as

$$p = \tan\alpha = \frac{f - g}{x}\,, \tag{1.166}$$

from which we get

$$g = f - xp\,. \tag{1.167}$$

By using the inverted formula $x = x(p)$, we arrive at

$$\boxed{g(p) = f[x(p)] - x(p)p}\,, \tag{1.168}$$

which is the sought function that contains all the information as the original $f(x)$, but is expressed by means of p instead of x. This is called the *Legendre transform* of f and will be hereinafter denoted as

$$g(p) = \mathcal{L}[f(x)]\,. \tag{1.169}$$

Let us now summarize the process by the following three steps:

1. We start with $f = f(x)$.
2. We calculate $p(x) = \mathrm{d}f/\mathrm{d}x$ and invert it into $x = x(p)$.
3. We obtain the Legendre transform of f as $g(p) = f[x(p)] - x(p)p$.

Applied to the previously presented example, we proceed as follows:

1. We start with $f = \mathrm{e}^x$.
2. We calculate $p(x) = \mathrm{e}^x$ and invert it into $x = \ln(p)$.
3. The last step then yields $g(p) = p - p\ln(p)$.

This should now be the correct Legendre transform of $f(x) = \mathrm{e}^x$, i.e., a different function of the variable p but carrying exactly the same information. We shall now prove that we are truly able to reconstruct $f(x)$ purely based on the knowledge of $g(p)$. First, we do this generally and then return to our example. So assume we have

$$g = g(p)\,, \tag{1.170}$$

and are asked to determine $f = f(x)$. By taking the differential of Eq. (1.167) we get

$$\begin{aligned} \mathrm{d}g &= \mathrm{d}f - x\mathrm{d}p - p\mathrm{d}x \\ &= p\mathrm{d}x - x\mathrm{d}p - p\mathrm{d}x \\ &= -x\mathrm{d}p\,, \end{aligned} \tag{1.171}$$

where in the second line we used

$$\mathrm{d}f = \frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x = p\mathrm{d}x\,. \tag{1.172}$$

From the last line of (1.171), we can see that

$$x = -\frac{\mathrm{d}g}{\mathrm{d}p}\,. \tag{1.173}$$

So we can take $x = x(p)$ and invert it as $p = p(x)$. Finally, from (1.167) we express

$$f = g + px \tag{1.174}$$

and substitute for p as

$$\boxed{f(x) = g[p(x)] + p(x)x}\,. \tag{1.175}$$

This is the original function $f(x)$, which will be hereinafter denoted as

$$f(x) = \mathcal{L}^{-1}[g(p)] \tag{1.176}$$

and called the *inverse Legendre transform* of g. Once again, to summarize the steps:

1. We start with $g = g(p)$.
2. We calculate $x(p) = -\mathrm{d}g/\mathrm{d}g$ and invert it into $p = p(x)$.
3. We obtain the inverse Legendre transform of g as $f(x) = g[p(x)] + p(x)x$.

Applying this to our example, we proceed as follows:

1. We start with $g(p) = p - p\ln(p)$.
2. We calculate $x(p) = \ln(p)$ and invert this into $p(x) = \mathrm{e}^x$.
3. The inverse Legendre transform is then $f(x) = \mathrm{e}^x$.

And this truly is the original function (1.160) that we started with.

As promised at the beginning of this section, the next thing we need to do is to extend the presented methodology to be applicable to multi-variable functions. But since the process is exactly the same (just a bit more tedious), we will directly present the resulting three steps of the Legendre transform:

1. At the beginning, we have $f = f(x_1, x_2, \dots)$.
2. We calculate $p_i(x_1, x_2, \dots) = \partial f/\partial x_i$ and invert this into $x_i = x_i(p_1, p_2, \dots)$.
3. We obtain the Legendre transform of f as

$$\boxed{g(p_1, p_2, \dots) = f[x_1(p_1, p_2, \dots), x_2(p_1, p_2, \dots), \dots] - \sum_i x_i(p_1, p_2, \dots) p_i} \,.$$

Similarly, the inverse Legendre transformation is then done by the following steps:

1. At the beginning, we have $g = f(p_1, p_2, \dots)$.
2. We calculate $x_i(p_1, p_2, \dots) = -\partial g/\partial p_i$ and invert this into $p_i = p_i(x_1, x_2, \dots)$.
3. We obtain the inverse Legendre transform of g as

$$\boxed{f(x_1, x_2, \dots) = g[p_1(x_1, x_2, \dots), p_2(x_1, x_2, \dots), \dots] + \sum_i p_i(x_1, x_2, \dots) x_i} \,.$$

There are definitely more compact ways to write this but, at this point, I wanted to be very explicit about the dependencies of various parameters on the others.

Of course, in case of a multi-variable function $f(x_1, x_2, \dots)$, there is no need to Legendre transform through all the x_i but we can freely choose any subset of those. So, e.g., if we have $f = f(x_1, x_2, x_3)$, we can only choose to replace $x_1 \to p_1$ and $x_3 \to p_3$, resulting in the transformed function $g = g(p_1, x_2, p_3)$, which is then referred to as the *partial Legendre transformation.* I will not try to formalize the corresponding steps for a general subset as that would be too cumbersome and highly unreadable. Instead, we will adopt the following notation:

$$g = \mathcal{L}[f; \dots] \,, \tag{1.177}$$

where "…" will be replaced by the respective list of x_i through which the transformation is being conducted. So in the above example, we would write $g(p_1, x_2, p_3) = \mathcal{L}[f(x_1, x_2, x_3); x_1, x_3]$, or simply $g = \mathcal{L}[f; x_1, x_3]$.

To conclude this mathematical intermezzo, we show the most typical use of the (partial) Legendre transformation in physics. In the course of analytical mechanics, we learn that the key function that contains all the information about a physical system is the lagrangian

$$L = L(x, \dot{x}, t)\,, \tag{1.178}$$

where $x = \{x_1, x_2, \dots\}$ and $\dot{x} = \{\dot{x}_1, \dot{x}_2, \dots\}$ stand for the (sets of) generalized coordinates and the corresponding generalized velocities, respectively. We then define the conjugate momenta p_i as

$$p_i = \frac{\partial L}{\partial \dot{x}_i}\,. \tag{1.179}$$

From the theoretical point of view, the conjugate momenta are much more practical than the generalized velocities, and hence, we might want to sought a different function that contains all the same information as the Lagrangian but conveniently replaces $\dot{x} \to p$. But this is just a textbook playground for using the Legendre transform. We therefore define

$$-H(x, p, t) = \mathcal{L}[L, \dot{x}] = L - \sum_i \dot{x}_i p_i\,, \tag{1.180}$$

where the "–" sign on the left is just conventional, leading to

$$H(x, p, t) = \sum_i \dot{x}_i p_i - L\,. \tag{1.181}$$

But that is exactly the definition of the Hamilton function representing the total energy of the system. By this we have ensured that no information contained in $L(x, \dot{x}, t)$ was lost and we can equally good describe our system by $H(x, p, t)$.

Now we are ready to move on to the specific uses of the Legendre transformation in thermodynamics.

1.25 Thermodynamic Potentials

Let us quickly remind ourselves what do we mean by the internal energy representation of a thermodynamical system. In such case, all the information about the system is carried by the function

$$U = U(S, V, N)\,. \tag{1.182}$$

Moreover, we define the intensive parameters

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}\,, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}\,, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}\,. \tag{1.183}$$

This is a perfectly valid representation usable for various theoretical calculations. In many cases, however, this turns out to be unpractical. E.g., the entropy is a very abstract quantity that is practically unmeasureable and we might rather have the system described by the temperature. Similarly, we sometimes might want to use the pressure instead of the volume, or the chemical potential instead of the number of particles. This is exactly the point where we can make use of the Legendre transformation, where

$$x_1 \equiv S\,, \quad x_2 \equiv V\,, \quad x_3 \equiv N\,, \tag{1.184}$$

and

$$p_1 \equiv T\,, \quad p_2 \equiv -P\,, \quad p_3 \equiv \mu\,. \tag{1.185}$$

Our task now is just to carry out the Legendre transformation through various subsets of the variables $\{S, V, N\}$.

1.25.1 Helmholtz Free Energy

We define the *Helmholtz free energy* as

$$\boxed{F(T,V,N) = \mathcal{L}[U(S,V,N);S]}\,. \tag{1.186}$$

This means that we take

$$T(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{1.187}$$

and invert this as

$$S = S(T,V,N)\,. \tag{1.188}$$

The corresponding Legendre transform then reads

$$F(T,V,N) = U[S(T,V,N),V,N] - S(T,V,N)\,T\,, \tag{1.189}$$

or simply

$$\boxed{F = U - TS}\,, \tag{1.190}$$

where I just changed the order of S and T as this is more traditional. Typically, those kind of expressions are written without explicitly denoting the dependence on the respective parameters (in this case (T,V,N)). However, it is important to keep in mind that the main reason for introducing the Legendre transformed quantities is to change from one set of parameters to another one, and so (1.189) is the truly correct form. To find the expressions for S, P, μ, we calculate the differential of Eq. (1.190) as

$$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - S\mathrm{d}T - T\mathrm{d}S \\ &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N - S\mathrm{d}T - T\mathrm{d}S \\ &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N\,, \end{aligned} \tag{1.191}$$

where in the second line we used (1.126). We can immediately see that

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}\,, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}\,, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}}\,. \tag{1.192}$$

Hence, the Helmholtz free energy F provides us with a representation where the equilibrium of s simple system is determined by (T,V,N). As we will see later, this is the key quantity describing the so called *canonical ensemble*.

1.25.2 Enthalpy

We define the *enthalpy* as

$$\boxed{H(S,P,N) = \mathcal{L}[U(S,V,N);V]}\,. \tag{1.193}$$

By taking

$$-P(S,V,N) = \left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{1.194}$$

and inverting into

$$V = V(S,P,N)\,, \tag{1.195}$$

the Legendre transformation reads

$$\begin{aligned} H(S,P,N) &= U[S,V(S,P,N),N] - V(S,P,N)(-P) \\ &= U[S,V(S,P,N),N] + V(S,P,N)\,P \end{aligned} \tag{1.196}$$

(notice the minus sign accompanying P according to (1.194)), or simply

$$\boxed{H = U + PV}\,. \tag{1.197}$$

Calculating the differential of the above yields

$$\begin{aligned} \mathrm{d}H &= \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \\ &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + P\mathrm{d}V + V\mathrm{d}P \\ &= T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N\,. \end{aligned} \tag{1.198}$$

From this, we get

$$\boxed{T = -\left(\frac{\partial H}{\partial S}\right)_{P,N}\,, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}\,, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}}\,. \tag{1.199}$$

If we now consider a quasi-static process at constant pressure ($P = const.$) and the number of particles ($N = const.$), (1.198) reads

$$\mathrm{d}H = T\mathrm{d}S = đQ\,. \tag{1.200}$$

Integrating the above then results in

$$Q = \int\limits_{\gamma_{A\to B}} đQ = \int\limits_{A}^{B} \mathrm{d}H = \Delta H\,, \tag{1.201}$$

meaning that the amount of heat withdrawn from a system during such process is equal to ΔH and that is why the enthalpy is sometimes referred to as the *heat content*. Nevertheless, we are not going to use enthalpy in this course as it does not play any significant role in the context of the statistical mechanics. (To my knowledge, this quantity is mostly relevant to chemistry.)

1.25.3 Gibbs Free Energy

The *Gibbs free energy* is defined as

$$\boxed{G(T,P,N) = \mathcal{L}[U(S,V,N);S,V]}\,. \tag{1.202}$$

Taking

$$T(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N}\,, \quad -P(S,V,N) = \left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{1.203}$$

and inverting into

$$S = S(T,P,N)\,, \quad V = V(T,P,N)\,, \tag{1.204}$$

the corresponding Legendre transformation reads

$$G(T,P,N) = U[S(T,P,N),V(T,P,N),N] - S(T,P,N)\,T + V(T,P,N)\,P\,, \tag{1.205}$$

or simply

$$\boxed{G = U - TS + PV}\,. \tag{1.206}$$

By calculating the differential, we get

$$\begin{aligned} \mathrm{d}G &= \mathrm{d}U - S\mathrm{d}T - T\mathrm{d}S + P\mathrm{d}V + V\mathrm{d}P \\ &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N - S\mathrm{d}T - T\mathrm{d}S + P\mathrm{d}V + V\mathrm{d}P \\ &= -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N\,, \end{aligned} \tag{1.207}$$

from which we obtain

$$\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}\,, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}\,, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}}\,. \tag{1.208}$$

Similarly as with the enthalpy, we are not going to use this quantity in this course.

1.25.4 Maxwell Relations

Let us now write together all the differentials of U, F, H, G considering $N = const.$ We get

$$\begin{aligned} \mathrm{d}U &= T\mathrm{d}S - P\mathrm{d}V\,, \\ \mathrm{d}F &= -S\mathrm{d}T - P\mathrm{d}V\,, \\ \mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}P\,, \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}P\,. \end{aligned} \tag{1.209}$$

From there, considering the property 5 of perfect differentials presented in Theorem 1, we immediately get

$$\begin{aligned}
-\left(\frac{\partial T}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial S}\right)_V ,\\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V ,\\
\left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P ,\\
-\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P .
\end{aligned} \tag{1.210}$$

These are called the *Maxwell relations* and might come in handy in various types of calculations.

1.25.5 Grand Canonical Potential

The last one of the Legendre transformed quantities is called the *grandcanonical potential* and is defined as

$$\boxed{\Phi_{\mathrm{G}}(T,V,\mu) = \mathcal{L}[U(S,V,N);S,N]}\,, \tag{1.211}$$

so by taking

$$T(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} , \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{1.212}$$

and inverting into

$$S = S(T,V,\mu)\,, \quad N = N(T,V,\mu) \tag{1.213}$$

the corresponding Legendre transformation reads

$$\Phi_{\mathrm{G}}(T,V,\mu) = U[S(T,V,\mu),V,N(T,V,\mu)] - S(T,V,\mu)\,T - N(T,V,\mu)\,\mu\,, \tag{1.214}$$

or simply

$$\boxed{\Phi_{\mathrm{G}} = U - TS - \mu N}\,. \tag{1.215}$$

Calculating the differential further yields

$$\begin{aligned}
\mathrm{d}\Phi_{\mathrm{G}} &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T - \mu\mathrm{d}N - N\mathrm{d}\mu\\
&= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N - T\mathrm{d}S - S\mathrm{d}T - \mu\mathrm{d}N - N\mathrm{d}\mu\\
&= -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu\,.
\end{aligned} \tag{1.216}$$

Hence,

$$\boxed{S = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial T}\right)_{V,\mu} , \quad P = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial V}\right)_{T,\mu} , \quad N = \left(\frac{\partial \Phi_{\mathrm{G}}}{\partial \mu}\right)_{T,V}}\,. \tag{1.217}$$

The grandcanonical potential is another key quantity that we will use later to describe the so called *grand-canonical ensemble.*

To conclude this section, we just note that the quantities U, F, H, G, Ω are called the *thermodynamic potentials.*

1.26 Why Statistical Physics?

To properly conclude this chapter, we explain why do we need the statistical physics. And the answer is pretty simple. Everything we have done so far assumes the a priori knowledge of the functional dependence of either

$$S = S(U, V, N)\,, \tag{1.218}$$

or any one of the following

$$\begin{aligned} U &= U(S, V, N)\,, \\ F &= F(T, V, N)\,, \\ H &= H(S, P, N)\,, \\ G &= G(T, P, N)\,, \\ \Phi_{\mathrm{G}} &= \Phi_{\mathrm{G}}(T, V, \mu)\,. \end{aligned} \tag{1.219}$$

(If we know one of these, we are always able to uniquely determine all of the others.) But we don't know that! And thermodynamics itself does not provide us with any way to discover this. Of course we could always conduct an experiment and try to estimate the correct formula, but such an approach is only empirical. And this is exactly the point where statistical physics comes into play. Hence, the purpose of statistical physics is to provide us with such formulas based on the underlying physical principles. And that's basically it.

1.27 Summary

Finally, we possess all the necessary background needed to proceed to the statistical part of these lecture notes. Please note that what we have covered here represents truly just the absolute minimum required for our purposes and there is so much that we have not touched, and so do not think for a second that you have now became an expert in thermodynamics.

Chapter 2

Basics of Theory of Probability

The next logical step in learning statistical physics is definitely the theory of probability. Hence, the purpose of this short chapter is to present the very basics of this topic, primarily aiming at the Shannon's concept of the information entropy.

2.1 Formal Definitions

We are going to start with some basic definitions. Assume we have a process that results in a random outcome, hereinafter referred to as the *random process* or *stochastic process*. The set of all possible outcomes of a random process is then called the *sample space* and denoted as Ω. E.g., if the random process is a flip of a coin, then

$$\Omega_{\text{coin}} = \{\text{heads}, \text{tails}\} , \tag{2.1}$$

or in case of a throw with a 6-sided dice

$$\Omega_{\text{dice}} = \{1, 2, 3, 4, 5, 6\} . \tag{2.2}$$

Note that if we decided to flip the coin twice, that must be taken as a different random process with

$$\Omega_{\text{coin (2x)}} = \{\text{heads} - \text{heads}, \text{heads} - \text{tails}, \text{tails} - \text{heads}, \text{tails} - \text{tails}\} . \tag{2.3}$$

Next, we define the *event space* $\mathcal{F}$ to be the set of all the subsets of $\mathscr{S}$. In case of the coin flipping, that would be

$$\mathcal{F}_{\text{coin}} = \Big\{\emptyset, \{\text{heads}\}, \{\text{tails}\}, \{\text{heads}, \text{tails}\}\Big\} . \tag{2.4}$$

(We are oversimplifying things here a bit, as actually the event space must form something called the sigma algebra to avoid potential mathematical problems, but we do not need to be as precise in this course.) An element of the event space $E \in \mathcal{F}$ is then called an *event* (how surprising). Each event then has some (physical) meaning. E.g., in the case with the dice, the event $\{1, 3, 5\}$ can be interpreted as "the output is an odd number", or $\{4,5,6\}$ as "the output is greater than 3".

Finally, we define the *probability* P to be a function (more precisely the *measure*) that assigns to each event a real number

$$P : \mathcal{F} \to \mathbb{R}\,, \tag{2.5}$$

such that the following conditions are met:

1. $P(E) \in [0,1]$;
2. $P(A \cup B) = P(A) + P(B)$ for any disjoint events, i.e., $A \cap B = \emptyset$;
3. $P(\Omega) = 1$, i.e., the random process must have some output.

To fully specify the probability function, we actually only need to determine the probabilities of all the singleton subsets of Ω (a singleton is a set containing exactly one element), that is

$$P\big(\{\omega_i\}\big)\,, \quad \omega_i \in \Omega. \tag{2.6}$$

The probabilities of each other event can then always be reconstructed based on the second property of P. In the case of the dice (assuming it's fair), we would have

$$P_{\text{dice}}\big(\{1\}\big) = \cdots = P_{\text{dice}}\big(\{6\}\big) = 1/6\,. \tag{2.7}$$

If we then want to calculate, e.g., the probability that the output is an even number, we would get

$$\begin{aligned} P_{\text{dice}}\big(\{2,4,6\}\big) &= P_{\text{dice}}\big(\{2\} \cup \{4\} \cup \{6\}\big) \\ &= P_{\text{dice}}\big(\{2\}\big) + P_{\text{dice}}\big(\{4\}\big) + P_{\text{dice}}\big(\{6\}\big) = \frac{1}{2}\,, \end{aligned} \tag{2.8}$$

as expected. Further, notice that the probabilities of all the singleton subsets add up to one:

$$P_{\text{dice}}\big(\{1\}\big) + \cdots + P_{\text{dice}}\big(\{6\}\big) = 1\,. \tag{2.9}$$

This must always be the case, as

$$\Omega = \bigcup_i \{\omega_i\}\,, \tag{2.10}$$

and

$$\{\omega_i\} \cap \{\omega_j\} = \emptyset \quad \text{for} \quad i \neq j\,, \tag{2.11}$$

allowing us to combine the second and the third property of P to get

$$\sum_i P\big(\{\omega_i\}\big) = P\left(\bigcup_i \{\omega_i\}\right) = P(\Omega) = 1\,. \tag{2.12}$$

Moreover,

$$1 = P(\Omega) = P(\Omega \cup \emptyset) = P(\Omega) + P(\emptyset) = 1 + P(\emptyset)\,, \tag{2.13}$$

i.e.,

$$P(\emptyset) = 0\,, \tag{2.14}$$

which is just another way of saying that the process must have some output.

Finally, the triplet $(\Omega, \mathcal{F}, P)$ is called the *probability space* and represents the formal mathematical structure required to properly deal with random processes mathematically.

Now lets move on to another important object in context of the theory of probability, being the *random variable*. A random variable is basically an arbitrary function that assigns to each element of the sample space a real number, i.e.,

$$X : \Omega \to \mathbb{R}\,. \tag{2.15}$$

(Similarly as with the event space $\mathcal{F}$, there are actually some formal mathematical restrictions that such a function must obey.) So, e.g., for the coin, we can define

$$X_{\text{coin}} = \begin{cases} 0, & \text{for heads} \\ 1, & \text{for tails} \end{cases} \tag{2.16}$$

Here, the random variable serves just as a label with no sensible interpretation. However, we could consider a different case where we flip the coin twice and define the random variable as the total number of heads, i.e.,

$$X_{\text{coin (2x)}} = \begin{cases} 2, & \text{heads} - \text{heads} \\ 1, & \text{heads} - \text{tails} \vee \text{tails} - \text{heads} \\ 0, & \text{tails} - \text{tails} \end{cases} \tag{2.17}$$

Such a random variable now has a proper meaning, whereas this will always be the case in physics. The last bit we are going to need is the inverse of the random variable. However, we cannot take this to be the inverse function, since – as you can see from the above example – the random variable does not need to be one-to-one (both heads-tails and tails-heads are mapped to the same number 1), and in such case, the inverse function is not properly defined. Hence, we will make use of the generalized form of the inverse function being the inverse image (or preimage). The definition is as follows. Assume a function

$$f : \mathrm{D}(f) \to \mathrm{R}(f)\,. \tag{2.18}$$

Then, we define the inverse image of $B \subseteq \mathrm{R}(f)$ as

$$f^{-1}(B) = \{x \in \mathrm{D}(f) : f(x) \in B\}\,. \tag{2.19}$$

So, e.g., for

$$f(x) = x^2\,, \tag{2.20}$$

we have

$$f^{-1}\big(\{4\}\big) = \{-2, 2\}\,, \tag{2.21}$$

as both

$$(-2)^2 = 2^2 = 4\,. \tag{2.22}$$

Notice that both the input and the output of the inverse image are sets and not just numbers. At this point, we separate the upcoming text into the two parts based on the character of the random variable.

2.2 Discrete Random Variable

In this case, the random variable can take on only discrete values in $\mathbb{R}$, which we can express as

$$\mathrm{R}(X) = \{X_1, X_2, \ldots, X_N\} = \{X_i\}_{i=1}^N\,, \tag{2.23}$$

where the fact that we started indexing from $i = 1$ is purely conventional and definitely not necessary; and N can go up to infinity. We then define the *probability distribution* of X as

$$w_i = P\Big[X^{-1}\big(\{X_i\}\big)\Big]\,. \tag{2.24}$$

(The object inside the round brackets represents a singleton set containing just one of the X_i and not the whole range of X.) Note that one typically uses p_i instead of w_i, but as in this course we will frequently deal with the pressure P and it can be problematic to distinguish between small and capital "P" especially when writing on a board, we will stick with w_i. Also this is consistent with my previous lecture notes on Quantum Mechanics. Now let us see how does this work on the example with the coin. In this case, we have

$$\mathrm{R}(X_{\text{coin}}) = \{X_0, X_1\} = \{0, 1\}\,, \tag{2.25}$$

(This is exactly the case where it makes sense to start indexing from $i = 0$ instead of 1 to avoid confusions). Then,

$$X_{\text{coin}}^{-1}\big(\{0\}\big) = \{\text{heads}\}\,. \tag{2.26}$$

But this is a valid element of $\mathcal{F}_{\text{coin}}$ to which the probability function P_{coin} assigns the value

$$P_{\text{coin}}(\{\text{heads}\}) = \frac{1}{2}\,, \tag{2.27}$$

and as such,

$$w_0 = P_{\text{coin}}\Big[X^{-1}\big(\{0\}\big)\Big] = P_{\text{coin}}\big(\{\text{heads}\}\big) = \frac{1}{2}\,. \tag{2.28}$$

Similarly, then,

$$w_1 = P_{\text{coin}}\Big[X^{-1}\big(\{1\}\big)\Big] = P_{\text{coin}}\big(\{\text{tails}\}\big) = \frac{1}{2}\,. \tag{2.29}$$

Let us also work out the case where we flip the coin twice, where

$$\mathrm{R}\left(X_{\text{coin (2x)}}\right) = \{X_0, X_1, X_2\} = \{0, 1, 2\}\,. \tag{2.30}$$

(Once again, we start indexing from $i = 0$ to avoid confusions.) Then,

$$\begin{aligned} w_0 &= P_{\text{coin (2x)}}\Big[X^{-1}_{\text{coin (2x)}}\big(\{0\}\big)\Big] = P_{\text{coin (2x)}}\big(\{\text{tails} - \text{tails}\}\big) = \frac{1}{4}\,, \\ w_1 &= P_{\text{coin (2x)}}\Big[X^{-1}_{\text{coin (2x)}}\big(\{1\}\big)\Big] = P_{\text{coin (2x)}}\big(\{\text{heads} - \text{tails}, \text{tails} - \text{heads}\}\big) \\ &= P_{\text{coin (2x)}}\big(\{\text{heads} - \text{tails}\}\big) + P_{\text{coin (2x)}}\big(\{\text{tails} - \text{heads}\}\big) = \frac{1}{4} + \frac{1}{4} = \frac{1}{2}\,, \\ w_2 &= P_{\text{coin (2x)}}\Big[X^{-1}_{\text{coin (2x)}}\big(\{2\}\big)\Big] = P_{\text{coin (2x)}}\big(\{\text{heads} - \text{heads}\}\big) = \frac{1}{4}\,. \end{aligned} \tag{2.31}$$

Notice that in the second line the inverse image of $\{2\}$ gives a set of two elements, which is exactly the case where the use of a just the inverse function would not work. As we can observe, the probability distribution in both the cases sums up to one, which is what we would intuitively expect, but lets prove this generally. First, it should be obvious that

$$X^{-1}\big(\{X_i\}\big) \cap X^{-1}\big(\{X_j\}\big) = \emptyset \quad \text{for} \quad i \neq j\,, \tag{2.32}$$

since X is a function and, as such, each element of $\mathrm{D}(f)$ has exactly one image in $\mathrm{R}(f)$. But then, we must be able to make use of the second property of the probability function P to express

$$\sum_i w_i = \sum_i P\Big[X^{-1}\big(\{X_i\}\big)\Big] = P\left[\bigcup_i X^{-1}\big(\{X_i\}\big)\right] = P(\Omega) = 1\,. \tag{2.33}$$

Hence,

$$\boxed{\sum_i w_i = 1}\,, \tag{2.34}$$

which we will hereinafter refer to as the *normalization condition.* Last but not least, even though Eq. (2.24) represents the mathematically correct expression, it is not very elegant, and hence, in most textbooks, you just find something like

$$w_i = P\big(X = X_i\big)\,, \tag{2.35}$$

which is much more readable and we will use this notation hereinafter.

Up to this point, for each of the previously mentioned examples, we acted like the values of the probabilities corresponding to various events were obvious. And of course, in simple intuitive cases, this is true. But let's now try to be a little more thorough. Also, from now on, whenever talking about probabilities, we will basically mean the probability distributions, as that is what physics typically works with. Generally, there are two ways to determine the probabilities w_i.

1. *Objectively / Experimentally:* Assuming a random process and a corresponding discrete random variable X, we repeat the process N times and write down

$$N_i = \text{how many times we got the value } X_i\,. \tag{2.36}$$

The probabilities w_i are then calculated as a limit

$$w_i = \lim_{N\to\infty} \frac{N_i}{N} \,. \tag{2.37}$$

But of course, this can never be done with infinite precision.

2. *Subjectively / Theoretically:* Here we basically guess the values of w_i based on the apriori given knowledge about the process. E.g., in the case of the dice, if there is no reason to question it's fairness, then we assume that each of the possible outcomes is equally likely.

Moving on, assume we have a random process with a discrete random variable X and the corresponding probability distribution w_i. If we repeat the process N times, the average value of X is given by the arithmetic mean formula

$$\bar{X} = \frac{1}{N}\sum_i N_i X_i \,, \tag{2.38}$$

Now similarly as before, let's impose the limit $N \to \infty$ and define

$$\langle X\rangle = \lim_{N\to\infty} \bar{X} = \lim_{N\to\infty} \frac{1}{N}\sum_i N_i X_i \,. \tag{2.39}$$

By moving both the factor $1/N$ and the limit inside the sum, we get

$$\langle X\rangle = \sum_i \left(\lim_{N\to\infty} \frac{N_i}{N}\right) X_i \,. \tag{2.40}$$

But the term inside the round brackets is exactly our definition of the probability as given by Eq. (2.37), and hence,

$$\boxed{\langle X\rangle = \sum_i w_i X_i} \,. \tag{2.41}$$

This is called the *expected value* of X. The key difference between $\bar{X}$ and $\langle X\rangle$ is that $\bar{X}$ characterizes an actual experiment, while $\langle X\rangle$ is calculated purely based on the a priori knowledge of the probability distribution, and therefore characterizes the corresponding probabilistic model. By repeating exactly the same steps as above, it is then trivial to show that if instead of the expectation value of X itself we would want the expectation value of some function $f = f(X)$, the result is simply

$$\boxed{\big\langle f(X)\big\rangle = \sum_i w_i f(X_i)} \,. \tag{2.42}$$

As an example, we can take X_{dice} and calculate

$$\langle X_{\text{dice}}\rangle = \sum_{i=1}^{6} w_i X_i = \frac{1}{6}\sum_{i=1}^{6} i = \frac{21}{6} = 3.5 \,. \tag{2.43}$$

In reality, the more times we actually throw the dice, the closer we should get to this value. Note that we can conduct a similar calculation with X_{coin}, resulting in

$$\langle X_{\text{coin}} \rangle = w_0 X_0 + w_1 X_1 = 0.5\,. \tag{2.44}$$

However, as the random variable was chosen purely as a label, the expectation value has no sensible interpretation here.

To introduce another important quantity relevant to the probability distributions, we propose the following example. Assume two random processes 1 and 2 which we repeat 10×, resulting in the outcomes:

$$\begin{aligned} X^{(1)} &= \{9, 12, 8, 8, 10, 9, 11, 12, 10, 11\}\,, \\ X^{(2)} &= \{3, 15, 17, 5, 11, 14, 8, 2, 18, 7\}\,, \end{aligned} \tag{2.45}$$

see Fig. 2.1.

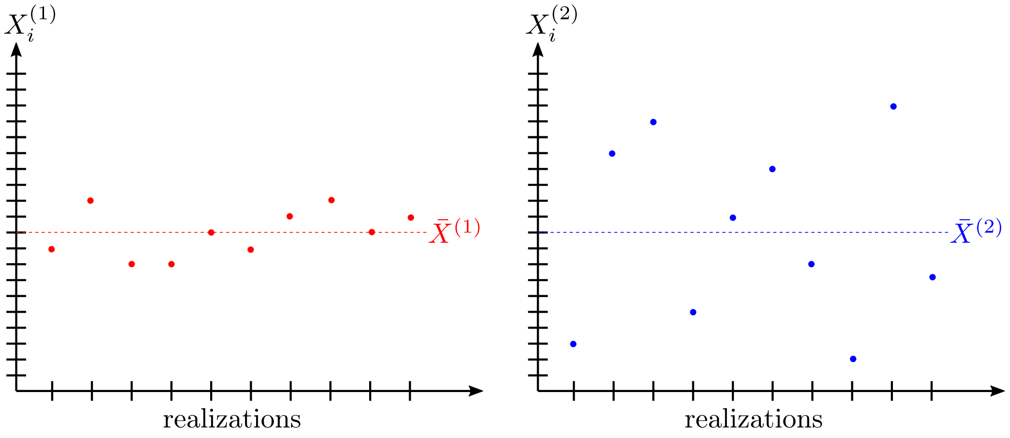

Figure 2.1: Two random processes with the same average.

In both the cases,

$$\bar{X}^{(1)} = \bar{X}^{(2)} = 10\,. \tag{2.46}$$

However, just by looking at Fig. 2.1, there is definitely a qualitative difference between the two, being that all the outcomes in the process 1 seem to lie much closer to the average value than in the process 2. Our task is to come up with a quantity that can be used to quantify the "spreadness" of the outputs around the average value. The first attempt might be as follows. We define a new random variable

$$\Delta X = X - \bar{X} \tag{2.47}$$

representing the difference between each outcome and the average value $\bar{X}$, and calculate the average, resulting in

$$\overline{\Delta X} = \frac{1}{N} \sum_i N_i \left(X_i - \bar{X} \right) = \frac{1}{N} \sum_i N_i X_i - \bar{X} = \bar{X} - \bar{X} = 0\,. \tag{2.48}$$

Evidently, this is not a good choice. The problem lies in the fact that the definition (2.47) contains both positive and negative values that average to 0. The simplest way to fix that would be to take the absolute value of the difference, i.e.,

$$\Delta X = \left|X - \bar{X}\right| \,, \tag{2.49}$$

which can now be interpreted as the distance between each output and the average. This would work, however, due to various reasons that we will not explain in this text, the more appropriate definition turns out to be

$$\Delta X^2 = \left(X - \bar{X}\right)^2 \,, \tag{2.50}$$

and the quantity representing the "spreadness" then

$$s = \sqrt{\frac{1}{N-1}\sum_i N_i \left(X_i - \bar{X}\right)^2} \,. \tag{2.51}$$

This is called the *sample standard deviation* and for the presented examples gives

$$s^{(1)} \approx 1.5 \,, \quad s^{(2)} \approx 5.8 \,. \tag{2.52}$$

Now you probably want to ask: why the heck is there $N-1$ instead of N in the denominator? Or in other words, why isn't this just the square root of the average of ΔX^2? The answer to this is provided later in the text. Right now, you just need to believe me. Similarly as with the expectation value, we now let $N \to \infty$ and define the *variance* of X as

$$\begin{aligned}
\sigma_X^2 &= \lim_{N\to\infty} \frac{1}{N-1}\sum_i N_i \left(X_i - \bar{X}\right)^2 \\
&= \sum_i \left(\lim_{N\to\infty} \frac{N_i}{N}\right)\left[X_i - \left(\lim_{N\to\infty} \bar{X}\right)\right]^2 \\
&= \sum_i w_i \big(X_i - \langle X\rangle\big)^2 \,,
\end{aligned} \tag{2.53}$$

where we substituted the expressions (2.37), (2.39); and further used the fact that

$$N - 1 \to N \quad \text{as} \quad N \to \infty \tag{2.54}$$

in the second line. By comparing the above result with the definition of the expectation value (2.42), we can write

$$\boxed{\sigma_X^2 = \sum_i w_i \big(X_i - \langle X\rangle\big)^2 = \Big\langle \big(X_i - \langle X\rangle\big)^2 \Big\rangle} \,. \tag{2.55}$$

while the square root of the variance, i.e.,

$$\boxed{\sigma_X = \sqrt{\sum_i w_i \big(X_i - \langle X\rangle\big)^2} = \sqrt{\Big\langle \big(X_i - \langle X\rangle\big)^2 \Big\rangle}} \,, \tag{2.56}$$

is then called the *standard deviation* of X. Note that by calculating

$$\left\langle \left(X_i - \langle X\rangle\right)^2 \right\rangle = \left\langle X_i^2 - 2X_i\langle X\rangle + \langle X\rangle^2 \right\rangle = \langle X_i^2\rangle - 2\langle X\rangle^2 + \langle X\rangle^2 \,, \tag{2.57}$$

we get an alternative formula for the variance

$$\sigma_X^2 = \langle X_i^2\rangle - \langle X\rangle^2 \tag{2.58}$$

which might come in handy sometimes. The difference between s^2 and σ_X^2 is then exactly the same as with $\bar{X}$ and $\langle X\rangle$. The summary of the newly introduced quantities is provided in Tab. 2.1.

experiment	**probabilistic model**
$\bar{X} = \frac{1}{N}\sum_i N_i X_i$	$\langle X\rangle = \sum_i w_i X_i$
$s^2 = \frac{1}{N-1}\sum_i N_i (X_i - \bar{X})^2$	$\sigma_X^2 = \sum_i w_i (X_i - \langle X\rangle)^2$

Table 2.1: Mutually analogous quantities related to the experiment and to the corresponding probabilistic model.

2.3 Common Discrete Distributions

In this section, we provide a list of some of the most important discrete probability distributions.

2.3.1 Discrete Uniform Distribution

Assuming a random process with discrete random variable X that has n possible outcomes, each one of those being equally probable, we have

$$w_i = \frac{1}{n} \,. \tag{2.59}$$

This is the *uniform distribution.* Further, if

$$\mathrm{R}(X) = \{a, a+1, \ldots, b-1, b\} \,, \quad a, b \in \mathbb{Z} \,, \tag{2.60}$$

then the expectation value

$$\langle X\rangle = \frac{a+b}{2} \,, \tag{2.61}$$

and the variance

$$\sigma_X^2 = \frac{(b-a+1)^2 - 1}{12} = \frac{n^2 - 1}{12} \,. \tag{2.62}$$

An example of the uniform distribution is the fair 6-sided dice.

2.3.2 Bernoulli Distribution

Assume a random process with only two possible outcomes

$$\Omega = \{\mathrm{A}, \mathrm{B}\}\,; \tag{2.63}$$

and the random variable

$$X = \begin{cases} 1\,, & \text{for A} \\ 0\,, & \text{for B} \end{cases} \quad . \tag{2.64}$$

The corresponding probability distribution must then be

$$w_1 = p\,, \quad w_0 = 1 - p\,, \quad p \in [0,1]\,. \tag{2.65}$$

This is called the *Bernoulli distribution.* The mean value

$$\langle X \rangle = p\,, \tag{2.66}$$

and the variance

$$\sigma_X^2 = p(1-p)\,. \tag{2.67}$$

However, this is exactly the case where one needs to be careful with the interpretation, as the random variable here serves purely as a label. Note that in the extreme cases where either $p = 0$ or $p = 1$, we would get $\sigma_X^2 = 0$, which should be obvious, as if all the results are either $X = 0$ or $X = 1$, then there is zero spread in the resulting values. (But technically, such a process would not be random anymore.)

2.3.3 Binomial Distribution

Assume a random process described by the Bernoulli distribution with some $p \in [0,1]$. We then define a new random process as follows. We repeat the original process n times and define the random variable X as the number of how many times we got the output A. So, e.g., if $n = 10$ and the result after $10\times$ repeating the original Bernoulli process was ABBABBABAB, then $X = 4$. In such case,

$$\mathrm{R}(X) = \{0, \dots, n\}\,, \tag{2.68}$$

with the probability distribution given by

$$w_k = \begin{pmatrix} n \\ k \end{pmatrix} p^k (1-p)^{n-k}\,, \quad k = 0, \dots, n\,. \tag{2.69}$$

This is called the *binomial distribution.* Further,

$$\langle X \rangle = np\,, \tag{2.70}$$

which is actually quite intuitive, and

$$\sigma_X^2 = np(1-p)\,. \tag{2.71}$$

An example of this can be the coin flipping, whereas if the coin is fair, we would have $p = 1 - p = 1/2$.

2.3.4 Poisson Distribution

Assume a phenomenon that happens randomly in time, and the average rate λ of how many times does it occur in a defined time interval. Let's take the random process to be waiting such time interval and counting the occurrences. The random variable X then represents the corresponding number, i.e.,

$$\mathrm{R}(X) = \{0, 1, 2, \dots\}\,. \tag{2.72}$$

The corresponding probability distribution is then given by

$$w_k = \frac{\lambda^k \mathrm{e}^{-\lambda}}{k!} \tag{2.73}$$

and called the *Poisson distribution*, with

$$\langle X \rangle = \lambda\,, \tag{2.74}$$

(logically), and

$$\sigma_X^2 = \lambda\,. \tag{2.75}$$

Here is an example. My best friend's hobby is to take photographs of wildlife animals, and especially the kingfisher, see Fig. 2.2.

Figure 2.2: Kingfisher (photo by J. Kolomaznik).

He told me that, on average, he observes 3 kingfishers during one photo session (assuming, of course, that each photo session takes the same amount of time for the Poisson distribution to work). I.e., $\lambda = 3$. Now he might ask, what is the probability that he sees 5 kingfishers in one session. The answer is then, simply,

$$w_5 = \frac{3^5 \mathrm{e}^{-3}}{5!} \approx 0.1\,. \tag{2.76}$$

Here our list of the example discrete distributions ends. We are probably not going to make use of all of these in this text, but it would feel somehow incomplete not to mention them in context of this chapter.

2.4 Multiple Random Variables

In this section, we will briefly extend our framework of a single discrete random variable to the case of multiple random variables. And to make things simpler, we will just stick with two random variables, as the generalization to three or more is then straightforward. So assume a random process with the sample space Ω for which we define

$$X : \Omega \to \mathbb{R}\,, \quad Y : \Omega \to \mathbb{R}\,. \tag{2.77}$$

The above can also be combined as

$$(X, Y) : \Omega \to \mathbb{R}^2\,. \tag{2.78}$$

As an example, assume the random process to be throwing a dice and flipping a coin at the same time. Here,

$$\Omega = \{(1, \text{heads}), (1, \text{tails}), (2, \text{heads}), \ldots, (6, \text{tails})\}\,. \tag{2.79}$$

The random variables can then be chosen as follows

$$\begin{aligned} X &= \text{“the number on the dice”}\,, \\ Y &= \begin{cases} 1, & \text{for heads} \\ 0, & \text{for tails} \end{cases}\,. \end{aligned} \tag{2.80}$$

So, e.g.,

$$(3, \text{tails}) \to (3, 0)\,, \quad (4, \text{heads}) \to (4, 1)\,, \quad \text{etc.} \tag{2.81}$$

In such case, we define the *joint probability distribution*

$$w_{ij} = P\big(X = X_i, Y = Y_j\big)\,. \tag{2.82}$$

For the above example, we would get

$$w_{ij} = \frac{1}{12}\,, \quad \forall i, j\,. \tag{2.83}$$

In many cases, however, we might actually be interested only in the probability distributions of one of the random variables, regardless of the others. We then define the *marginal probability distributions* as

$$w_i^{(X)} = \sum_j w_{ij}\,, \quad w_j^{(Y)} = \sum_i w_{ij}\,. \tag{2.84}$$

For our example, that would be

$$w_i^{(X)} = \sum_{j=0}^{1} \frac{1}{12} = \frac{2}{12} = \frac{1}{6}\,, \quad \forall i\,; \tag{2.85}$$

and

$$w_i^{(Y)} = \sum_{j=1}^{6} \frac{1}{12} = \frac{6}{12} = \frac{1}{2}\,, \quad \forall j\,. \tag{2.86}$$

This brings us to a very important definition. We say that X, Y are *independent* if

$$w_{ij} = w_i^{(X)} w_j^{(Y)}\,, \quad \forall i, j\,. \tag{2.87}$$

It is trivial to see that this holds true in the preceding example, which should be obvious, as the result on the dice does not affect the result on the coin and vice versa. But let us show a different example where this is not true. Assume the random process to be just the throw of a dice, while

$$X = \begin{cases} 1, & \text{for odd} \\ 0, & \text{for even} \end{cases}\,, \qquad Y = \begin{cases} 1\,, & \text{for} \leq 3 \\ 0\,, & \text{otherwise} \end{cases}\,. \tag{2.88}$$

Here

$$w_1^{(X)} = P[X = 1] = \frac{1}{2}\,, \quad w_1^{(Y)} = P[Y = 1] = \frac{1}{2}\,, \tag{2.89}$$

but

$$w_{11} = P[X = 1, Y = 1] = P\big(\{1, 3\}\big) = \frac{2}{6} = \frac{1}{3}\,. \tag{2.90}$$

We can see that

$$w_1^{(X)} w_1^{(Y)} \neq w_{11}\,, \tag{2.91}$$

and as such, X, Y are not independent.

Moving on, we define the expected values of X as

$$\langle X \rangle = \sum_{i,j} X_i w_{ij} = \sum_i X_i \left(\sum_j w_{ij} \right) = \sum_i X_i w_i^{(X)}\,, \tag{2.92}$$

and Y:

$$\langle Y \rangle = \sum_{i,j} Y_j w_{ij} = \sum_j Y_i \left(\sum_i w_{ij} \right) = \sum_j Y_j w_j^{(Y)}\,. \tag{2.93}$$

It is trivial to show that the expectation value is a linear operation, i.e.,

$$\langle \alpha X + \beta Y \rangle = \alpha \langle X \rangle + \beta \langle Y \rangle\,, \quad \alpha, \beta \in \mathbb{R}\,. \tag{2.94}$$

Further, for independent X, Y, we have

$$\langle XY \rangle = \sum_{i,j} X_i Y_j w_{ij} = \sum_{i,j} X_i Y_j w_i^{(X)} w_j^{(Y)} = \left(\sum_i X_i w_i^{(X)} \right) \left(\sum_i Y_j w_j^{(Y)} \right) = \langle X \rangle \langle Y \rangle\,, \tag{2.95}$$

which we just rewrite compactly as

$$\langle XY\rangle = \langle X\rangle\langle Y\rangle\,, \quad \text{for} \quad w_{ij} = w_i^{(X)} w_j^{(Y)} \tag{2.96}$$

For a general multi-variable function $f(X,Y)$, the mean value is then

$$\big\langle f(X,Y)\big\rangle = \sum_{i,j} f(X_i,Y_j) w_{ij}\,. \tag{2.97}$$

Of course, in case where f depends only on one of those, we would get

$$\big\langle f(X)\big\rangle = \sum_i f(X_i) w_i^{(X)}\,, \quad \big\langle f(Y)\big\rangle = \sum_j f(Y_j) w_j^{(Y)}\,. \tag{2.98}$$

Similarly as in Eq. (2.96), for independent X, Y and $f(X,Y)$ separable as

$$f(X,Y) = g(X)h(Y)\,, \tag{2.99}$$

then

$$\big\langle g(X)h(Y)\big\rangle = \big\langle g(X)\big\rangle\big\langle h(Y)\big\rangle\,, \quad \text{for} \quad w_{ij} = w_i^{(X)} w_j^{(Y)}\,. \tag{2.100}$$

2.5 Bessel's Correction

Now we possess all the necessary information to properly explain the weird factor $1/(N-1)$ in Eq. (2.51), so let's do this. First, assume a random process with a discrete random variable X. Then, we define a new random process as follows. We repeat the original process n times and define n random variables as

$$X^{(i)} = \text{"the value of } X \text{ at } i\text{-th realization"}\,, \quad i = 1\ldots n\,. \tag{2.101}$$

So, e.g., if the original process is the roll of a dice and we choose $n = 5$, if the result after 5 rolls is $(6, 2, 5, 1, 2)$, then

$$X^{(1)} = 6\,, \quad X^{(2)} = 2\,, \quad X^{(3)} = 5\,, \quad X^{(4)} = 1\,, \quad X^{(5)} = 2\,. \tag{2.102}$$

Now if this one realization of the new process (i.e., the n realizations of the original process) represented the only data we had available about the original process, then according to (2.51), we would say that

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X^{(i)}\,, \tag{2.103}$$

and

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}\Big(X^{(i)} - \bar{X}\Big)^2 \tag{2.104}$$

are the sample variance and the arithmetic mean of the original process, respectively. (We are going to work with the sample variance instead of the sample standard deviation purely for convenience reasons.) Our task now is to show that

$$\langle s^2 \rangle = \sigma_X^2 \,, \tag{2.105}$$

where by the expectation value on the left hand side we mean the expectation value relative to the new process, while on the right hand side the σ_X^2 represents the variance of the original process. If we are able to prove this, then the formula (2.51) truly represents the correct estimation of the standard deviation of a random process. It is crucial that you fully understand this idea, otherwise the upcoming calculation would not make any sense. For that purpose, I tried to explain it graphically in Fig. 2.3. (Ignore the dashed blue rectangle for now.)

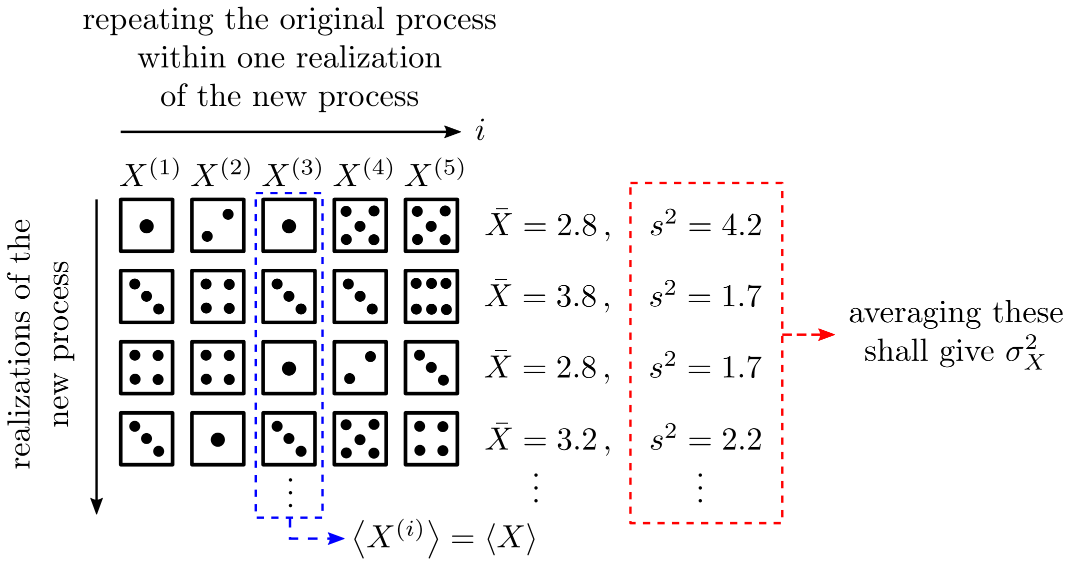

Figure 2.3: Bessel correction visualization. (I truly rolled the dice here.)

We start by expressing

$$\begin{aligned}
\langle s^2 \rangle &= \left\langle \frac{1}{n-1} \sum_{i=1}^{n} \left(X^{(i)} - \bar{X} \right)^2 \right\rangle \\
&= \frac{1}{n-1} \sum_{i=1}^{n} \left\langle \left(X^{(i)} - \frac{1}{n} \sum_{j=1}^{n} X^{(j)} \right)^2 \right\rangle \\
&= \frac{1}{n-1} \sum_{i=1}^{n} \left\langle \left(\frac{1}{n} \sum_{j=1}^{n} X^{(i)} - \frac{1}{n} \sum_{j=1}^{n} X^{(j)} \right)^2 \right\rangle
\end{aligned}$$

$$= \frac{1}{n^2(n-1)} \sum_{i=1}^{n} \left\langle \left(\sum_{j=1}^{n} X^{(i)} - \sum_{j=1}^{n} X^{(j)} \right)^2 \right\rangle$$

$$= \frac{1}{n^2(n-1)} \sum_{i=1}^{n} \left\langle \left(\sum_{j=1}^{n} \left(X^{(i)} - X^{(j)} \right) \right)^2 \right\rangle = \frac{1}{n^2(n-1)} \sum_{i=1}^{n} \langle \cdots \rangle \,. \tag{2.106}$$

(Try to keep track of the indices.) Lets focus only on the expectation value term. We can rewrite this as

$$\begin{aligned}
\langle \cdots \rangle &= \left\langle \left(\sum_{j=1}^{n} \left(X^{(i)} - X^{(j)} \right) \right) \left(\sum_{k=1}^{n} \left(X^{(i)} - X^{(k)} \right) \right) \right\rangle \\
&= \left\langle \sum_{j=1}^{n} \sum_{k=1}^{n} \left(X^{(i)} - X^{(j)} \right) \left(X^{(i)} - X^{(k)} \right) \right\rangle \\
&= \sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle \left(X^{(i)} \right)^2 - X^{(i)} X^{(k)} - X^{(i)} X^{(j)} + X^{(j)} X^{(k)} \right\rangle \\
&= \sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle \left(X^{(i)} \right)^2 \right\rangle - 2 \sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle X^{(i)} X^{(k)} \right\rangle + \sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle X^{(j)} X^{(k)} \right\rangle \,,
\end{aligned} \tag{2.107}$$

where in the last line we made use of the fact that the second and third term in the line above are symmetric under $j \leftrightarrow k$. Lets go term by term. The first one is simple:

$$\sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle \left(X^{(i)} \right)^2 \right\rangle = n^2 \left\langle \left(X^{(i)} \right)^2 \right\rangle \,, \tag{2.108}$$

since the summation goes over j, k while the term being summed contains only i. Now comes the key point. As all of the $X^{(i)}$ represent the results of realizations of the same original process, we must have

$$\left\langle X^{(i)} \right\rangle = \langle X \rangle \,, \tag{2.109}$$

where the expectation value on the right hand side is meant for the original process. This is visualized in Fig. 2.3 by the dashed blue rectangle. Similarly,

$$\left\langle \left(X^{(i)} \right)^2 \right\rangle = \left\langle X^2 \right\rangle \,, \tag{2.110}$$

which allows us to express the final form of the first term as

$$n^2 \left\langle X^2 \right\rangle \,. \tag{2.111}$$

The second term is a bit more complicated. We rewrite it as

$$-2 \sum_{j=1}^{n} \sum_{k=1}^{n} \left\langle X^{(i)} X^{(k)} \right\rangle = -2n \left\langle \left(X^{(i)} \right)^2 \right\rangle - 2n \sum_{\substack{k=1 \\ k \neq i}}^{n} \left\langle X^{(i)} X^{(k)} \right\rangle \,, \tag{2.112}$$

where the n comes out of the first sum over j. But $X^{(i)}$ and $X^{(k)}$ must be independent, as the i-th realization of the original process must not have an effect on any of the subsequent ones. (The roll of a dice does not affect any subsequent roll.) Hence, we make use of Eq. (2.96) to write

$$-2n\left\langle\left(X^{(i)}\right)^2\right\rangle - 2n\sum_{\substack{k=1\\k\neq i}}^{n}\left\langle X^{(i)}X^{(k)}\right\rangle = -2n\left\langle\left(X^{(i)}\right)^2\right\rangle - 2n\sum_{\substack{k=1\\k\neq i}}^{n}\left\langle X^{(i)}\right\rangle\left\langle X^{(k)}\right\rangle\,. \tag{2.113}$$

Further, we take Eqs. (2.109), (2.110) to express the final form of the second term as

$$-2n\left\langle X^2\right\rangle - 2n(n-1)\left\langle X\right\rangle^2\,. \tag{2.114}$$

Lastly, the third term yields

$$\begin{aligned}\sum_{j=1}^{n}\sum_{k=1}^{n}\left\langle X^{(j)}X^{(k)}\right\rangle &= \sum_{j=1}^{n}\left\langle\left(X^{(j)}\right)^2\right\rangle + \sum_{j=1}^{n}\sum_{\substack{k=1\\k\neq j}}^{n}\left\langle X^{(j)}\right\rangle\left\langle X^{(k)}\right\rangle \\ &= n\left\langle X^2\right\rangle + n(n-1)\langle X\rangle^2\,.\end{aligned} \tag{2.115}$$

Combining everything together, we are left with

$$\langle\cdots\rangle = n(n-1)\left[\left\langle X^2\right\rangle - \left\langle X\right\rangle^2\right] = n(n-1)\sigma_X^2\,, \tag{2.116}$$

while putting this back into (2.106) gives

$$\left\langle s^2\right\rangle = \frac{1}{n^2(n-1)}\sum_{i=1}^{n} n(n-1)\sigma_X^2 = \sigma_X^2\,. \tag{2.117}$$

Hence,

$$\left\langle s^2\right\rangle = \sigma_X^2\,, \tag{2.118}$$

and the statement of Eq. (2.51) is justified. If on the other hand one used the intuitive factor of $1/N$, we would not get this equality.

Strictly speaking, we are not going to need this for the purposes of the statistical physics, but as this is supposed to be an undergraduate advanced course, I thought it would be nice to explain it properly and not just leave it with the comment that you blindly need to trust me.

2.6 Shannon Entropy

Now we are finally getting to the most important part of why are we are doing all of this, being the (in)famous entropy. Claude Elwood Shannon (1916-2001) was trying to come up with a quantity that somehow measures the amount of disorder in a random process. Mathematically, that would be a function

$$S = S(w_1, \dots, w_N) \tag{2.119}$$

which we refer to as the *entropy*, hereinafter. (At this point, there is no relevance to the entropy introduced in context of thermodynamics.) For this purpose, he formulated four axioms (usually referred to as the Shannon-Khinchin axioms) that such a function must obey

1. Entropy is a continuous function in all of it's arguments.
2. Entropy is reaches maximum for uniform distribution, i.e., when all the outputs of a random process are equally probable.
3. Entropy remains the same when a new possible outcome is added with zero probability.
4. For multiple independent random variables, the total entropy is additive over the marginal probability distributions.

Let us comment on some of those. The purpose of the first property is as follows. If we were to change the probability distribution infinitesimally as, e.g.,

$$w_i \to w_i + \delta\,, \quad w_k \to w_k - \delta\,, \quad \text{for some } i, k\,, \tag{2.120}$$

then it would be weird if the value of the entropy jumped by a finite difference. Second, it should be intuitive that the uniform distribution must contain the maximum amount of disorder, as if each output is equally probable, then we basically cannot make any assumptions about the result, as opposed to, e.g., throwing a cat onto the floor, while even though still being a random process, we know almost certainly that it will land on it's feet. Third, if we add another possible output to the random process but with zero probability, then of course the entropy should not change, as this practically changes nothing about the process. (This should be taken as more of a mathematical requirement.) And finally, for two or more independent variables, which essentially means that the knowledge about X tells us nothing about Y and vice versa, then it seems logical to just add up the individual entropies. As opposed to this, consider the random process to be the weather outside, with X being the temperature and Y just 1 if it is snowing and 0 if it's not. If we then measure X to be 15° C, then we almost certainly know it is not snowing, so this knowledge of X significantly reduced the disorder in Y, and hence, the respective entropies would not add up anymore.

We are not going to replicate Shannon's work here and rather just provide the answer. There exists a unique function possessing all of the above stated requirements, being

$$\boxed{S = -k \sum_i w_i \ln(w_i)}\,, \tag{2.121}$$

with k being an arbitrary positive constant. Note that due to this arbitrariness, it does not matter what base of the logarithm we use, as

$$\log_a x = \frac{\log_b x}{\log_b a}\,, \tag{2.122}$$

so by choosing

$$k = \frac{k'}{\ln a}\,, \tag{2.123}$$

Eq. (2.121) becomes

$$S = -k' \sum_i w_i \log_a(w_i)\,. \tag{2.124}$$

Our task now is to show that this truly meets all the requirements. (As the second one is hardest to prove, we leave it to the end).

1. This one is trivial, as w_i and $\ln(w_i)$ are both continuous functions of w_i, and hence so must be the product of the two $w_i \ln(w_i)$.

3. Assume a probability distribution

$$w_1 \ldots w_N \tag{2.125}$$

with the entropy given by (2.121) as

$$S = -k \sum_{i=1}^{N} w_i \ln(w_i)\,. \tag{2.126}$$

Now we add a new outcome of zero probability. But instead of $w_{N+1} = 0$, we must do $w_{N+1} \to 0^+$, as $\ln(0)$ is not defined. The new entropy then becomes

$$S_{\text{new}} = -k \sum_{i=1}^{N+1} w_i \ln(w_i) = -k \sum_{i=1}^{N} w_i \ln(w_i) - k w_{N+1} \ln(w_{N+1}) = S - k \lim_{\xi \to 0^+} \xi \ln(\xi)\,. \tag{2.127}$$

Now we rewrite the last term as

$$-k \lim_{\xi \to 0^+} \xi \ln(\xi) = k \lim_{\xi \to 0^+} \frac{\ln(\xi)}{-\xi^{-1}}\,. \tag{2.128}$$

As this would result in an expression of the form ∞/∞, we can use the l'Hôpital's rule, i.e., differentiate both the numerator and the denominator by ξ, resulting in

$$k \lim_{\xi \to 0^+} \frac{\ln(\xi)}{-\xi^{-1}} \overset{\text{l'H}}{=} k \lim_{\xi \to 0^+} \frac{\xi^{-1}}{\xi^{-2}} = k \lim_{\xi \to 0^+} \xi = 0\,. \tag{2.129}$$

Hence,

$$S_{\text{new}} = S\,. \tag{2.130}$$

4. Assuming two independent random variables X, Y, i.e.,

$$w_{ij} = w_i^{(X)} w_j^{(Y)} \,, \tag{2.131}$$

we can write the following for the corresponding entropy:

$$\begin{aligned} S &= -k \sum_{i,j} w_{ij} \ln(w_{ij}) = -k \sum_{i,j} w_i^{(X)} w_j^{(Y)} \ln\left(w_i^{(X)} w_j^{(Y)}\right) \\ &= -k \sum_{i,j} w_i^{(X)} w_j^{(Y)} \left[\ln\left(w_i^{(X)}\right) + \ln\left(w_j^{(Y)}\right)\right] \\ &= -k \left(\sum_j w_j^{(Y)}\right)\left(\sum_i w_i^{(X)} \ln\left(w_i^{(X)}\right)\right) - k \left(\sum_i w_i^{(X)}\right)\left(\sum_j w_j^{(Y)} \ln\left(w_j^{(Y)}\right)\right) \\ &= -k \sum_i w_i^{(X)} \ln\left(w_i^{(X)}\right) - k \sum_j w_j^{(Y)} \ln\left(w_j^{(Y)}\right) = S^{(X)} + S^{(Y)} \,. \end{aligned} \tag{2.132}$$

Hence,

$$S = S^{(X)} + S^{(Y)} \,, \tag{2.133}$$

which is what we wanted to show.

Now before dealing with the second requirement, we must briefly remind ourselves about one very powerful method from the multi-variable calculus, being the method of Lagrange multipliers. If you are familiar with this topic, feel free to skip the following section.

2.6.1 An Aside: Lagrange Multipliers

The method of *Lagrange multipliers* is a powerful tool in multi-variable calculus to find local extrema of a function $f(x_1, \ldots, x_n)$ with N constraints of the form

$$g_i(x_1, \ldots, x_n) = 0 \,, \quad i = 1, \ldots, N \,. \tag{2.134}$$

The main idea is as follows. For simplicity, assume just one constraint

$$g(x_1, \ldots, x_n) = 0 \,. \tag{2.135}$$

Such a constraint then defines a $N-1$ dimensional hypersurface in the $(x_1, \ldots, x_N)$ space

$$\Gamma = \{\mathbf{x} : g(\mathbf{x}) = 0\} \,, \tag{2.136}$$

where $\mathbf{x} = (x_1, \ldots, x_N)$. Denoting the point of the local extrema as

$$\mathbf{x}^{(0)} = \left(x_1^{(0)}, \ldots, x_N^{(0)}\right) \,, \tag{2.137}$$

the corresponding necessary condition reads

$$\mathrm{d}f = \sum_i \left.\frac{\partial f}{\partial x_i}\right|_{\mathbf{x}^{(0)}} \mathrm{d}x_i = \left.\boldsymbol{\nabla} f\right|_{\mathbf{x}^{(0)}} \cdot \mathrm{d}\mathbf{x} \overset{!}{=} 0 \,, \tag{2.138}$$

where

$$\boldsymbol{\nabla} f=\left(\frac{\partial f}{\partial x_1},\ldots,\frac{\partial f}{\partial x_N}\right)\,, \tag{2.139}$$

and

$$\mathrm{d}\mathbf{x}=(\mathrm{d}x_1,\ldots,\mathrm{d}x_N)\ . \tag{2.140}$$

This means that we must have

$$\boldsymbol{\nabla} f\Big|_{\mathbf{x}^{(0)}}\perp \mathrm{d}\mathbf{x}\,. \tag{2.141}$$

At the same time, differentiating (2.135) gives

$$\mathrm{d}g=\boldsymbol{\nabla} g\cdot\mathrm{d}\mathbf{x}=0\,, \tag{2.142}$$

and so

$$\boldsymbol{\nabla} g\perp \mathrm{d}\mathbf{x}\,,\quad \forall\mathbf{x}\in\Gamma\,, \tag{2.143}$$

see Fig. 2.4

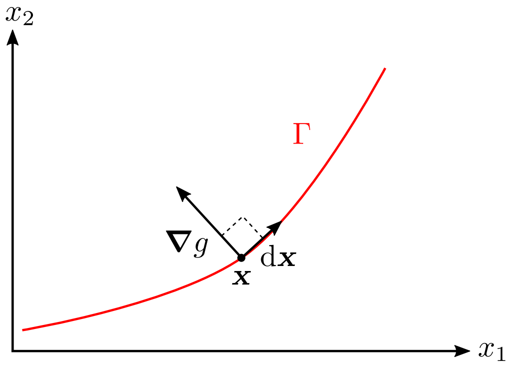

Figure 2.4: Lagrange multipliers.

By comparing Eq. (2.141) with (2.143), we get

$$\boldsymbol{\nabla} f\Big|_{\mathbf{x}^{(0)}}\propto \boldsymbol{\nabla} g\Big|_{\mathbf{x}^{(0)}}\,, \tag{2.144}$$

which is conventionally written as

$$\boldsymbol{\nabla} f\Big|_{\mathbf{x}^{(0)}}+\lambda\boldsymbol{\nabla} g\Big|_{\mathbf{x}^{(0)}}=0\,, \tag{2.145}$$

where λ is called the *Lagrange multiplier*. Hence, to find the local extrema of $f(\mathbf{x})$ under the condition $g(\mathbf{x})=0$, we must solve the system of $N+1$ equations

$$\boldsymbol{\nabla} f+\lambda\boldsymbol{\nabla} g=0\quad\wedge\quad g(\mathbf{x})=0\,. \tag{2.146}$$

This is then typically formalized as follows. We define the *Lagrangian* as

$$\mathcal{L}(\mathbf{x},\lambda)=f(\mathbf{x})+\lambda g(\mathbf{x})\,, \tag{2.147}$$

with the corresponding system of equations becoming

$$\nabla\mathcal{L} = 0 \quad \wedge \quad \frac{\partial\mathcal{L}}{\partial\lambda} = 0\,. \tag{2.148}$$

By inserting (2.147) into the above, it is then trivial to show that this exactly reproduces (2.146). Lastly, note that having two or more constraints

$$g_i(\mathbf{x}) = 0\,, \quad i = 1, 2, \dots\,, \tag{2.149}$$

we then simply extend the Lagrangian by

$$\mathcal{L}(\mathbf{x}, \lambda) = f(\mathbf{x}) + \sum_i \lambda_i g_i(\mathbf{x}) \tag{2.150}$$

and proceed further the same as before, i.e.,

$$\nabla\mathcal{L} = 0 \quad \wedge \quad \frac{\partial\mathcal{L}}{\partial\lambda_i} = 0\,. \tag{2.151}$$

2.6.2 Maximizing Entropy

Now lets use the method of Lagrange multipliers to show that the uniform distribution truly maximizes the entropy. Our task is to find the local extrema of the function

$$S(w_1, \dots, w_N) = -k\sum_{i=1}^{N} w_i \ln(w_i) \tag{2.152}$$

under the normalization constraint

$$g(w_1, \dots, w_N) = \sum_{i=1}^{N} w_i - 1 = 0\,. \tag{2.153}$$

The corresponding Lagrangian is

$$\mathcal{L}(w_1, \dots, w_N) = -k\sum_{i=1}^{N} w_i \ln(w_i) + \lambda\left(\sum_{i=1}^{N} w_i - 1\right)\,. \tag{2.154}$$

Setting

$$\frac{\partial\mathcal{L}}{\partial w_i} = -k\ln(w_i) - k + \lambda = 0 \tag{2.155}$$

allows us to express

$$w_i = \mathrm{e}^{\frac{\lambda}{k} - 1}\,. \tag{2.156}$$

Further, the last equation of (2.151) yields

$$\frac{\partial\mathcal{L}}{\partial\lambda} = \sum_{i=1}^{N} w_i - 1 = 0\,, \tag{2.157}$$

whereas substituting (2.156) for w_i then results in

$$\sum_i \mathrm{e}^{\frac{\lambda}{k}-1} - 1 = N\mathrm{e}^{\frac{\lambda}{k}-1} - 1 = 0\,, \tag{2.158}$$

i.e.,

$$\lambda = k + k\ln\left(\frac{1}{N}\right)\,. \tag{2.159}$$

Finally, putting this back into Eq. (2.156) gives

$$w_i = \frac{1}{N}\,, \tag{2.160}$$

which is the uniform distribution. The corresponding value of the entropy is then

$$S^{(\text{uniform})} = -k\sum_{i=1}^{N}\frac{1}{N}\ln\left(\frac{1}{N}\right) = k\ln(N)\,, \tag{2.161}$$

which we put into the box due to it's importance:

$$\boxed{S^{(\text{uniform})} = k\ln(N)}\,. \tag{2.162}$$

Now technically, this only guarantees the uniform distribution to represent the extremum of S and not strictly the maximum. Without diving deeper into the rigorous mathematics of the Lagrange multipliers, we can do the following. First, let us assume the distribution

$$w_i^\star = \begin{cases} 1\,, & \text{for } i = i^\star \\ 0\,, & \text{otherwise} \end{cases}\,, \tag{2.163}$$

i.e., a process that always results in $X_{i^\star}$, which is technically not a random process anymore. It is trivial to show that, in such case, $S^\star = 0$, which is what we would expect as, in that case, there is no disorder if the system behaves deterministically (not randomly). But then, if the entropy of the uniform distribution is extremum and, at the same time, there exists another distribution for which $S^\star < S^{(\text{uniform})}$, the fact that the uniform distribution is being the only extremum implies it must be the maximum.

By this, we have proven that the definition (2.121) satisfies all the Shannon-Khinchin axioms.

2.7 Continuous Random Variable

The last remaining bit is to extend our theory considering so far only discrete distributions to the continuous case, meaning that

$$\mathrm{R}(X) \subseteq \mathbb{R}\,. \tag{2.164}$$

And to keep things as simple as possible, instead of deriving everything again from the beginning, we just replace all the object of a discreet character with the appropriate analogies from the continuous world. So first, instead of the discrete index i, we use the continuous variable x:

$$X_i \to X(x)\,. \tag{2.165}$$

However, it is almost always the case that we use just

$$X(x) = x\,, \tag{2.166}$$

and we will do so hereinafter. As opposed to the discrete case where we directly defined the probability distribution w_i, here we typically start with the so called *cumulative distribution function*

$$F(x) = P(X \le x)\,, \tag{2.167}$$

the derivative of which

$$w(x) = \frac{\mathrm{d}F}{\mathrm{d}x} \tag{2.168}$$

is then called the *probability density function* whose interpretation can be deduced by rewriting the above as

$$w(x) = \frac{F(x+\mathrm{d}x) - F(x)}{\mathrm{d}x}\,, \tag{2.169}$$

i.e.,

$$w(x)\,\mathrm{d}x = F(x+\mathrm{d}x) - F(x)\,, \tag{2.170}$$

and hence,

$$\boxed{w(x)\,\mathrm{d}x = P\big(X \in [x, x+\mathrm{d}x]\big)}\,. \tag{2.171}$$

The probability density function $w(x)$ then plays a similar role as the discrete distribution w_i does. To translate from the discrete world to the continuous one, we then simply replace

$$w_i \to w(x)\,, \qquad \sum_i \to \int \cdots \,\mathrm{d}x\,. \tag{2.172}$$

Accordingly, the normalization condition reads

$$\int\limits_{\mathrm{R}(X)} w(x)\,\mathrm{d}x = 1\,, \tag{2.173}$$

Further, we define the expectation value of x as

$$\langle X\rangle = \int\limits_{\mathrm{R}(X)} x\,w(x)\,\mathrm{d}x\,, \tag{2.174}$$

or for a general function $f(X)$ as

$$\langle f(X)\rangle = \int\limits_{\mathrm{R}(X)} f(x)\,w(x)\,\mathrm{d}x\,. \tag{2.175}$$

Moreover, the variance of X is given by

$$\sigma_X^2 = \int\limits_{\mathrm{R}(X)} \big(x - \langle X\rangle\big)^2 w(x)\,\mathrm{d}x\,, \tag{2.176}$$

with σ_X being the standard deviation. Finally, the formula for the entropy becomes

$$S = -k \int\limits_{\mathrm{R}(X)} w(x)\ln w(x)\mathrm{d}x\,. \tag{2.177}$$

2.8 Common Continuous Distributions

In this section, we provide a list of some of the most important continuous probability distributions.

2.8.1 Continuous Uniform Distribution

Assuming a random process with continuous random variable X such that

$$\mathrm{R}(X) = [a, b]\,, \tag{2.178}$$

the probability density of the *uniform distribution* is given by

$$w(x) = \frac{1}{b-a}\,. \tag{2.179}$$

And as the name suggests, this is basically just a continuous analogy to the discrete uniform distribution. The expectation value is

$$\langle X\rangle = \frac{a+b}{2} \tag{2.180}$$

and the variance

$$\sigma_X^2 = \frac{(b-a)^2}{12}\,. \tag{2.181}$$

As an example, if measure the current in an electric circuit, the result of the multimeter shall be read as

$$I = (\text{displayed value } \pm \delta)\,\mathrm{A}\,. \tag{2.182}$$

This means that true value

$$\{I\} \in [\text{displayed value } - \delta, \text{displayed value } + \delta]\,. \tag{2.183}$$

Typically, then, the corresponding probability density is considered uniform (that would be specified by the manufacturer).

2.8.2 Normal or Gaussian Distribution

Assuming

$$\mathrm{R}(X) = \mathbb{R}\,, \tag{2.184}$$

the probability density of the *normal distribution* is given by

$$w(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \equiv \mathcal{N}(\mu, \sigma) \tag{2.185}$$

with the expected value

$$\langle X \rangle = \mu\,, \tag{2.186}$$

and the variance

$$\sigma_X^2 = \sigma^2\,. \tag{2.187}$$

This has so many applications that it is hard to select one specific case for demonstration. Nevertheless, I think that one of the most important properties is the relevance to the *central limit theorem*, which states the following. The playground is almost the same as with the Bessel's correction, so we assume a random process with a (discrete or continuous) random variable X such that

$$\langle X \rangle = \mu\,, \quad \sigma_X^2 = \sigma\,. \tag{2.188}$$

Then, we define a new random process where we repeat the original process n times and define

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X^{(i)}\,. \tag{2.189}$$

The central limit theorem then states that if we take $\bar{X}$ to be the random variable of the new process, then

$$w(\bar{X}) \to \mathcal{N}(\mu, \sigma/n) \quad \text{as} \quad n \to \infty\,. \tag{2.190}$$

2.9 Multiple Continuous Random Variables

For multiple continuous random variables (once again, we do this only for two) X, Y, we define the *joint cumulative distribution function*

$$F(x, y) = P\left(X \leq x, Y \leq y\right) \tag{2.191}$$

and the *joint probability density function*

$$w(x, y) = \frac{\partial^2 F}{\partial y \partial x}\,. \tag{2.192}$$

Expressing the above as

$$w(x, y) = \frac{1}{\mathrm{d}x\,\mathrm{d}y}\Big[F(x+\mathrm{d}x, y+\mathrm{d}y) - F(x+\mathrm{d}x, y) - F(x, y+\mathrm{d}y) + F(x, y)\Big]\,, \tag{2.193}$$

the interpretation is then

$$w(x,y)\,\mathrm{d}x\,\mathrm{d}y = P\big(X\in[x,x+\mathrm{d}x], Y\in[y,y+\mathrm{d}y]\big)\,. \tag{2.194}$$

The normalization condition therefore reads

$$\int\limits_{\mathrm{R}[X]\times\mathrm{R}[Y]} w(x,y)\,\mathrm{d}x\,\mathrm{d}y = 1\,. \tag{2.195}$$

The *marginal probability densities* become

$$w^{(X)}(x) = \int\limits_{\mathrm{R}(Y)} w(x,y)\,\mathrm{d}y\,,\quad w^{(Y)}(y) = \int\limits_{\mathrm{R}(X)} w(x,y)\,\mathrm{d}x\,. \tag{2.196}$$

while if X, Y are independent, it must hold that

$$w(x,y) = w^{(X)}(x)\,w^{(Y)}(y)\,. \tag{2.197}$$

Further, the expectation values are

$$\langle X\rangle = \int\limits_{\mathrm{R}[X]} x\,w^{(X)}(x)\,\mathrm{d}x\,,\quad \langle Y\rangle = \int\limits_{\mathrm{R}[Y]} y\,w^{(Y)}(y)\,\mathrm{d}x\,, \tag{2.198}$$

and so on.

2.10 Summary

Well, this section turned out to be a bit longer than I initially expected. Of course, we could have done everything much simpler, similarly as, e.g., in my lecture notes on Quantum Mechanics. But on the other hand, I came up to the conclusion that if there is one topic in theoretical physics that deserves a proper walkthrough the theory of probability, it must definitely be the Statistical Physics. But let's stop wasting any more time and let us finally get to the part you all have been awaiting from the beginning.

Chapter 3

Statistical Physics

As already mentioned in the discussion present at the end of the first chapter, the main purpose of statistical physics is to find the expression for either the entropy S or one of the thermodynamic potentials $(U, F, H, G, \Phi_{\mathrm{G}})$ as a function of the corresponding triplet of determining parameters. (This will be hereinafter referred to as the *fundamental relation.*) In these lecture notes, we are going to learn three different ways to approach this problem called the *micro-canonical*, *canonical* and *grand-canonical* formalism. Accordingly, this chapter is divided into the three corresponding parts. But before we start, here is an important note. In all of those formalisms, we assume the system of particles to be confined to some finite volume V. At the same time, quantum mechanics teaches us that such a confinement basically always implies the allowed energy levels of the system to be discrete. Therefore, in all of our upcoming derivations, we will always start by assuming a discrete energy spectrum, while the classical case would then be taken as some sort of a continuous limit. This part is mostly based on D. Tong's lecture notes on statistical physics.

3.1 Fundamental Principles

In our framework, the starting point of any calculation in statistical physics is always to formulate the problem macroscopically by using the language of thermodynamics. This can be summarized by the following three steps:

1. We select a (typically simple) system, hereinafter referred to as the *studied system*, for which we want to determine the fundamental relation.
2. We take the studied system to be a part of an externally isolated composite system in equilibrium.
3. Based on the equilibrium conditions, we choose a suitable triplet of determining parameters and the corresponding quantity (S or one of the potentials).

Now let us investigate what is going on at the microscopic level. The quantum mechanics teaches us that a general system is always in some microstate $|\psi_i\rangle$ with the corresponding value of energy E_i such that

$$\hat{\mathbf{H}} \left|\psi_i\right\rangle = E_i \left|\psi_i\right\rangle \, . \tag{3.1}$$

However, since the system as a whole is isolated, it is constrained by

$$E = const. \, , \tag{3.2}$$

and hence, the only accessible microstates are those that satisfy

$$\hat{\mathbf{H}} \left|\psi_i\right\rangle = E \left|\psi_i\right\rangle \, . \tag{3.3}$$

Further, let us denote Ω as the number of the accessible microstates, which is just the degeneracy factor

$$\Omega = g(E) \, . \tag{3.4}$$

Now comes the key idea of the whole concept of statistical physics. In an ideal world, if an isolated system sits in one of the eigenstates of the Hamilton operator, it will stay there forever. (We are silently assuming $\hat{\mathbf{H}}$ not being explicitly dependent on time, but since we are dealing with equilibrium – i.e., a macroscopically static state – then this is basically required.) However, in reality, there is no such thing as perfect isolation, and what actually happens is that the system is constantly being subjected to various forms of random interactions with the surrounding world. (This can be traced down to the fact that even the vacuum is filled with random fluctuations of the fundamental quantum fields.) As a result of this, a real system continuously and rapidly transitions randomly among all the accessible microstates. (This is the point where randomness comes into play.) However, we cannot just give up the idea of a system being isolated as that is one of the key properties that conditions the applicability of the postulates of thermodynamics. To get out of this, we propose the following.

> The random interactions are so weak that they do not alter the set of accessible microstates to the system, which remains identical to that of a perfectly isolated system. Their only effect is to induce random transitions among those microstates.

This then immediately raises the following question: What are the probabilities corresponding to the individual microstates? First, let's explain what do we mean by the probabilities. Assume that the system stays in equilibrium for a finite time interval τ and denote τ_i as the amount of time spent in the i-th microstate. Then, in analogy with our earlier definition of the objective/experimental way of determining probabilities,

$$w_i = \lim_{\tau \to \infty} \frac{\tau_i}{\tau} \, . \tag{3.5}$$

The answer is then provided by the fundamental postulate of the statistical physics:

> In an externally isolated system in equilibrium, all the accessible microstates are equally probable.

Or in other words,

$$\boxed{w_i = \frac{1}{\Omega}}\,. \tag{3.6}$$

(Note that this is tightly connected to the so called *ergodic hypothesis*, which is something you might encounter during your studies.) Now recall that thermodynamics defines the entropy as the quantity that is maximized in equilibrium. But at the same time, (3.6) is a uniform distribution and we have already shown that a uniform distribution maximizes the Shannon entropy

$$S = -k \sum_{i=1}^{\Omega} w_i \ln(w_i) = k \ln \Omega\,. \tag{3.7}$$

Therefore, we identify

$$\boxed{S(E) = k_{\mathrm{B}} \ln \Omega(E)} \tag{3.8}$$

as the entropy of an externally isolated system, where

$$\boxed{k_{\mathrm{B}} = 1.380649 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}} \tag{3.9}$$

is called the *Boltzmann constant* whose value is chosen to reproduce the Kelvin temperature scale. This is the famous *Boltzmann entropy formula.* This is also the point where we have taken two initially unrelated definitions of the entropy and declared them as one simply based on their common property of reaching maximum in equilibrium.

3.2 Micro-canonical Formalism

In the *micro-canonical* formalism, we assume having just the studied system (externally isolated) in equilibrium with the determining parameters (U, V, N). Hence, our goal is to find the fundamental relation in the form

$$S = S(U, V, N)\,. \tag{3.10}$$

Once again, the external isolation imposes the constraint

$$E = \mathit{const.}\,, \tag{3.11}$$

so the accessible microstates must obey

$$\hat{\mathbf{H}} \left| \psi_i \right\rangle = E \left| \psi_i \right\rangle\,. \tag{3.12}$$

Recall that thermodynamics knows only the internal energy U. But since all of the accessible microstates have the same energy $(E_i = E)$, it shall be obvious that

$$\boxed{E = U}\,. \tag{3.13}$$

Hence, to calculate the entropy, we determine the accessible microstates by solving

$$\hat{\mathbf{H}} \left| \psi \right\rangle = U \left| \psi \right\rangle\,, \tag{3.14}$$

count them, i.e.,

$$\Omega = g(U)\,, \tag{3.15}$$

and finally – according to Eq. (3.8) – express

$$\boxed{S(U) = k_\mathrm{B} \ln \Omega(U)}\,. \tag{3.16}$$

This is the sought fundamental relation. (As we will see, S will also depend on N and sometimes on V.)

Now assume having two individually isolated simple systems in equilibrium with the respective values of the internal energies $U^{(1)}$ and $U^{(2)}$, see Fig. 3.1.

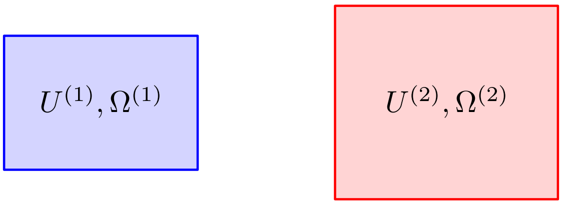

Figure 3.1: Two isolated systems.

Denoting

$$\Omega^{(1)} = g^{(1)}\left(U^{(1)}\right)\,, \quad \Omega^{(2)} = g^{(2)}\left(U^{(2)}\right)\,, \tag{3.17}$$

the total number of accessible microstates to the combined system must be

$$\Omega_\mathrm{tot} = \Omega^{(1)}\Omega^{(2)}\,. \tag{3.18}$$

Calculating the total entropy of the combined system then gives

$$S_\mathrm{tot} = k_\mathrm{B} \ln \Omega_\mathrm{tot} = k_\mathrm{B} \ln\left(\Omega^{(1)}\Omega^{(2)}\right) = k_\mathrm{B} \ln \Omega^{(1)} + k_\mathrm{B} \ln \Omega^{(2)} = S^{(1)} + S^{(2)}\,. \tag{3.19}$$

This is the additivity of entropy.

3.2.1 An Aside: Stirling's Approximation

During various calculations in statistical physics, one often encounters an expression of the form

$$\ln N! \tag{3.20}$$

However, we do not want our formulas to contain factorials as they are not very pleasant to work with mathematically. Fortunately, there is a nice way to approximate the above for large N, which will basically always be the case (recall that, typically, $N \sim 10^{23}$). First, we express

$$\ln N! = \sum_{n=1}^{N} \ln n\,. \tag{3.21}$$

Then, we approximate

$$\begin{aligned}\sum_{n=1}^{N} \ln n \approx \int_{1}^{N} \mathrm{d}x \ln x = (x \ln x - x)\Big|_{1}^{N} &= N \ln N - N - 1 \\ &\approx N \ln N - N = N(\ln N - 1) \approx N \ln N\,,\end{aligned} \tag{3.22}$$

see Fig. 3.2.

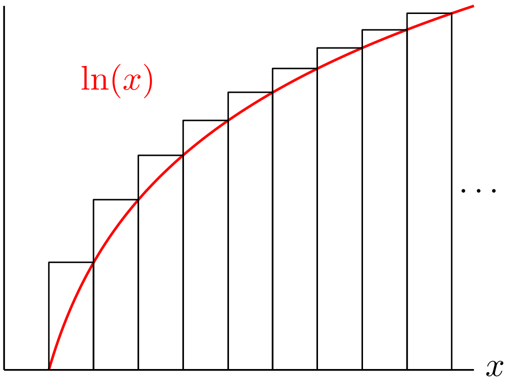

Figure 3.2: Stirling's approximation.

By combining (3.21) and (3.22), we get the desired result

$$\boxed{\ln N! \approx N \ln N}\,, \tag{3.23}$$

which is the *Stirling's approximation.*

3.2.2 Two-level System

The two-level system is probably the simplest possible model situation that we can analyze. So assume our simple system to be consisting of N atoms fixed in space, while each one of those can take on only one of the two possible values of the energy, being

$$\varepsilon_0 = 0\,, \quad \varepsilon_1 = \varepsilon\,, \tag{3.24}$$

hereinafter referred to as the ground state and the excited state, respectively. (We use ε instead of E to stress out that we are talking here only about one particle and not the system as a whole.) This then essentially represents the simplest possible model of solid. The internal energy of such system must then be expressible as

$$U = \varepsilon N_\varepsilon\,, \tag{3.25}$$

where N_ε stands for the total number of excited particles. The external isolation imposes the constraint

$$U = const.\,, \tag{3.26}$$

i.e.,

$$N_\varepsilon = const. \tag{3.27}$$

The question now is: How many microstates are there that all correspond to the internal energy U? The answer is simply the number of combinations of selecting N_ε excited atoms from the total number of N, i.e.,

$$\Omega = \begin{pmatrix} N \\ N_\varepsilon \end{pmatrix} = \frac{N!}{(N - N_\varepsilon)!N_\varepsilon!}\,. \tag{3.28}$$

Combining this with (3.25), we get

$$\Omega = \frac{N!}{(N - \frac{U}{\varepsilon})!\frac{U}{\varepsilon}!}\,, \tag{3.29}$$

To calculate the entropy, we employ Eq. (3.16) and obtain

$$S = k_\mathrm{B} \ln \Omega = k_\mathrm{B} \ln N! - k_\mathrm{B} \ln \left(N - \frac{U}{\varepsilon}\right)! - k_\mathrm{B} \ln \frac{U}{\varepsilon}!\,. \tag{3.30}$$

First, it is easy to check that for both the extreme cases, i.e., $U = 0$ or $U = N/\varepsilon$, we get $S = 0$, which should be intuitive, as this implies either all the atoms being in the ground state or all being excited, and hence, there is no disorder. Now we make an assumption of $N, N_\varepsilon \gg 1$, allowing us to make use of the Stirling's approximation, by which the above becomes

$$\begin{aligned} S &\approx k_\mathrm{B} N \ln N - k_\mathrm{B}\left(N - \frac{U}{\varepsilon}\right) \ln \left(N - \frac{U}{\varepsilon}\right) - k_\mathrm{B} \frac{U}{\varepsilon} \ln \frac{U}{\varepsilon} \\ &= -k_\mathrm{B} N \left[\left(1 - \frac{U}{\varepsilon N}\right) \ln \left(1 - \frac{U}{\varepsilon N}\right) + \frac{U}{\varepsilon N} \ln \frac{U}{\varepsilon N}\right]\,, \end{aligned} \tag{3.31}$$

Notice that now we have

$$S = S(U, N)\,, \tag{3.32}$$

meaning that we know everything about the system. So let's calculate the temperature. We get

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{k_\mathrm{B}}{\varepsilon} \ln \left(\frac{\varepsilon N}{U} - 1\right)\,. \tag{3.33}$$

It is trivial to show that $[T] = \mathrm{K}$. Further, let's invert the above as

$$U = \frac{\varepsilon N}{1 + \exp \frac{\varepsilon}{k_\mathrm{B} T}} = \frac{\varepsilon N}{1 + \mathrm{e}^{\beta \varepsilon}}\,, \tag{3.34}$$

where we substituted

$$\boxed{\beta \equiv \frac{1}{k_\mathrm{B} T}}\,. \tag{3.35}$$

(This is one of the most commonly used substitutions in statistical physics and we will use it very often). Dividing (3.34) by N, the average energy per atom is then

$$u \equiv \frac{U}{N} = \frac{\varepsilon}{1 + \mathrm{e}^{\beta\varepsilon}} \,. \tag{3.36}$$

In the limit of high temperatures, we get

$$\lim_{T \to \infty} U = \lim_{\beta \to 0} \frac{\varepsilon N}{1 + \mathrm{e}^{\beta\varepsilon}} = \frac{\varepsilon N}{2} \,, \tag{3.37}$$

meaning that half of the atoms are excited. Now this might seem a bit counterintuitive at first, so let's see why is that. Assume that we were to raise the temperature of our system by adding heat quasi-statically at constant N. But the formula for the quasi-static heat

$$\mathrm{d}S = \frac{\text{đ}Q}{T} \tag{3.38}$$

tells us that adding heat to the system increases the entropy. Hence, heating up to the limit of infinite temperatures essentially means increasing the entropy up to the maximum possible value. Looking back at Eq. (3.33), we can see that the maximum of the entropy is truly reached for $U = \varepsilon N/2$.

Last but not least, there is one more quantity that we are usually interested by, being the heat capacity. There are various types of heat capacities used in the world of thermodynamics, but the most typical one is the capacity at constant volume, defined as

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}} \,. \tag{3.39}$$

In this specific case, we get

$$C_V = N \frac{\varepsilon^2}{k_\mathrm{B} T^2} \frac{\exp\left(\frac{\varepsilon}{k_\mathrm{B} T}\right)}{\left[1 + \exp\left(\frac{\varepsilon}{k_\mathrm{B} T}\right)\right]^2} \,, \tag{3.40}$$

or

$$c_V \equiv \frac{C_V}{N} = \frac{\varepsilon^2}{k_\mathrm{B} T^2} \frac{\exp\left(\frac{\varepsilon}{k_\mathrm{B} T}\right)}{\left[1 + \exp\left(\frac{\varepsilon}{k_\mathrm{B} T}\right)\right]^2} \tag{3.41}$$

on average per atom. We see that

$$\lim_{T \to \infty} C_V = 0 \,. \tag{3.42}$$

To calculate the limit $T \to \infty$, we rewrite (3.40) using β as

$$C_V = N k_\mathrm{B} \varepsilon^2 \beta^2 \frac{\exp(\beta\varepsilon)}{\left[1 + \exp(\beta\varepsilon)\right]^2} \tag{3.43}$$

and proceed as

$$\lim_{T\to 0} C_V = \lim_{\beta\to\infty} Nk_{\mathrm{B}}\varepsilon^2\beta^2 \frac{\exp(\beta\varepsilon)}{[1+\exp(\beta\varepsilon)]^2} = Nk_{\mathrm{B}}\varepsilon^2 \lim_{\beta\to\infty} \frac{\beta^2}{\exp(\beta\varepsilon)} = 0\,. \tag{3.44}$$

Also zero. This means that the heat capacity contains a maximum at some temperature $T_\star$, see Fig. 3.3.

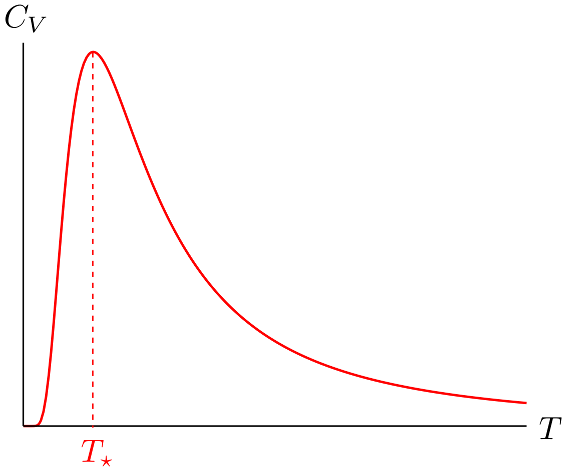

Figure 3.3: Shottky Anomaly.

This effect is called the *Shottky Anomaly* and can be observed in solid-state physics.

3.2.3 Einstein Model of Crystalline Solid

Of course, in a more realistic model of a solid, the atoms cannot be just assumed fixed in space. Hence, let us now analyse another model being the so-called *Einstein model of the crystalline solid*, where we assume each atom acting like a harmonic oscillator vibrating about a fixed point of the respective crystal lattice. From quantum mechanic, we know that the energy spectrum of a 1D harmonic oscillator is given by

$$E_n = \hbar\omega\left(\frac{1}{2}+n\right)\,, \quad n = 0,1,2,\dots\,, \tag{3.45}$$

ω being the angular frequency and $\hbar$ the Planck constant. However, atoms in solids are allowed to oscillate in three independent modes corresponding to the x, y, z axes, and hence, the energy spectrum of the i-th atom is

$$\varepsilon_i = \hbar\omega\left(\frac{3}{2}+n_{i1}+n_{i2}+n_{i3}\right) = \hbar\omega\left(\frac{3}{2}+\sum_{j=1}^{3} n_{ij}\right)\,, \quad n_{ij} = 0,1,2,\dots \tag{3.46}$$

with n_{i1} representing the number of energy quanta corresponding to the x-mode, and similarly for n_{i2}, n_{i3}. The total energy of the solid is then

$$U = \sum_{i=1}^{N} \varepsilon_i = \hbar\omega \sum_{i=1}^{N} \left(\frac{3}{2} + \sum_{j=1}^{3} n_{ij} \right) = \frac{3N\hbar\omega}{2} + \hbar\omega n \,, \tag{3.47}$$

with N being the number of atoms and

$$n = \sum_{i=1}^{N} \sum_{j=1}^{3} n_{ij} \tag{3.48}$$

the total amount of energy quanta. Our task now is to calculate the number of accessible microstates subject to the constraint

$$U = const. \,, \tag{3.49}$$

i.e.,

$$n = \frac{U}{\hbar\omega} - \frac{3N}{2} = const. \tag{3.50}$$

In other words, we must figure out how many ways are there to distribute n energy quanta between 3 oscillation modes of N atoms. The best way to visualise this is as follows. Imagine having n coins, each representing a single quantum of energy, which we place in a row on a table (a really long one). Then, we separate those coins using $3N-1$ matches into $3N$ slots, see Fig. 3.4.

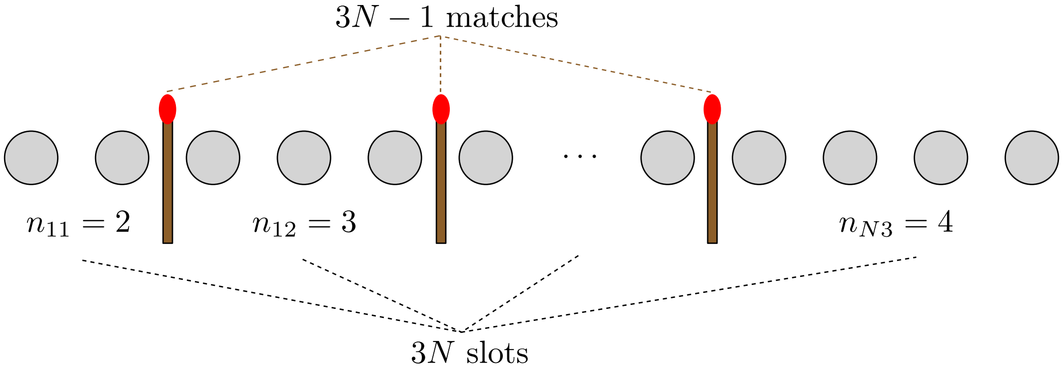

Figure 3.4: Einstein solid represented by coins and matches.

The k-th slot then represents the $[1+(k \bmod 3)]$-th mode of oscillation of the $(1+\lfloor k/3 \rfloor)$-th atom, and the number of coins in it the respective amount of energy quanta. Hence, the total number of accessible microstates is equal to the number of combinations of distributing $3N-1$ matches among $n+N-1$ possible places, i.e.,

$$\Omega = \binom{n+3N-1}{3N-1} = \frac{(n+3N-1)!}{n!(3N-1)!} \approx \frac{(n+3N)!}{n!(3N)!} \,. \tag{3.51}$$

The entropy is then

$$\begin{aligned} S &= k_{\rm B} \ln \Omega = k_{\rm B} \ln (n+3N)! - k_{\rm B} \ln n! - k_{\rm B} \ln(3N)! \\ &\approx k_{\rm B} (n+3N) \ln (n+3N) - k_{\rm B} n \ln n - k_{\rm B} (3N) \ln(3N) \\ &= 3N k_{\rm B} \left[\left(1 + \frac{n}{3N}\right) \ln \left(1 + \frac{n}{3N}\right) - \frac{n}{3N} \ln \frac{n}{3N} \right] . \end{aligned} \tag{3.52}$$

Calculating the temperature gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\partial S}{\partial n}\frac{{\rm d}n}{{\rm d}U} = \frac{1}{\hbar\omega}\frac{\partial S}{\partial n} = \frac{k_{\rm B}}{\hbar\omega} \ln\left(1 + \frac{3N}{n}\right) , \tag{3.53}$$

from which we obtain

$$n = \frac{3N}{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1} , \tag{3.54}$$

and further by substituting from (3.50)

$$U = 3N\frac{\hbar\omega}{2} + 3N\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1} . \tag{3.55}$$

See that in the limit

$$\lim_{T\to 0} U = \lim_{T\to 0} \left[\frac{3}{2}\hbar\omega N + \frac{3N\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1}\right] = 3N\frac{\hbar\omega}{2} , \tag{3.56}$$

meaning that all the oscillation modes are in the ground state. Next, the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3N(\hbar\omega)^2}{k_{\rm B}T^2}\frac{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1\right]^2} . \tag{3.57}$$

Defining the vibrational temperature

$$T_{\text{vib.}} = \frac{\hbar\omega}{k_{\rm B}} , \tag{3.58}$$

then for $T \gg T_{\text{vib.}}$, i.e.,

$$\frac{\hbar\omega}{k_{\rm B}T} \ll 1 , \tag{3.59}$$

we can Taylor expand

$$\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) \approx 1 + \frac{\hbar\omega}{k_{\rm B}T} \tag{3.60}$$

to get

$$C_V \approx 3Nk_{\rm B} \quad , \tag{3.61}$$

which is called the *Dulong-Petit law* (the heat capacity at high temperatures is approximately constant). Here we also can see the interpretation of the Boltzmann's constant. Expressing,

$$c_V = \frac{C_V}{3N} \approx k_\mathrm{B}\,, \tag{3.62}$$

we can see that k_B is just the average heat capacity per single oscillation mode. To calculate the limit $T \to 0$, we rewrite (3.57) using β as

$$C_V = 3Nk_\mathrm{B}(\hbar\omega)^2\beta^2 \frac{\exp{(\beta\hbar\omega)}}{\left[\exp{(\beta\hbar\omega)} - 1\right]^2} \tag{3.63}$$

and follow by

$$\lim_{T\to 0} C_V = \lim_{\beta\to\infty} 3Nk_\mathrm{B}(\hbar\omega)^2\beta^2 \frac{\exp{(\beta\hbar\omega)}}{\left[\exp{(\beta\hbar\omega)} - 1\right]^2} = 3Nk_\mathrm{B}(\hbar\omega)^2 \lim_{\beta\to\infty} \frac{\beta^2}{\exp{(\beta\hbar\omega)}} = 0\,. \tag{3.64}$$

The full profile of $C_V = C_V(T)$ is depicted in Fig. 3.5.

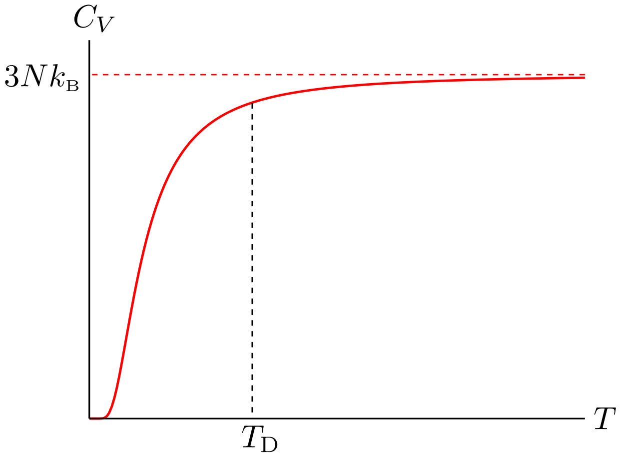

Figure 3.5: Heat capacity of the Einstein model of the crystalline solid.

3.2.4 Diathermal Contact

Assume having two initially isolated systems of internal energies $U_\mathrm{i}^{(1)}, U_\mathrm{i}^{(2)}$ and placing them together in a diathermal contact. After waiting some time, the combined system reaches a new equilibrium state with the total energy

$$E_\mathrm{tot} = U_\mathrm{i}^{(1)} + U_\mathrm{i}^{(2)}\,. \tag{3.65}$$

As the subsystems are allowed to exchange heat, their respective energies are no longer fixed, but it must still hold that

$$E^{(1)} + E^{(2)} = E_\mathrm{tot}\,. \tag{3.66}$$

The total number of accessible microstates to the combined system becomes

$$\Omega_{\text{tot}} = \sum_{E_n^{(1)}} \Omega^{(1)}\left(E_n^{(1)}\right)\, \Omega^{(2)}\left(E_{\text{tot}} - E_n^{(1)}\right) , \tag{3.67}$$

where the sum is now understood not over the microstates but over the energy levels of the first system. (We are cheating here a bit as connecting the two systems generally changes the set of microstates of each system and their corresponding energy levels, but if the mutual interactions are limited only to the boundaries where the number of particles mediating the interactions is small compared to the total numbers, this can be neglected.) Employing the Boltzmann entropy formula,

$$\Omega_{\text{tot}} = \sum_{E_n^{(1)}} \exp\left(\frac{S^{(1)}\left(E_n^{(1)}\right) + S^{(2)}\left(E_{\text{tot}} - E_n^{(1)}\right)}{k_{\text{B}}}\right) , \tag{3.68}$$

Now typically, the entropy scales as

$$S \sim N\, . \tag{3.69}$$

(We have seen this in both of the previous examples.) The terms being summed in (3.68) are therefore of the form

$$\exp\left[N f\left(E^{(1)}\right)\right] . \tag{3.70}$$

But for very large N, such an expression becomes extremely sharply peaked at the value of energy $E_\star$ which maximizes the argument of the exponential, i.e.,

$$E_\star = \arg\max_{E^{(1)}} \left[S^{(1)}\left(E^{(1)}\right) + S^{(2)}\left(E_{\text{tot}} - E^{(1)}\right)\right] , \tag{3.71}$$

see Fig. 3.6.

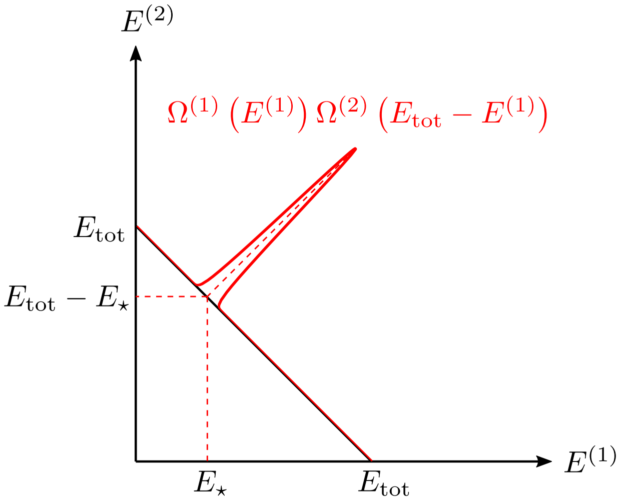

Figure 3.6: Diathermal contact.

In the above equation, we shall now recognize exactly the procedure of determining the values of equilibrium parameters introduced in the first chapter. I.e., take the entropies of the individual subsystems, add them up, and maximize w.r.t. the internal constraints. Therefore, we identify

$$U_{\mathrm{f}}^{(1)} = E_\star\,, \quad U_{\mathrm{f}}^{(2)} = E_{\mathrm{tot}} - E_\star\,, \tag{3.72}$$

meaning that the internal energies represent the most probable energies. At this point, we shall stress out that even though there of course exist microstates where the subsystems have different values of energies, their number is so negligible that, in reality, we would never observe them! Accordingly, we take

$$\Omega_{\mathrm{tot}} \approx \exp\left(\frac{S^{(1)}\left(U_{\mathrm{f}}^{(1)}\right) + S^{(2)}\left(U_{\mathrm{f}}^{(2)}\right)}{k_{\mathrm{B}}}\right) = \Omega^{(1)}\left(U_{\mathrm{f}}^{(1)}\right)\Omega^{(2)}\left(U_{\mathrm{f}}^{(2)}\right)\,, \tag{3.73}$$

while

$$S_{\mathrm{tot}} = S^{(1)}\left(U_{\mathrm{f}}^{(1)}\right) + S^{(2)}\left(U_{\mathrm{f}}^{(2)}\right) \geq S^{(1)}\left(U_{\mathrm{i}}^{(1)}\right) + S^{(2)}\left(U_{\mathrm{i}}^{(2)}\right)\,. \tag{3.74}$$

This is the second law. Moreover, expressing Eq. (3.71) as

$$\left.\frac{\partial S^{(1)}}{\partial E^{(1)}}\right|_{E_\star} = \left.\frac{\partial S^{(2)}}{\partial E^{(2)}}\right|_{E_{\mathrm{tot}}-E_\star} \tag{3.75}$$

and substituting from (3.72), we just get

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}\,, \tag{3.76}$$

which is exactly the condition on thermal equilibrium.

3.3 Canonical Formalism

In principle, the micro-canonical formalism must be sufficient to calculate the entropy of an arbitrary system. However, the problem is that the procedure of counting the total number of accessible microstates works only in scenarios where simple formulas from combinatorics can be applied. Hence, in this section, we introduce a different method called the *canonical formalism* which provides us with an alternative approach to obtain the desired fundamental relation that is arguably more practical.

In the canonical formalism, we assume having an externally isolated composite system consisting of the studied in diathermal contact with a large thermal reservoir of temperature T, see Fig. 3.7.

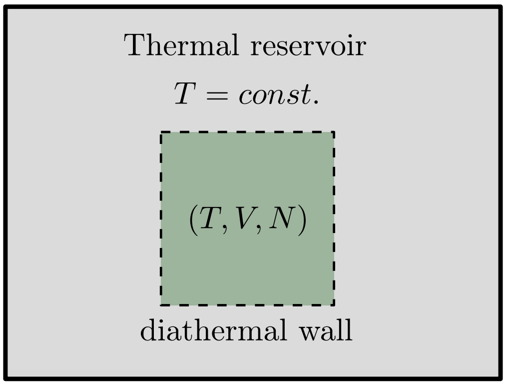

Figure 3.7: Canonical ensemble.

The thermal equilibrium further implies that the temperature of the studied system must be the same as the temperature of of the reservoir, and hence, the suitable triplet of parameters determining the equilibrium of the studied system is (T, V, N). Therefore, we are looking for the fundamental relation in the form

$$F = F(T, V, N)\,, \tag{3.77}$$

where F is the Helmholtz free energy.

The external isolation imposes the constraint

$$E^{(\mathrm{res})} + E = E_{\mathrm{tot}} = const.\,, \tag{3.78}$$

where E stands for the energy of the studied system. Our task is to determine the probability that the studied system is in a microstate with the corresponding energy E_i. But since all the accessible microstates to the composite system (studied system + reservoir) are equally probable, then this must be expressible as a fraction

$$w_i = \frac{\Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i)}{\Omega_{\mathrm{tot}}(E_{\mathrm{tot}})}\,, \tag{3.79}$$

where $\Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i)$ stands for the number of microstates accessible to the reservoir if it had energy $E_{\mathrm{tot}} - E_i$, and $\Omega_{\mathrm{tot}}(E_{\mathrm{tot}})$ is the total number of accessible microstates to the composite system. It is important to stress out that this represents the probability of an individual microstate of the studied system and not the whole energy level E_i. First, for the numerator, we can make use of the Boltzmann entropy formula to write

$$\Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i) = \exp\left(\frac{S^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i)}{k_{\mathrm{B}}}\right)\,. \tag{3.80}$$

The total number of accessible microstates then reads

$$\Omega_{\mathrm{tot}} = \sum_i \Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i)\,, \tag{3.81}$$

where the sum is understood as a sum over the microstates of the studied system. Using the Boltzmann's formula once again, this becomes

$$\Omega_{\text{tot}} = \sum_i \exp\left(\frac{S^{(\text{res})}(E_{\text{tot}} - E_i)}{k_{\text{B}}}\right) . \tag{3.82}$$

Next, note that

$$\frac{\partial S^{(\text{res})}}{\partial E^{(\text{res})}} = \frac{1}{T} = const. \,, \tag{3.83}$$

meaning that each higher order derivative must vanish. This allows us to Taylor expand

$$S^{(\text{res})}(E_{\text{tot}} - E_i) = S^{(\text{res})}(E_{\text{tot}}) - \frac{E_i}{T} . \tag{3.84}$$

Combining everything together, we finally arrive at

$$w_i = \frac{\exp\left(-\frac{E_i}{k_{\text{B}}T}\right)}{\sum\limits_i \exp\left(-\frac{E_i}{k_{\text{B}}T}\right)} . \tag{3.85}$$

The denominator is conventionally denoted as

$$\boxed{Z \equiv \sum_i \mathrm{e}^{-E_i/k_{\text{B}}T} = \sum_i \mathrm{e}^{-\beta E_i}} \tag{3.86}$$

and called the *partition function*, by which the expression for the probabilities becomes

$$\boxed{w_i = \frac{1}{Z}\,\mathrm{e}^{-E_i/k_{\text{B}}T} = \frac{1}{Z}\,\mathrm{e}^{-\beta E_i}} . \tag{3.87}$$

This is called the *Boltzmann distribution.* Notice that

$$\sum_i w_i = \frac{\sum\limits_i \mathrm{e}^{-\beta E_i}}{Z} = \frac{Z}{Z} = 1 \,, \tag{3.88}$$

which is just a sanity check that the Boltzmann distribution is correctly normalized.

3.3.1 Internal Energy

Previously, when dealing with diathermal contact in context of microcanonical formalism, we identified the internal energy as the most probable energy, which we obtained by maximizing the entropy. But here we don't know the entropy. Hence, we choose a slightly different approach and identify

$$U = \langle E \rangle = \sum_i w_i E_i = \frac{1}{Z} \sum_i \mathrm{e}^{-\beta E_i} E_i \,. \tag{3.89}$$

(We will show later that both the approaches are asymptotically equivalent.) This can be conveniently rewritten as

$$\boxed{U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z} \,. \tag{3.90}$$

Now let us calculate how much the actual energy fluctuates around U. For that purpose, we calculate

$$\begin{aligned} \sigma_E^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 &= \frac{1}{Z}\sum_i \mathrm{e}^{-\beta E_i} E_i^2 - \frac{1}{Z^2}\left(\sum_i \mathrm{e}^{-\beta E_i} E_i\right)^2 \\ &= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{\partial^2}{\partial \beta^2}\ln Z \,, \end{aligned} \tag{3.91}$$

that is

$$\sigma_E^2 = -\frac{\partial U}{\partial \beta} \,. \tag{3.92}$$

This can be further expressed as

$$\sigma_E^2 = -\frac{\partial U}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}\beta} = k_{\mathrm{B}} T^2 C_V \,, \tag{3.93}$$

But since typically

$$U \sim N \,, \quad C_V \sim N \,, \tag{3.94}$$

then

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \,, \tag{3.95}$$

and hence, for very large N,

$$E \approx U = \mathit{const.} \tag{3.96}$$

3.3.2 Entropy

Next, we focus on the entropy. From (3.79), we can express

$$\Omega_{\mathrm{tot}}(E_{\mathrm{tot}}) = \frac{\Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i)}{w_i} \,, \tag{3.97}$$

and further

$$\begin{aligned} S_{\mathrm{tot}}(E_{\mathrm{tot}}) &= k_{\mathrm{B}} \ln \Omega_{\mathrm{tot}}(E_{\mathrm{tot}}) \\ &= S^{(\mathrm{res})}(E_{\mathrm{tot}} - E_i) - k_{\mathrm{B}} \ln w_i \\ &= S^{(\mathrm{res})}(E_{\mathrm{tot}}) - \frac{E_i}{T} - k_{\mathrm{B}} \ln w_i \,. \end{aligned} \tag{3.98}$$

Calculating the expected value yields

$$\begin{aligned}S_{\text{tot}}(E_{\text{tot}}) &= S^{(\text{res})}(E_{\text{tot}}) - \frac{1}{T}\sum_i w_i E_i - k_{\text{B}}\sum_i w_i \ln w_i \\ &= S^{(\text{res})}(E_{\text{tot}}) - \frac{U}{T} - k_{\text{B}}\sum_i w_i \ln w_i \\ &= S^{(\text{res})}(E_{\text{tot}} - U) - k_{\text{B}}\sum_i w_i \ln w_i \,.\end{aligned} \tag{3.99}$$

But if U is the internal energy of the studied system, then

$$U^{(\text{res})} = E_{\text{tot}} - U \,, \tag{3.100}$$

and so

$$S_{\text{tot}}(E_{\text{tot}}) = S^{(\text{res})}\left(U^{(\text{res})}\right) - k_{\text{B}}\sum_i w_i \ln w_i \,. \tag{3.101}$$

Therefore, we identify

$$\boxed{S = -k_{\text{B}}\sum_i w_i \ln w_i} \tag{3.102}$$

as the entropy of the studied system, which is exactly the Shannon formula for the entropy. (In statistical physics, this is sometimes referred to as the Gibbs entropy formula.) Inserting the Boltzmann distribution into the above, we obtain

$$\begin{aligned}S &= -k_{\text{B}}\sum_i \frac{1}{Z}\mathrm{e}^{-\beta E_i} \ln\left(\frac{1}{Z}\,\mathrm{e}^{-\beta E_i}\right) \\ &= -k_{\text{B}}\beta\frac{1}{Z}\frac{\partial Z}{\partial\beta} + k_{\text{B}}\ln Z \\ &= -\frac{1}{T}\frac{\partial}{\partial\beta}\ln Z + k_{\text{B}}\ln Z \,.\end{aligned} \tag{3.103}$$

3.3.3 Maximizing Entropy

Since the first term on the right hand side of Eq. (3.101) is constant, then to maximize the total entropy we need to maximize S under the two constraints

$$\sum_i w_i = 1 \,, \quad \sum_i E_i\, w_i = U \,. \tag{3.104}$$

The corresponding Lagrangian reads

$$\mathcal{L} = -k_{\text{B}}\sum_i w_i \ln w_i + \lambda\left(\sum_i w_i - 1\right) + \mu\left(\sum_i E_i\, w_i - U\right) \,. \tag{3.105}$$

First, calculating

$$\frac{\partial\mathcal{L}}{\partial w_i} = -k_{\text{B}}\ln w_i - k_{\text{B}} + \lambda + \mu E_i = 0 \tag{3.106}$$

gives

$$w_i = \exp\left(\frac{\lambda + \mu E_i}{k_\mathrm{B}} - 1\right) , \tag{3.107}$$

and further

$$\frac{\partial \mathcal{L}}{\partial \lambda} = \sum_i w_i - 1 = 0 \tag{3.108}$$

leads to

$$\exp\left(\frac{\lambda}{k_\mathrm{B}} - 1\right) = \frac{1}{\sum\limits_i \mathrm{e}^{\mu E_i / k_\mathrm{B}}} . \tag{3.109}$$

Inserting the above into

$$\frac{\partial \mathcal{L}}{\partial \mu} = \sum_i E_i \, w_i - U = 0 \tag{3.110}$$

then results in

$$U = \sum_i \frac{\mathrm{e}^{\mu E_i / k_\mathrm{B}}}{\sum\limits_n \mathrm{e}^{\mu E_n / k_\mathrm{B}}} E_i \, . \tag{3.111}$$

Now comparing this with (3.89), we can immediately identify

$$\mu = -\frac{1}{T} , \tag{3.112}$$

and (3.107) becomes

$$w_i = \frac{1}{Z} \, \mathrm{e}^{-\beta E_i} \, . \tag{3.113}$$

Hence, we have shown that the Boltzmann distribution applied to the studied system truly maximizes the total entropy.

3.3.4 Helmholtz Free Energy

Finally, combining (3.90) with (3.103), we can express the Helmholtz free energy as

$$F = U - TS = -k_\mathrm{B} T \ln Z \, , \tag{3.114}$$

i.e.,

$$\boxed{F(T, V, N) = -k_\mathrm{B} T \ln Z} \, . \tag{3.115}$$

This is the sought fundamental relation. Now we know everything about the studied system, since based on the knowledge of F, we can calculate

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} , \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} , \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} , \tag{3.116}$$

and

$$U = F + TS \, . \tag{3.117}$$

3.3.5 Equivalence of Microcanonical and Canonical Formalisms

As promised earlier, the purpose of the following short discussion is to show that the microcanonical and canonical formalisms are asymptotically equivalent. The partition function of the studied system reads

$$Z = \sum_i \mathrm{e}^{-\beta E_i} \,. \tag{3.118}$$

This can be rewritten as a sum over energy levels

$$Z = \sum_{E_i} \Omega(E_i)\, \mathrm{e}^{-\beta E_i} = \sum_{E_i} \exp\left(\frac{S(E_i)}{k_\mathrm{B}} - \beta E_i\right) \,. \tag{3.119}$$

Since both

$$E \sim N \,, \quad S \sim N \,, \tag{3.120}$$

the summed terms are once again of the form

$$\exp\big[N f(E)\big] \,, \tag{3.121}$$

so we find $E_\star$ that maximizes the argument, i.e.,

$$\left.\frac{\partial S}{\partial E}\right|_{E_\star} = \frac{1}{T} \,, \tag{3.122}$$

and further identify

$$U_\mathrm{mc} = E_\star \tag{3.123}$$

as the internal energy in the micro-canonical formalism. Accordingly, we take

$$Z \approx \exp\left(\frac{S(U_\mathrm{mc})}{k_\mathrm{B}} - \beta U_\mathrm{mc}\right) \,, \tag{3.124}$$

which approaches the exact value as $N \to \infty$. Now using the canonical formalism, we define

$$\begin{aligned} U_\mathrm{c} = \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta}\left[\frac{S(U_\mathrm{mc})}{k_\mathrm{B}} - \beta U_\mathrm{mc}\right] \\ &= -\frac{1}{k_\mathrm{B}} \frac{\partial S}{\partial U_\mathrm{mc}} \frac{\partial U_\mathrm{mc}}{\partial \beta} + U_\mathrm{mc} + \beta \frac{\partial U_\mathrm{mc}}{\partial \beta} = U_\mathrm{mc} \,, \end{aligned} \tag{3.125}$$

and so

$$U_\mathrm{c} = U_\mathrm{mc} \,. \tag{3.126}$$

Similarly, using (3.103),

$$\begin{aligned} S_\mathrm{c} &= -\frac{1}{T}\frac{\partial}{\partial \beta} \ln Z + k_\mathrm{B} \ln Z \\ &= \frac{U_\mathrm{mc}}{T} + S(U_\mathrm{mc}) - k_\mathrm{B} \beta U_\mathrm{mc} \\ &= S(U_\mathrm{mc}) \,, \end{aligned} \tag{3.127}$$

i.e.,

$$S_\mathrm{c} = S_\mathrm{mc} \,. \tag{3.128}$$

3.3.6 Factorization of the Partition Function

Before moving on to some examples, there is a useful trick that we are going to make use of. Imagine that the energy of the studied system can be separated into mutually independent parts

$$E = E^{(1)} + E^{(2)} + E^{(3)} + \cdots . \tag{3.129}$$

The energy of each microstate can then be expressed as

$$E_I = E^{(1)}_{i_1} + E^{(2)}_{i_2} + E^{(3)}_{i_3} + \cdots , \tag{3.130}$$

where

$$I = \{i_1, i_2, i_3, \dots\} . \tag{3.131}$$

is a multi-index. In such case,

$$\begin{aligned} Z = \sum_I \mathrm{e}^{-\beta E_I} &= \sum_{\{i_1,i_2,i_3,\dots\}} \mathrm{e}^{-\beta\left(E^{(1)}_{i_1}+E^{(2)}_{i_2}+E^{(3)}_{i_3}+\cdots\right)} \\ &= \left(\sum_{i_1} \mathrm{e}^{-\beta E^{(1)}_{i_1}}\right)\left(\sum_{i_2} \mathrm{e}^{-\beta E^{(2)}_{i_2}}\right)\left(\sum_{i_3} \mathrm{e}^{-\beta E^{(3)}_{i_3}}\right)\cdots , \end{aligned} \tag{3.132}$$

i.e.,

$$Z = Z^{(1)} \cdot Z^{(2)} \cdot Z^{(3)} \cdots \tag{3.133}$$

Moreover,

$$\begin{aligned} F = -k_{\mathrm{B}}T \ln Z &= -k_{\mathrm{B}}T \ln\left(Z^{(1)} \cdot Z^{(2)} \cdot Z^{(3)} \cdots\right) \\ &= -k_{\mathrm{B}}T \ln Z^{(1)} - k_{\mathrm{B}}T \ln Z^{(2)} - k_{\mathrm{B}}T \ln Z^{(3)} \cdots \end{aligned} \tag{3.134}$$

and so

$$F = F^{(1)} + F^{(2)} + F^{(3)} + \cdots \tag{3.135}$$

The same would then apply to, e.g., the entropy

$$S = S^{(1)} + S^{(2)} + S^{(3)} + \cdots \tag{3.136}$$

and – most importantly – the internal energy

$$U = U^{(1)} + U^{(2)} + U^{(3)} + \cdots \tag{3.137}$$

3.3.7 Two-level System Revisited

Let us return back to the first example, being the two state system. First, since the total energy of the solid can be expressed as a sum over the individual atoms

$$E = \varepsilon^{(1)} + \varepsilon^{(2)} + \varepsilon^{(3)} + \cdots , \tag{3.138}$$

we can factorize the partition function as

$$Z = z^{(1)} \cdot z^{(2)} \cdot z^{(3)} \cdots = z^N \tag{3.139}$$

The partition function of a single atom can be expressed as

$$z = \sum_{i=0}^{1} \mathrm{e}^{-\beta\varepsilon_i} = \left(1 + \mathrm{e}^{-\beta\varepsilon}\right) , \tag{3.140}$$

and

$$Z = \left(1 + \mathrm{e}^{-\beta\varepsilon}\right)^N . \tag{3.141}$$

The Helmholtz free energy becomes

$$F = -k_{\mathrm{B}} T \ln Z = -k_{\mathrm{B}} T N \ln \left(1 + \mathrm{e}^{-\beta\varepsilon}\right) . \tag{3.142}$$

For the entropy, we can further write

$$S = -\frac{\partial F}{\partial T} = k_{\mathrm{B}} N \ln \left(1 + \mathrm{e}^{-\beta\varepsilon}\right) + k_{\mathrm{B}} N \frac{\beta\varepsilon}{1 + \mathrm{e}^{\beta\varepsilon}} . \tag{3.143}$$

Calculating the limit $T \to 0$ yields

$$\lim_{T \to 0} S = \lim_{\beta \to \infty} \left[k_{\mathrm{B}} N \ln \left(1 + \mathrm{e}^{-\beta\varepsilon}\right) + k_{\mathrm{B}} N \frac{\beta\varepsilon}{1 + \mathrm{e}^{\beta\varepsilon}} \right] = 0 \tag{3.144}$$

as expected. Finally, the internal energy is

$$U = F + TS = \frac{\varepsilon N}{1 + \mathrm{e}^{\beta\varepsilon}} , \tag{3.145}$$

which is exactly the result we got earlier.

3.3.8 Vibration

Assume the studied system to be an ensemble of N mutually non-interacting harmonic oscillators. The energy spectrum of a single oscillator is given as

$$\varepsilon_n = \frac{\hbar\omega}{2} + \hbar\omega n . \tag{3.146}$$

Expressing

$$z = \sum_n \mathrm{e}^{-\beta\varepsilon_n} = \mathrm{e}^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega n} = \mathrm{e}^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(\mathrm{e}^{-\beta\hbar\omega}\right)^n , \tag{3.147}$$

and using the formula for a geometric series

$$\sum_{n=0}^{\infty} \xi^n = \frac{1}{1 - \xi} , \tag{3.148}$$

we get

$$z = \mathrm{e}^{-\beta\hbar\omega/2} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}} . \tag{3.149}$$

The total partition sum becomes

$$Z = z^N = \left(\mathrm{e}^{-\beta\hbar\omega/2} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}} \right)^N , \tag{3.150}$$

and the Helmholtz free energy reads

$$F = -k_\mathrm{B} T \ln Z = N \frac{\hbar\omega}{2} + N k_\mathrm{B} T \ln \left(1 - \mathrm{e}^{-\beta\hbar\omega} \right) . \tag{3.151}$$

Now we can calculate the entropy

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = -N k_\mathrm{B} \ln \left(1 - \mathrm{e}^{-\beta\hbar\omega} \right) + N k_\mathrm{B} \frac{\beta\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} , \tag{3.152}$$

the limit of which as $T \to 0$ results in

$$\lim_{T\to 0} S = \lim_{\beta\to\infty} \left[-N k_\mathrm{B} \ln \left(1 - \mathrm{e}^{-\beta\hbar\omega} \right) + N k_\mathrm{B} \frac{\beta\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} \right] = 0 . \tag{3.153}$$

The internal energy is

$$U = F + TS = N \frac{\hbar\omega}{2} + N \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} . \tag{3.154}$$

Recalling that

$$T_\mathrm{vib.} = \frac{\hbar\omega}{k_\mathrm{B}} , \tag{3.155}$$

for $T \gg T_\mathrm{vib.}$,

$$U = N k_\mathrm{B} T , \tag{3.156}$$

and

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = N k_\mathrm{B} . \tag{3.157}$$

3.3.9 Einstein Model of Crystalline Solid Revisited

Considering that the Einstein model of a solid consists of $3N$ modes of independent harmonic oscillators, we can take Eq. (3.154) and simply replace $N \to 3N$ to get

$$U = 3N \frac{\hbar\omega}{2} + 3N \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} , \tag{3.158}$$

which is exactly the result as calculated previously.

3.3.10 Rotation

Let us now investigate the thermodynamical properties of N mutually non-interacting spinning particles. The kinetic energy of a single particle can be expressed as

$$\varepsilon = \frac{L^2}{2I}\,, \tag{3.159}$$

where L stands for the magnitude of angular momentum and I for the moment of inertia. From quantum mechanics, we further know that

$$L^2 = \ell(\ell+1)\hbar^2\,, \quad \ell = 0, 1, 2, \ldots \tag{3.160}$$

with

$$g(\ell) = (2\ell+1)\,. \tag{3.161}$$

The partition function for a single particle therefore reads

$$z = \sum_{\ell=0}^{\infty} (2\ell+1) \exp\left(-\frac{\ell(\ell+1)\hbar^2}{2Jk_{\mathrm{B}}T}\right)\,. \tag{3.162}$$

Unfortunately, this sum cannot be calculated analytically. However, we can at least approximate the result in the limit of low and high temperatures. Defining the *rotational temperature*

$$T_{\mathrm{R}} = \frac{\hbar^2}{2k_{\mathrm{B}}I}\,, \tag{3.163}$$

for $T \ll T_{\mathrm{R}}$, we keep only the first two terms of the sum

$$z \approx 1 + 3\exp\left(-2\frac{T_{\mathrm{R}}}{T}\right)\,. \tag{3.164}$$

Then,

$$Z = \left[1 + 3\exp\left(-2\frac{T_{\mathrm{R}}}{T}\right)\right]^N\,, \tag{3.165}$$

and

$$F = -Nk_{\mathrm{B}}T \ln\left[1 + 3\exp\left(-2\frac{T_{\mathrm{R}}}{T}\right)\right]\,. \tag{3.166}$$

The second term inside the logarithm is small, and hence, we use

$$\ln(1+x) \approx x \tag{3.167}$$

to get

$$F \approx -3Nk_{\mathrm{B}}T \exp\left(-2\frac{T_{\mathrm{R}}}{T}\right)\,. \tag{3.168}$$

Then,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = 3Nk_{\mathrm{B}}T \exp\left(-2\frac{T_{\mathrm{R}}}{T}\right) + 6Nk_{\mathrm{B}}\frac{T_{\mathrm{R}}}{T}\exp\left(-2\frac{T_{\mathrm{R}}}{T}\right)\,. \tag{3.169}$$

The internal energy reads

$$U = F + TS = 6Nk_{\mathrm{B}}T_{\mathrm{R}} \exp\left(-2\frac{T_{\mathrm{R}}}{T}\right) , \tag{3.170}$$

and the corresponding heat capacity

$$C_V = 12Nk_{\mathrm{B}} \left(\frac{T_{\mathrm{R}}}{T}\right)^2 \exp\left(-2\frac{T_{\mathrm{R}}}{T}\right) , \tag{3.171}$$

which in the limit $T \to 0$ approaches

$$\lim_{T\to 0} C_V = 0 . \tag{3.172}$$

Moving on to the second case, i.e., $T \gg T_{\mathrm{R}}$, we approximate the sum by an integral

$$z \approx \int\limits_0^\infty (2x+1) \exp\left(-x(x+1)\frac{T_{\mathrm{R}}}{T}\right) \mathrm{d}x , \tag{3.173}$$

Substituting

$$\xi = x(x+1) , \tag{3.174}$$

we get

$$z = \int\limits_0^\infty \exp\left(-\frac{T_{\mathrm{R}}}{T}\xi\right) \mathrm{d}\xi = \frac{T}{T_{\mathrm{R}}} . \tag{3.175}$$

Accordingly,

$$Z = \left(\frac{T}{T_{\mathrm{R}}}\right)^N , \tag{3.176}$$

$$F = -Nk_{\mathrm{B}}T \ln\left(\frac{T}{T_{\mathrm{R}}}\right) , \tag{3.177}$$

$$S = Nk_{\mathrm{B}} \left[1 + \ln\left(\frac{T}{T_{\mathrm{R}}}\right)\right] , \tag{3.178}$$

$$U = Nk_{\mathrm{B}}T , \tag{3.179}$$

$$C_V = Nk_{\mathrm{B}} . \tag{3.180}$$

We can see that – in the limit of high temperatures – the spinning particles exhibit the same thermodynamical behavior as the harmonic oscillators.

3.3.11 Classical Partition Function

In classical physics, a microstate of a system of N particles is represented by a point in the corresponding $6N$ dimensional phase space

$$q_1^{(a)}, q_2^{(a)}, q_3^{(a)}, p_1^{(a)}, p_2^{(a)}, p_3^{(a)}\,; \quad a = 1, \ldots, N\,, \tag{3.181}$$

with the energy

$$E = E(q, p)\,. \tag{3.182}$$

Hence, it might seem intuitive to replace the summation over microstates by the integral over the phase space as

$$Z = \sum_i \mathrm{e}^{-\beta E_i} \quad \to \quad Z' = \int\limits_\Omega \mathrm{e}^{-\beta E(q,p)}\, \mathrm{d}^{3N}q\, \mathrm{d}^{3N}p\,, \tag{3.183}$$

where Ω now stands for the $6N$-dimensional volume of the phase space accessible to the studied system. However, this is wrong. Recall that in order to calculate the Helmholtz free energy, we need to take the logarithm of Z, which requires Z being dimensionless. But since

$$p_i^{(a)} = \frac{\partial L}{\partial \dot{q}_i^{(a)}}\,, \tag{3.184}$$

then

$$\left[p_i^{(a)}\right] = \frac{\mathrm{J\,s}}{\left[q_i^{(a)}\right]}\,, \tag{3.185}$$

meaning that

$$\left[\mathrm{d}q_i^{(a)}\, \mathrm{d}p_i^{(a)}\right] = \mathrm{J\,s}\,, \tag{3.186}$$

and therefore

$$\left[Z'\right] = (\mathrm{J\,s})^{3N}\ . \tag{3.187}$$

Fortunately, there is a simple solution. We simply multiply Z' by an arbitrary constant α satisfying

$$[\alpha] = (\mathrm{J\,s})^{-3N}\ . \tag{3.188}$$

This will have no effect on U or P, since

$$\frac{\partial}{\partial \xi} \ln(\alpha Z') = \frac{\partial}{\partial \xi} \ln Z'\,, \tag{3.189}$$

but S and μ will be generally different. (But these cannot be measured anyway so we will not bother.) Now there exists a fundamental physical constant with exactly the right units, being the Planck constant, so we define

$$\boxed{Z = \frac{1}{(2\pi\hbar)^{3N}} \int\limits_\Omega \mathrm{e}^{-\beta E(q,p)}\, \mathrm{d}^{3N}q\, \mathrm{d}^{3N}p}\,. \tag{3.190}$$

At this point, this might seem as a completely random choice. However, we will show later that this actually makes a lot of sense. Accordingly, the Boltzmann distribution becomes

$$w(q,p) = \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{Z} \, \mathrm{e}^{-\beta E(q,p)} \, , \tag{3.191}$$

representing a joint probability distribution. We can check that the above is correctly normalized by calculating

$$\int\limits_{\Omega} w(q,p) \, \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p = \frac{1}{Z} \frac{1}{(2\pi\hbar)^{3N}} \int\limits_{\Omega} \mathrm{e}^{-\beta E(q,p)} \, \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p = \frac{Z}{Z} = 1 \, . \tag{3.192}$$

And that is basically all we need, as all the other formulas stay exactly the same, i.e.,

$$F = -k_{\mathrm{B}} T \ln Z \, , \tag{3.193}$$

and so on.

3.3.12 Classical Ideal Gas

The classical ideal gas represents the simplest possible model of a gas, defined by the following three assumptions:

1. Each particle can be treated as a point mass,
2. the particles mutually interact only by collisions,
3. each collision is perfectly elastic.

So assume having N particles of mass m enclosed in a container of volume V. Due to the collisions being perfectly elastic, the kinetic energy must be conserved, and as such, we can express the total energy as if the particles were non-interacting, i.e.,

$$E = \sum_{a=1}^{N} \frac{\left(p^{(a)}\right)^2}{2m} \, , \tag{3.194}$$

where

$$\left(p^{(a)}\right)^2 = \left(p_1^{(a)}\right)^2 + \left(p_2^{(a)}\right)^2 + \left(p_3^{(a)}\right)^2 \, . \tag{3.195}$$

But since the energy is separable in this way, we can calculate the partition function just for one particle and then express

$$Z = z^N \, . \tag{3.196}$$

So

$$\begin{aligned} z &= \frac{1}{(2\pi\hbar)^3} \int\limits_{\Omega} \exp\left(-\beta \frac{p^2}{2m}\right) \mathrm{d}^3x\, \mathrm{d}^3p \\ &= \frac{1}{(2\pi\hbar)^3} \left(\int\limits_V \mathrm{d}^3x\right) \left(\int\limits_{-\infty}^{\infty} \exp\left(-\beta\frac{p^2}{2m}\right) \mathrm{d}p\right)^3 \\ &= \frac{1}{(2\pi\hbar)^3} V \left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 = \frac{1}{(2\pi\hbar)^3} V \left(2\pi m k_\mathrm{B} T\right)^{3/2} \,, \end{aligned} \tag{3.197}$$

and

$$Z = \alpha^N V^N T^{3N/2} \,, \tag{3.198}$$

where

$$\alpha = \frac{1}{(2\pi\hbar)^3} \left(2\pi m k_\mathrm{B}\right)^{3/2} \,. \tag{3.199}$$

Finally, the Helmholtz free energy becomes

$$F(T, V, N) = -k_\mathrm{B} T \ln Z = -N k_\mathrm{B} T \ln\left(\alpha V T^{3/2}\right) \,, \tag{3.200}$$

Now we know everything. Calculating the entropy yields

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N k_\mathrm{B} \ln\left(\alpha V T^{3/2}\right) + \frac{3 N k_\mathrm{B}}{2} \,. \tag{3.201}$$

which allows us to express

$$U = F + TS = \frac{3}{2} N k_\mathrm{B} T \,, \tag{3.202}$$

or

$$u = \frac{U}{N} = \frac{3}{2} k_\mathrm{B} T \tag{3.203}$$

per particle on average. The corresponding heat capacity reads

$$C_V = \frac{3}{2} N k_\mathrm{B} \,. \tag{3.204}$$

Now notice that

$$\lim_{T \to 0} S = -\infty \,, \tag{3.205}$$

which might seem weird at first, but we must realize that, in this limit,

$$\lim_{T \to 0} U = 0 \,, \tag{3.206}$$

which is just wrong, as particles confined to a finite volume cannot have zero energy. Hence, at extremely low temperatures, we must consider the quantum behavior of particles, whereas this type of calculation simply fails. Further,

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_\mathrm{B} T}{V} \,, \tag{3.207}$$

i.e.,

$$PV = Nk_{\mathrm{B}}T\,, \tag{3.208}$$

which is the state equation of an ideal gas. Note that this is sometimes written in the form

$$PV = nRT\,, \tag{3.209}$$

where

$$n = \frac{N}{N_{\mathrm{A}}} \tag{3.210}$$

is the mole number,

$$N_A \approx 6.022 \cdot 10^{23}\,\mathrm{mol}^{-1} \tag{3.211}$$

the Avogadro's constant, and

$$R = N_{\mathrm{A}}k_{\mathrm{B}} \approx 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{3.212}$$

the universal gas constant.

3.3.13 Maxwell-Boltzmann Distribution

Let's express the joint probability density function for a single particle of the ideal gas as

$$w(\boldsymbol{x},\boldsymbol{p}) = \frac{1}{2\pi\hbar}\frac{1}{z}\,\mathrm{e}^{-\beta E} = \frac{1}{V\left(\sqrt{2\pi m k_{\mathrm{B}}T}\right)^3}\exp\left(-\beta\,\frac{p_1^2+p_2^2+p_3^2}{2m}\right)\,. \tag{3.213}$$

Now assume that we are not interested in the $\mathbf{x}$ dependence, so we calculate the marginal probability density

$$w(\boldsymbol{p}) = \int\limits_V w(x,p)\,\mathrm{d}^3\mathbf{x} = \frac{1}{\left(\sqrt{2\pi m k_{\mathrm{B}}T}\right)^3}\exp\left(-\beta\,\frac{p_1^2+p_2^2+p_3^2}{2m}\right)\,. \tag{3.214}$$

The interpretation is then that

$$w(\boldsymbol{p})\,\mathrm{d}^3\boldsymbol{p} = \frac{1}{\left(\sqrt{2\pi m k_{\mathrm{B}}T}\right)^3}\exp\left(-\beta\,\frac{p_1^2+p_2^2+p_3^2}{2m}\right)\,\mathrm{d}^3\boldsymbol{p}. \tag{3.215}$$

represents the probability

$$P\big(\boldsymbol{p} \in [p_1+\mathrm{d}p_1]\times[p_2+\mathrm{d}p_2]\times[p_3+\mathrm{d}p_3]\big)\,. \tag{3.216}$$

In calculus, we learn that having an integral of the form

$$\int f(x_1,x_2,x_3)\,\mathrm{d}^3\mathbf{x}\,, \tag{3.217}$$

we can switch to spherical coordinates

$$\begin{aligned} x_1 &= r\sin\theta\cos\varphi\,,\\ x_2 &= r\sin\theta\sin\varphi\,,\\ x_3 &= r\cos\theta\,, \end{aligned} \tag{3.218}$$

and rewrite (3.217) as

$$\int f\left[x_1(r,\theta,\varphi), x_2(r,\theta,\varphi), x_3(r,\theta,\varphi)\right] r^2 \sin\theta \,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi\,. \tag{3.219}$$

(Of course, we also need to adjust the integration limits accordingly.) Further, if

$$f = f\left(x_1^2 + x_2^2 + x_3^2\right) = f\left(r^2\right)\,, \tag{3.220}$$

we can integrate over the angles θ, φ to get

$$\int f\left(x_1^2 + x_2^2 + x_3^2\right)\,\mathrm{d}^3\mathbf{x} = 4\pi \int f\left(r^2\right)\,r^2\,\mathrm{d}r\,, \tag{3.221}$$

and hence,

$$f\left(x_1^2 + x_2^2 + x_3^2\right)\,\mathrm{d}^3\mathbf{x} \quad \longleftrightarrow \quad 4\pi f\left(r^2\right)\,r^2\,\mathrm{d}r\,. \tag{3.222}$$

But Eq. (3.215) is exactly in this form, allowing us to express

$$w(p)\,\mathrm{d}p = 4\pi\left(\frac{1}{2\pi m k_\mathrm{B} T}\right)^{3/2} p^2 \exp\left(-\beta\,\frac{p^2}{2m}\right)\,\mathrm{d}p\,, \tag{3.223}$$

where

$$p = |\boldsymbol{p}| = \sqrt{p_1^2 + p_2^2 + p_3^2} \tag{3.224}$$

is the magnitude of the momentum of the particle. Finally, using

$$p = mv\,, \tag{3.225}$$

the right hand side of Eq. (3.223) becomes

$$4\pi\left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right)\,\mathrm{d}v\,, \tag{3.226}$$

meaning that

$$w(v) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right) \tag{3.227}$$

represents the probability density of the particle having the magnitude of velocity v. This is the *Maxwell-Boltzmann distribution*, see Fig. 3.8

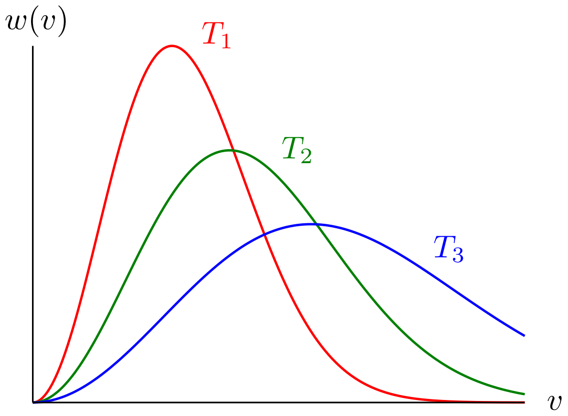

Figure 3.8: Maxwell-Boltzmann distribution for $T_1 > T_2 > T_3$.

Let us now calculate the three commonly used characteristic velocities that come out of the above.

1. The most probable velocity v_0 maximizes (3.227), i.e.,

$$\left.\frac{\partial w}{\partial v}\right|_{v_0} = 0 \qquad \longrightarrow \qquad v_0 = \sqrt{\frac{2k_\mathrm{B}T}{m}}\,. \tag{3.228}$$

2. The expected velocity

$$\langle v\rangle = \int\limits_0^\infty v\,w(v)\,\mathrm{d}v = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}}\,. \tag{3.229}$$

3. The root-mean-square velocity

$$v_\mathrm{rms} = \sqrt{\int\limits_0^\infty v^2\,w(v)\,\mathrm{d}v} = \sqrt{\frac{3k_\mathrm{B}T}{m}}\,. \tag{3.230}$$

We can see that all of those differ just by the numerical factor inside the square root, and hence, some authors then define the characteristic velocity as just

$$v_\mathrm{char.} = \sqrt{\frac{k_\mathrm{B}T}{m}}\,. \tag{3.231}$$

Note that there is a much simpler way to derive the expression for the v_rms. Recall that the internal energy of an ideal gas is just the sum of kinetic energies of all the constituent particles. Then,

$$N\frac{1}{2}mv_\mathrm{rms}^2 = \frac{3}{2}Nk_\mathrm{B}T\,, \tag{3.232}$$

and therefore

$$v_\mathrm{rms} = \sqrt{\frac{3k_\mathrm{B}T}{m}}\,. \tag{3.233}$$

3.3.14 Classical Vibration

Assume the studied system to be a collection of N independent classical harmonic oscillators. The energy of a single oscillator can be expressed as

$$\varepsilon = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \,. \tag{3.234}$$

The corresponding classical partition function can be expressed as

$$\begin{aligned} z &= \frac{1}{2\pi\hbar} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \exp\left(-\beta\frac{p^2}{2m} - \beta\frac{1}{2}m\omega^2 x^2\right) \mathrm{d}x\,\mathrm{d}p \\ &= \frac{1}{2\pi\hbar}\left(\int\limits_{-\infty}^{\infty} \exp\left(-\frac{m\omega^2 x^2}{2k_\mathrm{B}T}\right)\mathrm{d}x\right)\left(\int\limits_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2mk_\mathrm{B}T}\right)\mathrm{d}p\right) \\ &= \frac{1}{2\pi\hbar}\sqrt{\frac{2\pi k_\mathrm{B}T}{m\omega^2}}\sqrt{2\pi m k_\mathrm{B}T} = \frac{k_\mathrm{B}T}{\hbar\omega}\,, \end{aligned} \tag{3.235}$$

where we are neglecting the boundary effects since the term $\exp(-\alpha x^2)$ goes quickly to zero. (Unless the oscillator lies extremely close to the walls of the container, the integral over x can be very well approximated by the integral over the whole space.) For N such oscillators, we then have

$$Z = z^N = \left(\frac{k_\mathrm{B}T}{\hbar\omega}\right)^N \,. \tag{3.236}$$

Notice that this does not depend on m. Further,

$$F = -k_\mathrm{B}T\ln Z = -Nk_\mathrm{B}T\ln\left(\frac{k_\mathrm{B}T}{\hbar\omega}\right)\,, \tag{3.237}$$

and therefore

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_\mathrm{B} + \ln\left(\frac{k_\mathrm{B}T}{\hbar\omega}\right)\,. \tag{3.238}$$

Once again, this diverges towards $T \to 0$, since we are not considering the quantum effects. The internal energy is then

$$U = F + TS = Nk_\mathrm{B}T\,, \tag{3.239}$$

with the corresponding heat capacity

$$C_V = Nk_\mathrm{B}\,, \tag{3.240}$$

which is exactly the result of the previous calculation for $T \gg T_{\text{vib.}}$

3.3.15 Classical Rotation

The Lagrangian of a classical spinning particle expressed in spherical coordinates reads

$$L = \frac{1}{2} I \left[\dot{\theta}^2 + \sin^2(\theta)\, \dot{\varphi}^2 \right] . \tag{3.241}$$

Calculating the conjugate momenta

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = I\dot{\theta} , \quad p_\varphi = \frac{\partial L}{\partial \dot{\varphi}} = I \sin^2(\theta) \dot{\varphi} \tag{3.242}$$

allows us to express the energy of a single particle as

$$\varepsilon = \frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I \sin^2 \theta} . \tag{3.243}$$

The partition function for a single particle becomes

$$\begin{aligned} z &= \frac{1}{(2\pi\hbar)^2} \int \exp\left(-\beta \frac{p_\theta^2}{2I} - \beta \frac{p_\varphi^2}{2I \sin^2 \theta} \right) \mathrm{d}\theta \, \mathrm{d}\varphi \, \mathrm{d}p_\theta \, \mathrm{d}p_\varphi \\ &= \frac{1}{(2\pi\hbar)^2} \left(\sqrt{\frac{2\pi I}{\beta}} \right) \cdot (2\pi) \cdot \int_0^\pi \sqrt{\frac{2\pi I \sin^2 \theta}{\beta}} \, \mathrm{d}\theta \\ &= \frac{2 I k_\mathrm{B} T}{\hbar^2} . \end{aligned} \tag{3.244}$$

Therefore,

$$Z = \left(\frac{2 I k_\mathrm{B} T}{\hbar^2} \right)^N . \tag{3.245}$$

$$F = -N k_\mathrm{B} T \ln \left(\frac{2 I k_\mathrm{B} T}{\hbar^2} \right) , \tag{3.246}$$

$$S = N k_\mathrm{B} \ln \left(\frac{2 I k_\mathrm{B} T}{\hbar^2} \right) + N k_\mathrm{B} , \tag{3.247}$$

$$U = N k_\mathrm{B} T , \tag{3.248}$$

and

$$C_V = N k_\mathrm{B} . \tag{3.249}$$

This is exactly the result as obtained before for $T \gg T_\mathrm{R}$.

3.3.16 Diatomic Gas

A diatomic gas, as the name suggests, contains molecules consisting of two atoms. Such a molecule can move in the x, y, z directions, rotate and vibrate. Expressing the energy of single molecule as

$$\varepsilon = \varepsilon^{(\text{translation})} + \varepsilon^{(\text{rotation})} + \varepsilon^{(\text{vibration})} \tag{3.250}$$

and the total energy of the gas as

$$E = \sum_{a=1}^{N} \varepsilon^{(a)} , \tag{3.251}$$

we can immediately combine the results of the classical ideal gas, spinning particle and harmonic oscillator to express

$$U = U^{(\text{translation})} + U^{(\text{rotation})} + U^{(\text{vibration})} \tag{3.252}$$

and

$$C_V = C_V^{(\text{translation})} + C_V^{(\text{rotation})} + C_V^{(\text{vibration})} . \tag{3.253}$$

Since, typically,

$$T_{\text{vib.}} \gg T_{\text{R}} , \tag{3.254}$$

we can separate the temperature axis into the three corresponding regions, while

1. $C_V = \frac{3}{2} N k_{\text{B}}$ for $T < T_{\text{R}}$,
2. $C_V = \frac{5}{2} N k_{\text{B}}$ for $T_{\text{R}} < T < T_{\text{vib.}}$,
3. $C_V = \frac{7}{2} N k_{\text{B}}$ for $T > T_{\text{vib.}}$.

Note that for common diatomic gasses $(\text{N}_2, \text{O}_2, \text{H}_2, \text{CO}, \text{NO}, \dots)$ at room temperature, the second variant applies.

3.3.17 Equipartition Theorem

Assume that the energy of a single particle involves a separate term of the form

$$\varepsilon = \mathcal{C}\, \xi^2 + \text{other terms} , \tag{3.255}$$

where ξ is either a generalized coordinate or a conjugate momentum satisfying

$$\xi \in \mathbb{R} ; \tag{3.256}$$

and $\mathcal{C}$ an arbitrary constant. Such a term is called the *thermodynamic degree of freedom.* If there are f terms like this, i.e.,

$$\varepsilon = \mathcal{C}_1\, \xi_1^2 + \dots + \mathcal{C}_f\, \xi_f^2 + \text{other terms} , \tag{3.257}$$

we say the system has f thermodynamic degrees of freedom. Now for the k-th one, the corresponding part of the partition function reads

$$z_k \propto \int\limits_{-\infty}^{\infty} \mathrm{e}^{-\beta \mathcal{C} \xi^2}\, \mathrm{d}\xi = \sqrt{\frac{\pi}{\beta \mathcal{C}}}\,. \tag{3.258}$$

Then, the corresponding part of internal energy becomes

$$u_k = -\frac{\partial}{\partial \beta} \ln z_k = \frac{1}{2\beta}\,, \tag{3.259}$$

i.e.,

$$u_k = \frac{1}{2} k_{\mathrm{B}} T\,. \tag{3.260}$$

Hence, each thermodynamic degree of freedom adds $k_{\mathrm{B}}T/2$ to the total internal energy

$$u = \sum_k u_k = \frac{f}{2} k_{\mathrm{B}} T\,, \tag{3.261}$$

or

$$U = \frac{f}{2} N k_{\mathrm{B}} T\,, \tag{3.262}$$

which is the *equipartition theorem.* This, e.g., explains all the formulas related to the diatomic gas.

3.3.18 Adiabatic Process

Consider an ideal gas with the internal energy

$$U = \frac{f}{2} N k_{\mathrm{B}} T \tag{3.263}$$

undergoing a quasistatic adiabatic process

$$\mathrm{d}U = \text{đ}W = -P \mathrm{d}V\,, \tag{3.264}$$

i.e.,

$$\frac{f}{2} N k_{\mathrm{B}} \mathrm{d}T = -P \mathrm{d}V\,. \tag{3.265}$$

Using the equation of state, this becomes

$$\frac{f}{2}\left(P \mathrm{d}V + V \mathrm{d}P\right) = -P \mathrm{d}V\,, \tag{3.266}$$

and further rearranging yields

$$\frac{\mathrm{d}P}{P} + \left(1 + \frac{2}{f}\right) \frac{\mathrm{d}V}{V} = 0\,, \tag{3.267}$$

Integrating the above, we get the the *adiabatic equation*

$$PV^{\gamma} = const.\,, \tag{3.268}$$

where

$$\gamma = 1 + \frac{2}{f} \tag{3.269}$$

is called the *adiabatic exponent.* As mentioned earlier, for a typical diatomic gas at room temperature, $f = 5$, and therefore $\gamma = 1.4$.

3.3.19 Density of States

Assume having some sort of a linear 1D wave equation supporting a plane-wave solution

$$\psi(t, x) = A\,\mathrm{e}^{\mathrm{i}(\pm kx - \omega t)}\,, \tag{3.270}$$

where

$$\omega = \omega(k) \tag{3.271}$$

is the dispersion relation. If the domain is restricted to $x \in [0, L]$, the only allowed solutions are in the form of a superposition of right and left going waves of the same amplitudes, i.e.,

$$\psi(t, x) = A\cos(kx)\,\mathrm{e}^{-\mathrm{i}\omega t}\,, \tag{3.272}$$

where

$$k = \frac{\pi}{L} n\,, \quad n = 1, 2, \ldots \tag{3.273}$$

These are called *modes.* Extending the problem to 3D with the domain now being restricted to $\mathbf{x} \in [0, L_x] \times [0, L_y] \times [0, L_z]$, we would get

$$k_x = \frac{\pi}{L_x} n_x\,, \quad k_y = \frac{\pi}{L_y} n_y\,, \quad k_z = \frac{\pi}{L_z} n_z\,. \tag{3.274}$$

In the $\boldsymbol{k}$-space, each mode occupies the volume

$$\Delta k^3 = \frac{\pi^3}{V}\,, \quad V = L_x L_y L_z\,, \tag{3.275}$$

see Fig. 3.9.

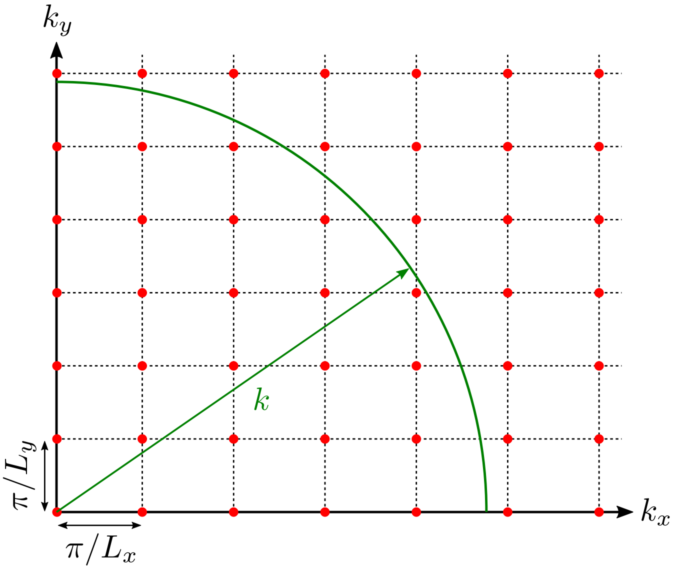

Figure 3.9: Allowed modes (red dots) represented as points in the $\boldsymbol{k}$-space.

Now lets define

$$\tilde{\Omega} = \tilde{\Omega}(k) \tag{3.276}$$

as the number of modes satisfying

$$k_x^2 + k_y^2 + k_z^2 \leq k^2\,, \tag{3.277}$$

i.e., the number of red dots within the 1/8 of the volume of the sphere of radius k represented by the green curve in the figure above. For sufficiently large k, this can be well approximated by

$$\tilde{\Omega}(k) \approx \frac{1}{\Delta k^3}\frac{1}{8}\frac{4}{3}\pi k^3 = V\frac{k^3}{6\pi^2}\,. \tag{3.278}$$

Differentiating the above w.r.t. k, we further define

$$\boxed{D(k)\,\mathrm{d}k = V\frac{k^2}{2\pi^2}\,\mathrm{d}k}\,, \tag{3.279}$$

representing the number of modes contained within the interval $[k, k+\mathrm{d}k]$. Such $D(k)$ is called the *density of states.*

3.3.20 Classical Partition Function Revisited

In quantum mechanics, a free particle is represented by a plane wave with

$$\varepsilon = \hbar\omega\,, \quad p = \hbar k. \tag{3.280}$$

Substituting into (3.279), we get

$$D(p)\,\mathrm{d}p = V\frac{4\pi p^2}{(2\pi\hbar)^3}\,\mathrm{d}p\,. \tag{3.281}$$

If we enclose the particle inside a box of volume V, each mode then represents an accessible microstate. The partition function therefore becomes

$$\begin{aligned} z &= \sum_n \mathrm{e}^{-\beta\varepsilon_n} = \sum_{\varepsilon_n}\Omega(\varepsilon_n)\,\mathrm{e}^{-\beta\varepsilon_n} = \sum_{p_n}\Omega(p_n)\,\mathrm{e}^{-\beta\varepsilon(p_n)} \\ &\approx \int_0^\infty \mathrm{e}^{-\beta\varepsilon(p)}D(p)\,\mathrm{d}p = V\frac{1}{(2\pi\hbar)^3}\int_0^\infty \mathrm{e}^{-\beta\varepsilon(p)}4\pi p^2\,\mathrm{d}p\,. \end{aligned} \tag{3.282}$$

But since

$$p^2 = p_x^2 + p_y^2 + p_z^2\,, \tag{3.283}$$

we can rewrite (3.282) as

$$z = V\frac{1}{(2\pi\hbar)^3}\int \mathrm{e}^{-\beta\varepsilon(\boldsymbol{p})}\,\mathrm{d}^3\boldsymbol{p}\,. \tag{3.284}$$

Moreover,

$$V = \int \mathrm{d}^3\mathbf{x}\,, \tag{3.285}$$

and so

$$z = \frac{1}{(2\pi\hbar)^3}\int \mathrm{e}^{-\beta\varepsilon(\boldsymbol{p})}\,\mathrm{d}^3\mathbf{x}\,\mathrm{d}^3\boldsymbol{p}\,. \tag{3.286}$$

Finally, for N particles,

$$Z = \frac{1}{(2\pi\hbar)^{3N}}\int \mathrm{e}^{-\beta E(p)}\,\mathrm{d}^{3N}x\,\mathrm{d}^{3N}p\,. \tag{3.287}$$

This shall serve as the motivation behind the constant introduced when defining the classical partition function.

3.3.21 Gibbs Paradox

We have already calculated the entropy of an ideal gas

$$S = Nk_\mathrm{B}\ln\left(\alpha VT^{3/2}\right) + \frac{3Nk_\mathrm{B}}{2}\,. \tag{3.288}$$

Now there is something weird. Recall that the entropy is supposed be an extensive quantity, meaning that scaling the system by λ should result in

$$S \to \lambda S\,. \tag{3.289}$$

However, this is clearly not the case here, as

$$V \to \lambda V\,, \quad N \to \lambda N \tag{3.290}$$

gives

$$S \to \lambda S + \lambda N k_{\mathrm{B}} \ln \lambda \neq \lambda S\,. \tag{3.291}$$

Let us see why this must be wrong. Consider two initially isolated identical copies of an ideal gas (Fig. 3.10 (a))

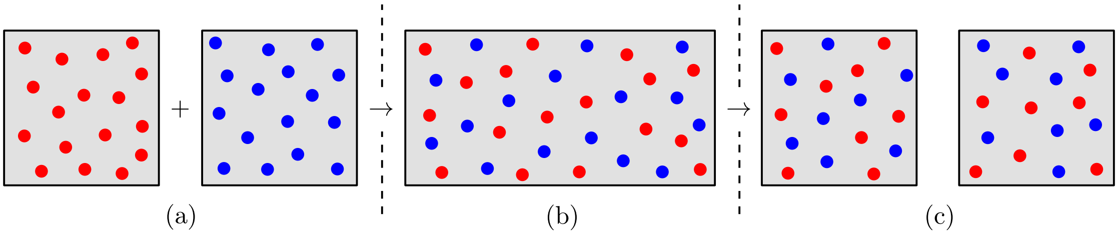

Figure 3.10: Gibbs paradox.

with the total entropy

$$S_{\mathrm{i}} = 2S_0\,, \tag{3.292}$$

S_0 being the entropy of a single copy. For the sake of the upcoming discussion, we use different colors for the particles within the two boxes, but keep in mind that physically they are identical. Now we join the copies together and let the particles mix up (Fig. 3.10 (b)). This must give the same result as having just one of the copies and scaling it by $\lambda = 2$, and hence, according to (3.291), the final entropy after the mixing becomes

$$S_{\mathrm{f}} = 2S_0 + 2N k_{\mathrm{B}} \ln 2\,. \tag{3.293}$$

Now notice that

$$S_{\mathrm{f}} > S_{\mathrm{i}}\,, \tag{3.294}$$

indicating that this ought to be an irreversible process. And it truly does seem so, as by dividing the mixed system once again into the two parts (Fig. 3.10 (c)), we will never get back the original state (the red and blue particles are irreversibly mixed up). But here comes the problem. Physically, if the particles are identical, there is no way of how we could possibly distinguish between the cases (a) and (c). (We cannot paint some particles red and the other ones blue.) And accordingly, such process should actually be fully reversible! This apparent contradiction is called the *Gibbs paradox* and our task now is to resolve it. For simplicity, assume having just 2 particles labeled as A and B. Now if

$$x^{(\mathrm{A})} = x\,, \quad p^{(\mathrm{A})} = p\,, \quad x^{(\mathrm{B})} = x'\,, \quad p^{(\mathrm{B})} = p'\,. \tag{3.295}$$

is an accessible microstate, then so must be

$$x^{(\mathrm{A})} = x'\,, \quad p^{(\mathrm{A})} = p'\,, \quad x^{(\mathrm{B})} = x\,, \quad p^{(\mathrm{B})} = p\,, \tag{3.296}$$

representing the interchange $A \leftrightarrow B$, and by using the expression

$$Z = z^N \tag{3.297}$$

we account for both of them. But if the particles are identical, then those two microstates cannot be distinguished and must be accounted for as just a single one! Accordingly, for N particles, there are $N!$ indistinguishable permutations, which can be resolved by correcting the previous formula into

$$Z = \frac{z^N}{N!}\,. \tag{3.298}$$

In such case,

$$\begin{aligned} F &= -k_\mathrm{B} T \ln\left(\frac{z^N}{N!}\right) = -N k_\mathrm{B} T \ln z + k_\mathrm{B} T \ln N! \\ &\approx -N k_\mathrm{B} T \ln z + N k_\mathrm{B} T \ln N \\ &= -N k_\mathrm{B} T \ln\left(\frac{z}{N}\right)\,. \end{aligned} \tag{3.299}$$

For the ideal gas, this gives us

$$S = N k_\mathrm{B} \ln\left(\alpha \frac{V T^{3/2}}{N}\right) + \frac{3 N k_\mathrm{B}}{2}\,, \tag{3.300}$$

which is now a perfectly extensive quantity.

3.3.22 Photon Gas

Assume the studied system to be an electromagnetic radiation of temperature T enclosed inside a cavity of volume V, hereinafter referred to as the *photon gas*. Since Maxwell equations are linear, the total energy can be expressed as a sum over the allowed modes, i.e.,

$$E = \sum_i E_i\,. \tag{3.301}$$

The same must then apply to the Helmholtz free energy, i.e.,

$$F = -k_\mathrm{B} T \sum_i \ln Z_i\,. \tag{3.302}$$

Denoting the frequency of the i-th mode as ω_i, the corresponding energy is quantized as

$$E_i = \hbar \omega_i n_i\,. \tag{3.303}$$

This allows us to calculate

$$Z(\omega_i) = \sum_{n_i=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega_i n_i} = \frac{1}{1 - \exp(-\beta \hbar \omega_i)}\,. \tag{3.304}$$

Now we rewrite the sum over the individual modes in Eq. (3.302) as a sum over the allowed frequencies

$$F = -k_\mathrm{B} T \sum_{\omega_i} \ln\left[Z(\omega_i)\right] \Omega(\omega_i)\,, \tag{3.305}$$

where $\Omega(\omega_i)$ stands for the number of modes with frequency ω_i. The above can be further approximated by

$$F \approx -k_\mathrm{B}T \int\limits_0^\infty \ln\left[Z(\omega)\right] D(\omega)\,\mathrm{d}\omega = k_\mathrm{B}T \int\limits_0^\infty \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) D(\omega)\,\mathrm{d}\omega\,. \tag{3.306}$$

The dispersion relation of electromagnetic waves reads

$$\omega = ck\,, \tag{3.307}$$

where c is the speed of light. Hence, substituting into Eq. (3.279) yields

$$D(\omega)\,\mathrm{d}\omega = V\frac{\omega^2}{2\pi^2 c^3}\,\mathrm{d}\omega\,. \tag{3.308}$$

But this is not quite right, since each mode can be further decomposed into the two orthogonal polarization states. Therefore, the correct formula reads

$$D(\omega)\,\mathrm{d}\omega = V\frac{\omega^2}{\pi^2 c^3}\,\mathrm{d}\omega\,. \tag{3.309}$$

Finally, the Helmholtz free energy becomes

$$F = k_\mathrm{B}T \int\limits_0^\infty V\frac{\omega^2}{\pi^2 c^3} \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)\,\mathrm{d}\omega\,. \tag{3.310}$$

Calculating the entropy yields

$$S = k_\mathrm{B} \int\limits_0^\infty V\frac{\omega^2}{\pi^2 c^3} \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)\,\mathrm{d}\omega + \frac{1}{T}\int\limits_0^\infty V\frac{\hbar}{\pi^2 c^3}\omega^3\frac{1}{\mathrm{e}^{\beta\hbar\omega}-1}\,\mathrm{d}\omega\,, \tag{3.311}$$

and

$$U = \int\limits_0^\infty V\frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{\mathrm{e}^{\beta\hbar\omega}-1}\,\mathrm{d}\omega\,. \tag{3.312}$$

Typically, this is then expressed in form of the energy density

$$u = \int\limits_0^\infty \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{\exp\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right)-1}\,\mathrm{d}\omega\,. \tag{3.313}$$

This is the famous *Planck radiation law*, see Fig. 3.11.

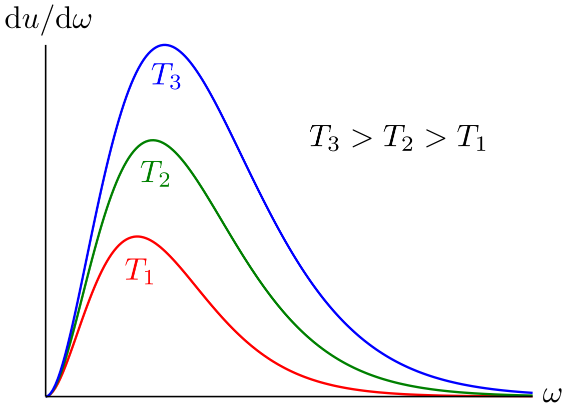

Figure 3.11: Planck radiation law.

Alternatively, we could take (3.313) and substitute for

$$\omega = 2\pi\nu \tag{3.314}$$

to get

$$u = \int_0^\infty \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right) - 1} \,\mathrm{d}\nu\,; \tag{3.315}$$

or

$$\nu = \frac{c}{\lambda}\,, \tag{3.316}$$

resulting in

$$u = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{k_\mathrm{B}T\lambda}\right) - 1} \,\mathrm{d}\lambda\,. \tag{3.317}$$

For $\hbar\omega \ll k_\mathrm{B}T$, we can approximate

$$\frac{\mathrm{d}u}{\mathrm{d}\omega} \approx \frac{\omega^2}{\pi^2 c^2} k_\mathrm{B}T\,. \tag{3.318}$$

This is the *Rayleigh-Jeans* law. We can see that the above diverges towards $\omega \to \infty$, which is called the *ultra-violet catastrophe*. In contrast, for $\hbar\omega \gg k_\mathrm{B}T$,

$$\frac{\mathrm{d}u}{\mathrm{d}\omega} \approx \frac{\hbar\omega^3}{\pi^2 c^3} \exp^{-1}\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right)\,. \tag{3.319}$$

This is the *Wien approximation*. Now let us calculate the frequency corresponding to the maximum of $\mathrm{d}u/\mathrm{d}\omega$. By setting

$$\frac{\mathrm{d}}{\mathrm{d}\omega}\left[\frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_\mathrm{B}T}\right) - 1}\right] \overset{!}{=} 0\,, \tag{3.320}$$

and substituting for

$$\xi \equiv \frac{\hbar\omega}{k_{\mathrm{B}}T}\,, \tag{3.321}$$

we get

$$3 - \xi = 3\,\mathrm{e}^{-\xi}\,. \tag{3.322}$$

The above equation does not possess an analytical solution, but can be solved numerically, yielding

$$\xi \approx 2.822\,, \tag{3.323}$$

and hence

$$\omega_{\max} = \frac{2.822 k_{\mathrm{B}}}{\hbar}\,T\,. \tag{3.324}$$

Similarly, we can do this for λ, resulting in

$$\lambda_{\max} = \frac{b}{T}\,, \quad b = 0.00289\,\mathrm{K\,m}\,. \tag{3.325}$$

This is the *Wien's displacement law.*

Next, we express the intensity

$$I = uc = \int_0^\infty \frac{\hbar\omega^3}{\pi^2 c^2} \frac{1}{\exp\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right) - 1}\,\mathrm{d}\omega\,. \tag{3.326}$$

Now imagine that there is a small hole dA at the surface of the cavity enclosing the photon gas, resulting in the energy being radiated outwards. For a specific direction of I, the radiation intensity reads

$$I_{\mathrm{rad},\theta} = I\cos\theta\,, \tag{3.327}$$

where θ is the angle between $\boldsymbol{I}$ and the normal $\boldsymbol{n}$ of dA, see Fig. 3.12.

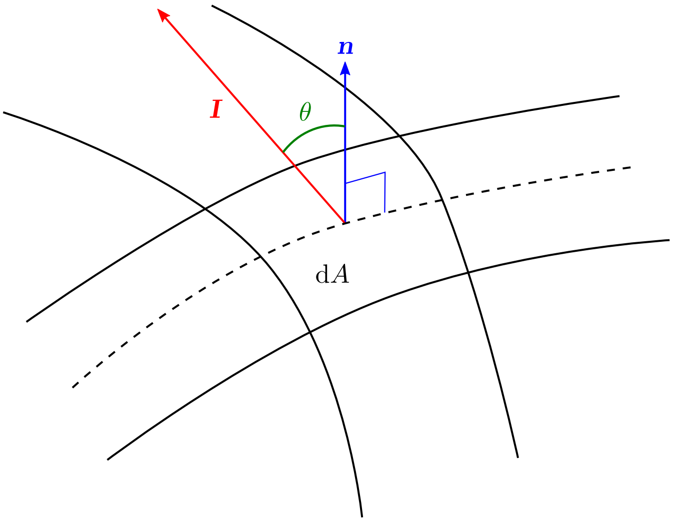

Figure 3.12: Cavity with a small hole.

Assuming the direction of I changes randomly with uniform distribution across the complete solid angle, we can express the average radiation intensity

$$I_{\text{rad}} = \frac{1}{4\pi} \int\limits_0^{2\pi} \int\limits_0^{\pi/2} I \cos\theta \, \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi = \frac{I}{4} \,, \tag{3.328}$$

Thus,

$$I_{\text{rad}} = \int\limits_0^{\infty} \frac{\hbar\omega^3}{4\pi^2 c^2} \frac{1}{\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right) - 1} \, \mathrm{d}\omega \,. \tag{3.329}$$

Using once again the substitution (3.321), we can rewrite the above as

$$I_{\text{rad}} = \frac{k_{\text{B}}^4}{4\hbar^3 \pi^2 c^2} T^4 \int\limits_0^{\infty} \frac{\xi^3}{\mathrm{e}^{\xi} - 1} \, \mathrm{d}\xi \,. \tag{3.330}$$

Further, it can be shown that

$$\int\limits_0^{\infty} \frac{\xi^3}{\mathrm{e}^{\xi} - 1} \, \mathrm{d}\xi = \frac{\pi^4}{15} \,, \tag{3.331}$$

(consult Maple or Mathematica), by which we finally arrive at

$$I_{\text{rad}} = \sigma T^4 \,, \quad \sigma = \frac{\pi^2 k_{\text{B}}^4}{60\hbar^3 c^2} \approx 5.670 \cdot 10^{-8} \, \mathrm{W\,m^{-2}\,K^{-4}} \,. \tag{3.332}$$

This is the *Stefan-Boltzmann law.*

The last bit we are going to investigate is the pressure. First, we take the expression for the free energy (3.310) and integrate by parts

$$F = -\frac{V}{3} \int\limits_0^{\infty} \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right) - 1} \, \mathrm{d}\omega \,. \tag{3.333}$$

Then,

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{1}{3} \int\limits_0^{\infty} \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right) - 1} \, \mathrm{d}\omega \,. \tag{3.334}$$

By comparing Eqs. (3.313) and (3.334), we get the famous formula

$$P = \frac{u}{3} \,. \tag{3.335}$$

Note that this is a real pressure that the photon gas exerts onto the walls of the cavity and in principle could be measured by standard methods.

3.4 Grand Canonical Formalism

The setup of the grand canonical formalism is as follows. Similarly as with the canonical formalism, we consider an externally isolated composite system consisting of the studied system in contact with a large reservoir, but this time we also allow the two to exchange particles, see Fig. 3.13.

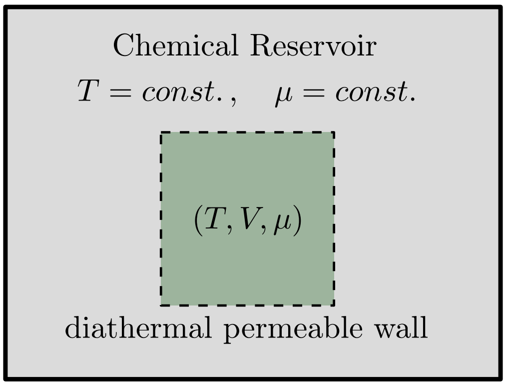

Figure 3.13: Grand-canonical formalism.

The "chemical" (this is probably not a well established term but who cares) reservoir is defined by

$$T = const.\,,\quad \mu = const.\,, \tag{3.336}$$

and the chemical equilibrium conditions imply that the temperature and chemical potential of the studied system must must be the same. The suitable triplet of equilibrium parameters is therefore (T, V, μ), with the fundamental relation taking the form

$$\Phi_{\mathrm{G}} = \Phi_{\mathrm{G}}(T, V, \mu)\,. \tag{3.337}$$

Now we can proceed basically the same as previously with the canonical formalism, just note that due to the number of particles no longer being fixed, we need two label each microstate by the pair of indices (i, N), such that

$$\hat{\mathbf{H}}\,|\psi_{nN}\rangle = E_{nN}\,|\psi_{nN}\rangle\ . \tag{3.338}$$

First, the external isolation ensures

$$E_{\mathrm{tot}} = E^{(\mathrm{res})} + E = const.\,, \tag{3.339}$$

$$N_{\mathrm{tot}} = N^{(\mathrm{res})} + N = const.. \tag{3.340}$$

The probability of (n, N)-th microstate is then

$$w_{nN} = \frac{\Omega^{(\mathrm{res})}(E_{\mathrm{tot}} - E_{nN}, N_{\mathrm{tot}} - N)}{\Omega_{\mathrm{tot}}(E_{\mathrm{tot}}, N_{\mathrm{tot}})}\,. \tag{3.341}$$

The numerator can be expressed as

$$\Omega^{(\mathrm{res})}(E_{\mathrm{tot}}-E_{nN},N_{\mathrm{tot}}-N)=\exp\left(\frac{S^{(\mathrm{res})}(E_{\mathrm{tot}}-E_{nN},N_{\mathrm{tot}}-N)}{k_{\mathrm{B}}}\right)\,,\tag{3.342}$$

while the denominator reads

$$\Omega_{\mathrm{tot}}=\sum_{n,N}\exp\left(\frac{S^{(\mathrm{res})}(E_{\mathrm{tot}}-E_{nN},N_{\mathrm{tot}}-N)}{k_{\mathrm{B}}}\right)\,.\tag{3.343}$$

Since

$$\frac{\partial S^{(\mathrm{res})}}{\partial E^{(\mathrm{res})}}=\frac{1}{T}=const.\,,\qquad\frac{\partial S^{(\mathrm{res})}}{\partial N^{(\mathrm{res})}}=-\frac{\mu}{T}=const.\,,\tag{3.344}$$

all the higher derivatives vanish and we can Taylor expand

$$S^{(\mathrm{res})}(E_{\mathrm{tot}}-E_{nN},N_{\mathrm{tot}}-N)=S^{(\mathrm{res})}(E_{\mathrm{tot}},N_{\mathrm{tot}})-\frac{E_{nN}}{T}+\frac{\mu N}{T}\,.\tag{3.345}$$

Combining everything together, we arrive at

$$w_{nN}=\frac{\exp\left(-\frac{E_{nN}-\mu N}{k_{\mathrm{B}}T}\right)}{\sum\limits_{i,N}\exp\left(-\frac{E_{nN}-\mu N}{k_{\mathrm{B}}T}\right)}\,.\tag{3.346}$$

The denominator

$$\boxed{\mathcal{Z}=\sum_{n,N}\mathrm{e}^{-\beta(E_{nN}-\mu N)}}\tag{3.347}$$

is called the *grand-canonical partition function*, using which (3.346) becomes

$$\boxed{w_{nN}=\frac{1}{\mathcal{Z}}\,\mathrm{e}^{-\beta(E_{nN}-\mu N)}}\,.\tag{3.348}$$

3.4.1 Number of Particles

In equilibrium, thermodynamics always assumes a fixed value of N, even if the system is constrained by permeable walls. Similarly as with the internal energy, this thermodynamical N is actually understood as $\langle N\rangle$. Unfortunately, there is a slight problem with the notation, since we do not have a different symbol for thermodynamical and statistical N. Nevertheless, we will see shortly that this is not much of a problem. First,

$$\langle N\rangle=\frac{1}{\mathcal{Z}}\sum_{nN}N\,\mathrm{e}^{-\beta(E_{nN}-\mu N)}=\frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu}\,,\tag{3.349}$$

i.e.,

$$\langle N\rangle=\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z}\,.\tag{3.350}$$

Now let's look at σ_N.

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2}\left[\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} + \frac{1}{\mathcal{Z}^2}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2\right] = \frac{1}{\beta^2}\frac{\partial}{\partial \mu}\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}\right), \tag{3.351}$$

so

$$\sigma_N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial \mu^2}\ln \mathcal{Z}\,. \tag{3.352}$$

Combining this with (3.350), we get

$$\sigma_N^2 = \frac{1}{\beta^2}\frac{\partial \langle N \rangle}{\partial \mu}\,. \tag{3.353}$$

Now we can express

$$\langle N \rangle = \langle N \rangle(T, V, \mu)\,. \tag{3.354}$$

Further, recall that $\langle N \rangle$ is extensive, meaning that that scaling the system by λ should give

$$\langle N \rangle \to \lambda \langle N \rangle\,. \tag{3.355}$$

But then, we must have

$$\langle N \rangle = V n(T, \mu)\,, \tag{3.356}$$

where $n(T, \mu)$ is intrinsically intensive. Accordingly,

$$\sigma_N^2 = \frac{V}{\beta^2}\frac{\partial n}{\partial \mu} = \langle N \rangle \frac{1}{\beta^2 n}\frac{\partial n}{\partial \mu}\,. \tag{3.357}$$

i.e.,

$$\sigma_N^2 \sim \langle N \rangle\,, \tag{3.358}$$

and therefore

$$\frac{\sigma_N}{\langle N \rangle} \sim \frac{1}{\sqrt{\langle N \rangle}}\,. \tag{3.359}$$

For very large $\langle N \rangle$, we can then simply write

$$N \approx \langle N \rangle = \mathit{const.}\,, \tag{3.360}$$

which is why in thermodynamics we use just N.

3.4.2 Internal Energy

The internal energy is once again defined as

$$\begin{aligned} U = \langle E \rangle &= \frac{1}{\mathcal{Z}}\sum_{n,N} E_{nN}\,\mathrm{e}^{-\beta(E_{nN}-\mu N)} \\ &= -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \beta} + \frac{\mu}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}\,, \end{aligned} \tag{3.361}$$

i.e.,

$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} + \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} \,. \tag{3.362}$$

Similarly as before, we could once again show that

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{\langle N \rangle}} \,, \tag{3.363}$$

and so

$$E \approx U = const. \tag{3.364}$$

3.4.3 Entropy

From Eq. (3.341) we express

$$\Omega_{\text{tot}}(E_{\text{tot}}) = \frac{\Omega^{(\text{res})}(E_{\text{tot}} - E_{nN}, N_{\text{tot}} - N)}{w_{nN}} \,, \tag{3.365}$$

and further by using the Boltzmann entropy formula together with (3.345) we get

$$S_{\text{tot}}(E_{\text{tot}}) = S^{(\text{res})}(E_{\text{tot}}, N_{\text{tot}}) - \frac{E_{nN}}{T} + \frac{\mu N}{T} - k_{\text{B}} \ln w_{nN} \,. \tag{3.366}$$

Calculating the expected value and undoing the Taylor expansion of $S^{(\text{res})}$ yields

$$S_{\text{tot}}(E_{\text{tot}}) = S^{(\text{res})}\left(U^{(\text{res})}, \left\langle N^{(\text{res})} \right\rangle\right) - k_{\text{B}} \sum_{n,N} w_{nN} \ln w_{nN} \,, \tag{3.367}$$

where

$$U^{(\text{res})} = E_{\text{tot}} - U \,, \tag{3.368}$$

and

$$\left\langle N^{(\text{res})} \right\rangle = N_{\text{tot}} - \langle N \rangle \,. \tag{3.369}$$

Hence, we identify

$$S = -k_{\text{B}} \sum_{n,N} w_{nN} \ln w_{nN} \tag{3.370}$$

as the entropy of the studied system, which is once again the Shannon formula. Further, inserting (3.348) into the above, we get

$$S = -\frac{1}{T} \frac{\partial}{\partial \beta} \ln \mathcal{Z} + k_{\text{B}} \ln \mathcal{Z} \,. \tag{3.371}$$

3.4.4 Maximizing Entropy

We will show that the distribution (3.348) maximizes the entropy

$$S = -k_{\mathrm{B}} \sum_{n,N} w_{nN} \ln w_{nN} \tag{3.372}$$

under the constraints

$$\sum_{n,N} w_{nN} = 1\,, \quad \sum_{n,N} E_{nN}\, w_{nN} = U\,, \quad \sum_{n,N} N\, w_{nN} = \langle N \rangle\,. \tag{3.373}$$

The corresponding Lagrangian reads

$$\begin{aligned}\mathcal{L} = -k_{\mathrm{B}} \sum_{n,N} w_{nN} \ln w_{nN} + \lambda_1 \left(\sum_{n,N} w_{nN} - 1 \right) \\ + \lambda_2 \left(\sum_{n,N} E_{nN}\, w_{nN} - U \right) + \lambda_3 \left(\sum_{n,N} N\, w_{nN} - \langle N \rangle \right)\,.\end{aligned} \tag{3.374}$$

Setting

$$\frac{\partial \mathcal{L}}{\partial w_{nN}} \overset{!}{=} 0 \tag{3.375}$$

yields

$$w_{nN} = \exp\left(\frac{\lambda_1 + \lambda_2 E_{nN} + \lambda_3 N}{k_{\mathrm{B}}} - 1 \right)\,, \tag{3.376}$$

and combining this with the first condition (3.373) results in

$$w_{nN} = \frac{\exp\left(\frac{\lambda_2 E_{nN} + \lambda_3 N}{k_{\mathrm{B}}} \right)}{\Xi}\,, \tag{3.377}$$

where we have denoted

$$\Xi(\lambda_2, \lambda_3) = \sum_{n,N} \exp\left(\frac{\lambda_2 E_{nN} + \lambda_3 N}{k_{\mathrm{B}}} \right)\,. \tag{3.378}$$

From the remaining two conditions (3.373), we further get

$$U = k_{\mathrm{B}} \frac{\partial}{\partial \lambda_2} \ln \Xi\,, \quad \langle N \rangle = k_{\mathrm{B}} \frac{\partial}{\partial \lambda_3} \ln \Xi\,. \tag{3.379}$$

Now we express the entropy as

$$S = k_{\mathrm{B}} \ln \Xi - \lambda_2 U - \lambda_3 \langle N \rangle\,. \tag{3.380}$$

Since $E_{nN} = E_{nN}(V)$, then keeping $V = \mathit{const.}$ allows us to express

$$\begin{aligned} \mathrm{d}S &= k_{\mathrm{B}}\mathrm{d}(\ln \Xi) - U\,\mathrm{d}\lambda_2 - \lambda_2\,\mathrm{d}U - \langle N\rangle\,\mathrm{d}\lambda_3 - \lambda_3\,\mathrm{d}\langle N\rangle \\ &= k_{\mathrm{B}}\frac{\partial}{\partial\lambda_2}\ln\Xi\,\mathrm{d}\lambda_2 + k_{\mathrm{B}}\frac{\partial}{\partial\lambda_3}\ln\Xi\,\mathrm{d}\lambda_3 - U\,\mathrm{d}\lambda_2 - \lambda_2\,\mathrm{d}U - \langle N\rangle\,\mathrm{d}\lambda_3 - \lambda_3\,\mathrm{d}\langle N\rangle \\ &= -\lambda_2\,\mathrm{d}U - \lambda_3\mathrm{d}\langle N\rangle\,, \end{aligned} \tag{3.381}$$

where we used (3.379) in the second equality. At the same time, Eq. (1.87) states that

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U - \frac{\mu}{T}\,\mathrm{d}\langle N\rangle\,. \tag{3.382}$$

Comparing the two, we can immediately identify

$$\lambda_2 = -\frac{1}{T}\,, \quad \lambda_3 = \frac{\mu}{T}\,, \tag{3.383}$$

by which

$$\Xi\left(-\frac{1}{T}, \frac{\mu}{T}\right) = \mathcal{Z}\,, \tag{3.384}$$

and

$$w_{nN} = \frac{1}{\mathcal{Z}}\,\mathrm{e}^{-\beta(E_{nN}-\mu N)}\,, \tag{3.385}$$

which is exactly the distribution (3.348).

3.4.5 Grand Canonical Potential

Finally, expressing

$$\Phi_{\mathrm{G}} = U - TS - \mu\langle N\rangle \tag{3.386}$$

and substituting from (3.350), (3.362) and (3.371), we get

$$\boxed{\Phi_{\mathrm{G}} = -k_{\mathrm{B}}T\ln\mathcal{Z}}\,, \tag{3.387}$$

from which we can further express anything, i.e.,

$$S = -\left(\frac{\partial\Phi_{\mathrm{G}}}{\partial T}\right)_{V,\mu}\,, \quad P = -\left(\frac{\partial\Phi_{\mathrm{G}}}{\partial V}\right)_{T,\mu}\,, \quad \langle N\rangle = \left(\frac{\partial\Phi_{\mathrm{G}}}{\partial\mu}\right)_{T,V} \tag{3.388}$$

and

$$U = \Phi_{\mathrm{G}} + TS + \mu\langle N\rangle\,. \tag{3.389}$$

3.4.6 Relation between Canonical and Grand Canonical Partition Functions

Notice that we can rewrite the grandcanonical partition function as

$$\mathcal{Z} = \sum_{n,N} \mathrm{e}^{-\beta(E_{nN}-\mu N)} = \sum_{N} \left(\sum_{n} \mathrm{e}^{-\beta E_{nN}} \right) \mathrm{e}^{\beta\mu N} \tag{3.390}$$

But the term inside the round brackets

$$Z_N \equiv \sum_n \mathrm{e}^{-\beta E_{nN}} \tag{3.391}$$

is just the canonical partition sum corresponding to N particles. Further, denoting

$$\zeta = \mathrm{e}^{\beta\mu}\,, \tag{3.392}$$

(3.390) becomes

$$\mathcal{Z} = \sum_N Z_N \zeta^N\,, \tag{3.393}$$

meaning that the grand canonical partition function can be represented by a power series in ζ with the coefficients Z_N.

3.4.7 Occupation Numbers

Let's pause here for a minute and focus on an important question that you might have been asking from the beginning of the introduction of the grand canonical formalism. At least to me, it seems quite weird and also impractical to consider the set of the parameters determining the equilibrium of the studied system to include the obscure chemical potential. Why would we want to do something like this? At the same time, recall that one of the primary reasons of introducing the canonical formalism was the limited applicability of the micro-canonical formalism. But the canonical formalism does not seem to have such limitations. So why are we doing all of this? The answer is related to the discussion about identical particles in context of the Gibbs paradox. It turns out that, generally, the corrected formula

$$Z = \frac{z^N}{N!} \tag{3.394}$$

is still not entirely correct. To demonstrate this, take the two level system

$$\varepsilon_0 = 0\,, \quad \varepsilon_1 = \varepsilon \tag{3.395}$$

with $N = 2$, and calculate

$$z = \sum_{i=0}^{1} \mathrm{e}^{-\beta\varepsilon_i} = 1 + \mathrm{e}^{-\beta\varepsilon}\,. \tag{3.396}$$

The original formula

$$Z = z^N = \left(1 + \mathrm{e}^{-\beta\varepsilon}\right)^2 = 1 + 2\,\mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon} \tag{3.397}$$

is wrong, because it considers

$$\varepsilon^{(\mathrm{A})} = 0\,, \quad \varepsilon^{(\mathrm{B})} = \varepsilon \quad \text{and} \quad \varepsilon^{(\mathrm{A})} = \varepsilon\,, \quad \varepsilon^{(\mathrm{B})} = 0 \tag{3.398}$$

as two distinct microstates. But our attempt to resolve this just by

$$Z = \frac{z^N}{N!} = \frac{1}{2}\left(1 + 2\,\mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}\right) = \frac{1}{2} + \mathrm{e}^{-\beta\varepsilon} + \frac{1}{2}\,\mathrm{e}^{-2\beta\varepsilon} \tag{3.399}$$

is not correct either, since even though we successfully got rid of the 2 accompanying the second term in (3.397), we also unintentionally damaged the other two terms that were originally correct. Obviously, the result we are aiming at is

$$Z = 1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}\,, \tag{3.400}$$

corresponding to the three physical microstates:

1. both particles in the ground state,
2. one excited particle,
3. both particles excited.

This motivates us to introduce the so called *occupation numbers* N_i representing the number of particles sitting at the i-th energy level. Specifying all the N_is then uniquely determines the microstate of a system of identical particles. E.g., in the above case, the three physical microstates can be represented by $\{N_0 = 2, N_1 = 0\}$, $\{N_0 = 1, N_1 = 1\}$, and $\{N_0 = 0, N_1 = 2\}$, respectively. The total energy of the system is given by

$$E = \sum_i \varepsilon_i N_i\,, \tag{3.401}$$

and the (finally correct) formula for the partition function corresponding to N particles becomes

$$Z = \sum_{\substack{N_1, N_2, N_3, \ldots \\ \sum_i N_i = N}} \exp\left(-\beta \sum_i \varepsilon_i N_i\right)\,, \tag{3.402}$$

meaning that we are summing over all the possible combinations of nonnegative integer values of N_i such that together they add up to

$$\sum_i N_i = N\,. \tag{3.403}$$

(3.402) now represents the truly correct formula, but unfortunately, it's general analytical evaluation is highly limited due to the presence of the constraint (3.403). And this is exactly the point where the grand canonical formalism comes into play, as it essentially relieves the constraint (3.403), allowing for a simple analytical evaluation of the corresponding grand canonical partition function, but at the cost of the results being dependent on the chemical potential. Let's see how this is done.

$$\begin{aligned}\mathcal{Z} &= \sum_{n,N} \mathrm{e}^{-\beta(E_{nN}-\mu N)} \equiv \sum_{N_1,N_2,N_3,\ldots} \exp\left[-\beta \sum_i (\varepsilon_i N_i - \mu N_i)\right] \\ &= \sum_{N_1,N_2,N_3,\ldots} \prod_i \exp[-\beta N_i(\varepsilon_i - \mu)] \\ &= \left(\sum_{N_1} \mathrm{e}^{-\beta N_1(\varepsilon_1-\mu)}\right)\left(\sum_{N_2} \mathrm{e}^{-\beta N_2(\varepsilon_2-\mu)}\right)\left(\sum_{N_3} \mathrm{e}^{-\beta N_3(\varepsilon_3-\mu)}\right)\cdots \\ &= \prod_i \sum_{N_i} \mathrm{e}^{-\beta N_i(\varepsilon_i-\mu)}\,.\end{aligned} \tag{3.404}$$

Denoting

$$\boxed{\mathcal{Z}_i = \sum_{N_i} \mathrm{e}^{-\beta N_i(\varepsilon_i-\mu)}}\,, \tag{3.405}$$

allows us to express

$$\mathcal{Z} = \prod_i \mathcal{Z}_i\,, \tag{3.406}$$

and since

$$\Phi_{\mathrm{G}} = -k_{\mathrm{B}} T \ln \mathcal{Z}\,, \tag{3.407}$$

we can further write

$$\Phi_{\mathrm{G}} = \sum_i \Phi_{\mathrm{G}}^{(i)}\,, \quad \Phi_{\mathrm{G}}^{(i)} = -k_{\mathrm{B}} T \ln \mathcal{Z}_i\,. \tag{3.408}$$

Accordingly,

$$S = \sum_i S_i\,, \quad S_i = -\left(\frac{\partial \Phi_{\mathrm{G}}^{(i)}}{\partial T}\right)_{V,\mu}\,; \tag{3.409}$$

$$P = \sum_i P_i\,, \quad P_i = -\left(\frac{\partial \Phi_{\mathrm{G}}^{(i)}}{\partial V}\right)_{T,\mu}\,; \tag{3.410}$$

$$\langle N \rangle = \sum_i \langle N_i \rangle\,, \quad \langle N_i \rangle = -\left(\frac{\partial \Phi_{\mathrm{G}}^{(i)}}{\partial \mu}\right)_{T,V}\,. \tag{3.411}$$

Moreover, without any further calculation, it should be obvious that

$$U = \sum_i \varepsilon_i \langle N_i \rangle\,. \tag{3.412}$$

Now we need to separate the upcoming calculations based on the character of the identical particles.

3.4.8 Bose-Einstein Statistics

Bosons are particles with integer spin and symmetric wavefunction that do not obey Pauli's exclusion principle. This means that there can be

$$N_i = 0, 1, 2, \dots \tag{3.413}$$

particles sitting at each energy level ε_i. Hence,

$$\mathcal{Z}_i = \sum_{N_i=0}^{\infty} \mathrm{e}^{-\beta N_i(\varepsilon_i - \mu)} = \frac{1}{1 - \exp\left[-\beta(\varepsilon_i - \mu)\right]} \,. \tag{3.414}$$

Note that in order for the above series to converge, we must have

$$\mu < \varepsilon_i \quad \forall i \,. \tag{3.415}$$

Next, we express

$$\Phi_{\mathrm{G}}^{(i)} = -k_{\mathrm{B}} T \ln \mathcal{Z}_i = k_{\mathrm{B}} T \ln\left(1 - \mathrm{e}^{-\beta(\varepsilon_i - \mu)}\right) \,, \tag{3.416}$$

from which

$$\boxed{\langle N_i \rangle = \frac{1}{\exp\left[\beta(\varepsilon_i - \mu)\right] - 1}} \,. \tag{3.417}$$

This is the *Bose-Einstein statistics*, see Fig. 3.14

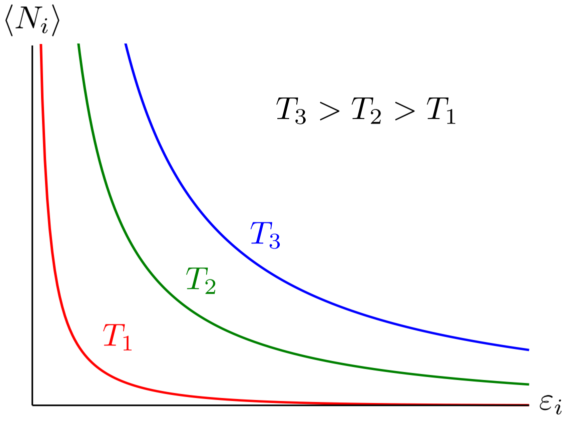

Figure 3.14: Bose-Einstein statistics.

3.4.9 Fermi-Dirac Statistics

Fermions are particles with half-integer spin and antisymmetric wavefunction that obey Pauli's exclusion principle. This means that there can be only

$$N_i = 0, 1 \tag{3.418}$$

particles sitting at each energy level. Accordingly,

$$\mathcal{Z}_i = \sum_{N_i=0}^{1} \mathrm{e}^{-\beta N_i(\varepsilon_i - \mu)} = 1 + \mathrm{e}^{-\beta(\varepsilon_i - \mu)} \,. \tag{3.419}$$

In contrast to the previous case, there is now no condition on μ. Moving on,

$$\Phi_{\mathrm{G}}^{(i)} = -k_{\mathrm{B}} T \ln \mathcal{Z}_i = -k_{\mathrm{B}} T \ln \left(1 + \mathrm{e}^{-\beta(\varepsilon_i - \mu)}\right) \,, \tag{3.420}$$

and finally

$$\boxed{\langle N_i \rangle = \frac{1}{\exp\left[\beta(\varepsilon_i - \mu)\right] + 1}} \,. \tag{3.421}$$

This is the *Fermi-Dirac statistics*, see Fig. 3.15.

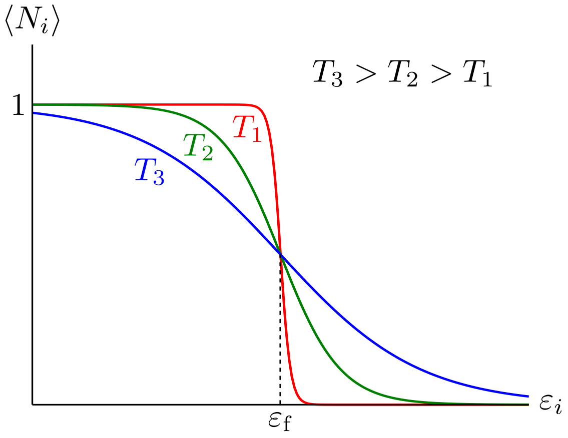

Figure 3.15: Fermi-Dirac statistics.

3.4.10 Getting Rid of Chemical Potential

The time has finally come to get rid of the chemical potential. Formally, this would be done by using the Legendre transform as follows:

1. starting with the fundamental relation

$$\Phi_{\mathrm{G}} = \Phi_{\mathrm{G}}(T, V, \mu) \,, \tag{3.422}$$

2. we calculate
$$\langle N\rangle = \left(\frac{\partial \Phi_{\mathrm{G}}}{\partial \mu}\right)_{T,V} = \langle N\rangle(T,V,\mu)\,, \tag{3.423}$$
invert this into
$$\mu = \mu\big(T,V,\langle N\rangle\big)\,, \tag{3.424}$$
3. and express
$$\begin{aligned} F\big(T,V,\langle N\rangle\big) &= \mathcal{L}^{-1}[\Phi(T,V,\mu);\mu] \\ &= \Phi\big[T,V,\mu\big(T,V,\langle N\rangle\big)\big] + \mu\big(T,V,\langle N\rangle\big)\langle N\rangle\,. \end{aligned} \tag{3.425}$$
(Note that this is an inverse Legendre transform since in thermodynamics we understand $\langle N\rangle$ as the primary variable.)

But unfortunately, the reality is not as simple. In our case, Eq. (3.423) can be written compactly for Bosons and Fermions together as

$$\langle N\rangle = \sum_i \frac{1}{\exp\left[\beta(\varepsilon_i - \mu)\right] \pm 1}\,, \tag{3.426}$$

while recalling that the dependence on the volume is hidden in

$$\varepsilon_i = \varepsilon_i(V)\,. \tag{3.427}$$

And the problem is that (3.426) cannot be generally inverted into (3.424), which essentially prevents us from performing the (inverse) Legendre transform. And if you are expecting some clever trick to get around this then I must disappoint you, as there is no such thing. However, there are at least cases where we are able to eliminate μ from the resulting expressions, which we will demonstrate by the following example.

3.4.11 Fermion Gas

Assume the studied system to be a gas of fermions confined to some container of volume V. Limiting ourselves to non-relativistic case, the energy of a single fermion reads

$$\varepsilon = \frac{p^2}{2m}\,. \tag{3.428}$$

Substituting for

$$p = \hbar k \tag{3.429}$$

allows us to express the density of states (3.279) as a function of the energy

$$D(\varepsilon)\,\mathrm{d}\varepsilon = \frac{g\, m^{3/2}}{\sqrt{2}\pi^2\hbar^3} V\varepsilon^{1/2}\,\mathrm{d}\varepsilon = \alpha V \varepsilon^{1/2}\,\mathrm{d}\varepsilon\,, \tag{3.430}$$

where g stands for a possible degeneracy factor (e.g., each electron of given energy comes in two variants with opposite spin). Now we approximate

$$\begin{aligned}\Phi_{\mathrm{G}} &= \sum_i \Phi_{\mathrm{G}}^{(i)} = \sum_{\varepsilon_i} \Phi_{\mathrm{G}}^{(i)} \Omega(\varepsilon_i) \\ &\approx \int\limits_0^\infty \Phi_{\mathrm{G}}(\varepsilon) D(\varepsilon)\,\mathrm{d}\varepsilon = -k_{\mathrm{B}} T \int\limits_0^\infty \ln\left(1 + \mathrm{e}^{-\beta(\varepsilon-\mu)}\right) \alpha V \varepsilon^{1/2}\,\mathrm{d}\varepsilon\,.\end{aligned} \tag{3.431}$$

Integrating by parts and discarding the boundary term, the above becomes

$$\Phi_{\mathrm{G}} = -\frac{2}{3}\,\alpha V \int\limits_0^\infty \frac{\varepsilon^{3/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,. \tag{3.432}$$

Now we can calculate the pressure

$$P = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial V}\right)_{T,\mu} = \frac{2}{3}\,\alpha \int\limits_0^\infty \frac{\varepsilon^{3/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,. \tag{3.433}$$

Repeating the same procedure as above,

$$\langle N\rangle \approx \int\limits_0^\infty \langle N(\varepsilon)\rangle D(\varepsilon)\,\mathrm{d}\varepsilon = \alpha V \int\limits_0^\infty \frac{\varepsilon^{1/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,, \tag{3.434}$$

and

$$U \approx \int\limits_0^\infty \varepsilon\langle N(\varepsilon)\rangle D(\varepsilon)\,\mathrm{d}\varepsilon = \alpha V \int\limits_0^\infty \frac{\varepsilon^{3/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,. \tag{3.435}$$

These can be further rewritten as densities

$$\langle n\rangle = \alpha \int\limits_0^\infty \frac{\varepsilon^{1/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,, \tag{3.436}$$

$$u = \alpha \int\limits_0^\infty \frac{\varepsilon^{3/2}}{\exp\left[\beta(\varepsilon-\mu)\right]+1}\,\mathrm{d}\varepsilon\,. \tag{3.437}$$

We can immediately see that

$$P = \frac{2}{3} u\,. \tag{3.438}$$

Now let us show how we can get rid of the chemical potential at absolute zero. Since the integral in Eq. (3.434) cannot be solved analytically, there is no way of how we could possibly invert it to obtain the desired formula

$$\mu = \mu(T, V, \langle N\rangle)\,. \tag{3.439}$$

Nevertheless, such a dependence must exist at least implicitly, and so from now on, we will understand $\langle N\rangle$ as the independent equilibrium parameter. First, we define the *Fermi energy*

$$\boxed{\varepsilon_{\mathrm{f}} \equiv \lim_{T\to 0} \mu\big(T, V, \langle N\rangle\big)}\,, \tag{3.440}$$

whose meaning can be seen by calculating

$$\begin{aligned} \lim_{T\to 0}\langle N(\varepsilon)\rangle &= \lim_{T\to 0} \frac{1}{\exp\Big[\beta\big(\varepsilon - \mu(T, V, \langle N\rangle)\big)\Big] + 1} \\ &= \lim_{T\to 0} \frac{1}{\exp\left[\beta(\varepsilon - \varepsilon_{\mathrm{f}})\right] + 1} \\ &= \begin{cases} 1\,, & \varepsilon < \varepsilon_{\mathrm{f}} \\ 0\,, & \varepsilon > \varepsilon_{\mathrm{f}} \end{cases} \quad . \end{aligned} \tag{3.441}$$

I.e., at absolute zero, each energy level below the Fermi energy is occupied and vice versa. Further, using this limit allows us to solve the integrals (3.434) and (3.433) analytically:

$$\langle N_0\rangle = \lim_{T\to 0}\langle N\rangle = \alpha V \int\limits_0^{\varepsilon_{\mathrm{f}}} \varepsilon^{1/2}\,\mathrm{d}\varepsilon = \frac{2}{3}\alpha V \varepsilon_{\mathrm{f}}^{3/2}\,, \tag{3.442}$$

$$P_0 = \lim_{T\to 0} P = \frac{2}{3}\alpha \int\limits_0^{\varepsilon_{\mathrm{f}}} \varepsilon^{3/2}\,\mathrm{d}\varepsilon = \frac{4}{15}\alpha\, \varepsilon_{\mathrm{f}}^{5/2}\,. \tag{3.443}$$

By combining the two, we finally arrive at

$$P_0 \propto \langle n_0\rangle^{5/3}\,, \tag{3.444}$$

which is an equation of state being completely devoid of the chemical potential, which is what we were aiming at. Last but not least, there is an important observation. The equation of state for a classical ideal gas can be written as

$$P = n k_{\mathrm{B}} T\,, \tag{3.445}$$

telling us the pressure should vanish as $T \to 0$. But that is clearly not the case with the fermion gas, which exhibits non-zero pressure even at absolute zero. This type of pressure is a direct consequence of the Pauli's exclusion principle and does not have a classical counterpart. It is also this type of pressure that prevents a neutron star or a white dwarf from collapsing into a black hole.