



# Statistical Mechanics

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**ABSTRACT:** This is my study notebook for a the course Statistical Mechanics taught by Prof. Carlos E. Fiore at the University of São Paulo's Institute of Physics (IFUSP) on the second semester of 2022. It was written as a way of keeping up with the course and correspond to my lecture notes with some additions from extra bibliography and sometimes slightly different notation. These notes are not endorsed by Prof. Fiore or IFUSP.

**KEYWORDS:** Statistical Mechanics, Thermodynamics, Stochastic Dynamics.

**VERSION:** September 13, 2022.

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## 1 Non-Equilibrium Thermodynamics

### 1.1 Phenomenological Description

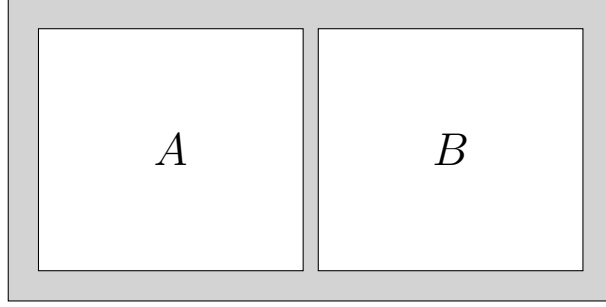
Thermodynamical systems can be in equilibrium or out of equilibrium. While most systems are not in equilibrium, some of them are. Introductory courses on Thermodynamics and Statistical Mechanics will often focus on equilibrium processes, so in order to understand how to describe non-equilibrium process, it is important for us to first understand what are the differences between each situation.

To obtain a general description, let us begin by considering an isolated system composed of two parts,  $A$  and  $B$ , as illustrated in Fig. 1 on the following page.

Let us consider some thermodynamic variable  $x_k$ , with  $x_k^A$  being associated to the subsystem  $A$  and  $x_k^B$  being associated to  $B$ .  $x_k$  can be either the internal energy  $U$ , the volume  $V$ , or the number of particles  $N$  of the constituents of the system\*. Notice that due to the system being isolated,  $x_k^A$  or  $x_k^B$  might change, but their sum  $x_k^A + x_k^B$  always remains constant (which is just another way of stating the First Law of Thermodynamics).

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\*We could be more general and assume many chemical components inside each subsystem, so we'd need to consider the number of particles of each one separately, but our treatment can be easily generalized.



**Figure 1:** *An isolated system composed of two parts, A and B. The wall in between the parts can be removed so that they interact.*

In a differential formulation, we get

$$dx_k^A + dx_k^B = 0. \quad (1.1)$$

Notice that this expression holds true for the internal energy, volume, and particle number, but might fail for other quantities, such as temperature and entropy.

We know that to each of the system's we can attribute entropy functions  $S^A = S^A(U^A, V^A, N^A)$  and  $S^B = S^B(U^B, V^B, N^B)$ . We know that the total entropy of the system is also given by  $S = S^A + S^B$ . Hence, we know that

$$dS = dS^A + dS^B. \quad (1.2)$$

The Second Law of Thermodynamics ensures that  $dS \geq 0$ .

Due to the First Law, we know that the extensive quantities associated to  $A$  are related to those of  $B$ . This leads to the consequence that

$$\left( \frac{\partial S}{\partial x_k^A} \right) = \left( \frac{\partial S^A}{\partial x_k^A} \right) + \left( \frac{\partial S^B}{\partial x_k^A} \right), \quad (1.3a)$$

$$= \left( \frac{\partial S^A}{\partial x_k^A} \right) - \left( \frac{\partial S^B}{\partial x_k^B} \right). \quad (1.3b)$$

This quantity can be interpreted as a sort of “thermodynamical force” (not as a mechanical force). Notice that, if each side is in equilibrium, then this expression leads us to the particular cases

$$\left( \frac{\partial S}{\partial U^A} \right)_{V^A, N^A} = \frac{1}{T^A} - \frac{1}{T^B}, \quad (1.4a)$$

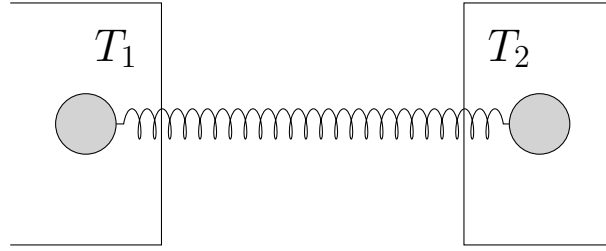
$$\left( \frac{\partial S}{\partial V^A} \right)_{U^A, N^A} = \frac{P^A}{T^A} - \frac{P^B}{T^B}, \quad (1.4b)$$

and

$$\left( \frac{\partial S}{\partial N^A} \right)_{U^A, V^A} = -\frac{\mu^A}{T^A} + \frac{\mu^B}{T^B}, \quad (1.4c)$$

and therefore non-vanishing “thermodynamical forces” will lead to an energy, volume, or particle number flux between the subsystems once the wall is removed.

If we remove the barrier between the subsystems  $A$  and  $B$  and let them interact, they will then eventually reach equilibrium and a steady state. A different situation is illustrated in Fig. 2, where one has two particles, each of them subject to a thermal bath, connected by a spring. Even though the system will eventually evolve to a steady state, it is never in equilibrium, for energy keeps continuously flowing from the hot bath to the cold one.



**Figure 2:** A system composed of two particles connected by a spring. Each particle is subject to a thermal bath. If the temperatures of the baths are unequal, the system is always in non-equilibrium, even though it evolves to a steady state in which energy keeps flowing from the hotter reservoir to the colder one.

How can we generally distinguish between equilibrium and non-equilibrium then? To see this, let us consider the differential expression

$$dS = \sum_k \left( \frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} \right) dx_k^A. \quad (1.5)$$

For thermal equilibrium, we have  $dS = 0$ . In this situation, we often have\*

$$\frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} = 0. \quad (1.6)$$

Since  $dS \geq 0$ , if we hold all extensive variables constant but one of them, we'll have that  $\frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} > 0$  if, and only if,  $dx_k^A > 0$ . Similarly,  $\frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} < 0$  if, and only if,  $dx_k^A < 0$ . This implies that energy will flow from hot to cold, volume will flow from low pressure to high pressure, particles will flow from large chemical potential to small chemical potential.

Why can't I have  $dx_k^A = 0$ ?

If  $dS > 0$ , then for at least one value of  $k$  we have  $F_k \equiv \frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} \neq 0$ . In this case, notice that we'll have a non-vanishing flux  $J_k \equiv \frac{dx_k^A}{dt}$ . Hence, for  $dS > 0$ , we have a flux if, and only if, we have a thermodynamical force.

Is this condition necessary?

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\*Since equilibrium only requires  $dS = 0$ , we may still have  $\left( \frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} \right) dx_k^A \neq 0$  for different values of  $k$ , as long as their sum vanishes. This can happen, for example, for a Carnot engine.

This leads us to the following definition: a system is in equilibrium when its entropy production  $\sigma$ , defined as

$$\sigma \equiv \frac{dS}{dt} = \sum_k \left( \frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} \right) \frac{dx_k^A}{dt} = \sum_k F_k J_k, \quad (1.7)$$

vanishes, but out of equilibrium when it doesn't.

The importance of entropy production is that it will, for example, generalize to more complicated systems, including small systems (as opposed with systems whose number of particles is comparable to Avogadro's number). However, it will still be positive for equilibrium and strictly positive for non-equilibrium\*.

One can show that in the spring system of Fig. 2 on the preceding page the entropy production is proportional to  $(T_1 - T_2)^2$ , so the system is out of equilibrium whenever the temperatures are different. The direction of the energy flux is determined by the sign of the temperature difference.

In most situations, the entropy production can't be attributed to the subsystem  $A$  or  $B$ , but rather it is a property of the whole composite system. There is, though, a specific situation in which we can discuss the entropy production due to a subsystem: when one of the subsystems is much larger than the other.

Suppose for example that  $B$  is much larger than  $A$ . Then we can treat  $B$  as a reservoir, with  $\frac{\partial S^B}{\partial x_k^B}$  being approximately constant. In this situation, we can write

$$\frac{dS}{dt} = \sum_k \left( \frac{\partial S^A}{\partial x_k^A} - \frac{\partial S^B}{\partial x_k^B} \right) \frac{dx_k^A}{dt}, \quad (1.8a)$$

$$= \sum_k \frac{\partial S^A}{\partial x_k^A} \frac{dx_k^A}{dt} + \phi, \quad (1.8b)$$

$$= \frac{dS^A}{dt} + \phi, \quad (1.8c)$$

where  $\phi$  is called the entropy flux and is due only to the bath. It will be given in terms of the heat flux of the reservoir as  $\phi = \frac{\dot{Q}}{T}$  (conferatur the Clausius relation). In this situation, we can interpret

$$\frac{dS^A}{dt} = \frac{dS}{dt} - \phi = \sigma - \phi \quad (1.9)$$

as the entropy production due to  $A$ . Notice that while the Second Law implies  $\frac{dS}{dt} \geq 0$ , there is no restriction on the sign of  $\frac{dS^A}{dt}$ .

At a steady state, we'll have  $\frac{dS^A}{dt} = 0$ , *id est*, the system's entropy will no longer depend on time. This then implies  $\sigma = \phi$ . We can then still have equilibrium or non-equilibrium, depending on whether  $\sigma = \phi = 0$  (equilibrium) or  $\sigma = \phi > 0$  (non-equilibrium). Notice that  $\sigma = 0$  doesn't mean nothing is happening: it means only that on average, the effects cancel out.

Hence, while there are other definitions, the difference between a system being or not in equilibrium is whether the entropy production vanishes or not. As for the difference between equilibrium and steady state, it boils down to the fact that in steady state the quantities no longer change with time on average (*id est*, macroscopically).

Should I comment on this?

Typically, systems will evolve to a steady state, be it in equilibrium or not. To distinguish between them, we can compute the entropy production. But how do we do that?

## 1.2 Markovian Systems and the Master Equation

In order to be able to do computations, it is interesting for us to reformulate these phenomenological concepts in an stochastic\* language. This will allow us, for example, to treat more general systems. Some references that might be useful are Tomé and M. J. de Oliveira [2014](#), [2015](#); Van den Broeck and Esposito [2015](#).

Check this definition of stochastic (is quantum stochastic?)

Since we can't describe large numbers of particles with just Classical or Quantum Mechanics, we often resort to statistical methods to describe large systems. For example, if a system is in thermal equilibrium at fixed inverse temperature  $\beta$ , we assign to its microstates probabilities according to the Gibbs distribution,

$$p_n = \frac{e^{-\beta E_n}}{Z}. \quad (1.10)$$

However, how can we do this in systems that are not in equilibrium?

In order to achieve that, we'll begin by describing the so-called Markovian systems. A Markovian system is a system whose probabilities on a given step depend only on the conditions of the previous step, as opposed to depending on the entire history of the system. Markovian processes are way simpler to describe and they are able to describe a wide range of phenomena, so it is interesting to consider them.

For a Markovian system with  $l$  steps, we can write the probability of getting the outcomes  $\{n_k\}$  as

$$P_l(n_l, n_{l-1}, \dots, n_0) = P_l(n_l | n_{l-1}, n_{l-2}, \dots, n_0) P_{l-1}(n_{l-1}, n_{l-2}, \dots, n_0), \quad (1.11a)$$

$$= P_l(n_l | n_{l-1}) P_{l-1}(n_{l-1}, n_{l-2}, \dots, n_0) \quad (1.11b)$$

where in the first step we used Bayes' rule and in the second we used the hypothesis that the system is Markovian. If we keep repeating this argument, we get to

$$P_l(n_l, n_{l-1}, \dots, n_0) = P_l(n_l | n_{l-1}) P_{l-1}(n_{l-1} | n_{l-2}) \cdots P_1(n_1 | n_0) P_0(n_0). \quad (1.12)$$

Therefore, if we know the transition rates  $P_k(n_k | n_{k-1})$  and the initial probability  $P_0(n_0)$ , we can reconstruct the entire evolution.

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\*In fact, fluctuations can lead to a measurement of negative entropy production (Crooks [1998](#), [1999](#)). We shall discuss this later in the course.

\*A stochastic system is any system that is not deterministic.

Some remarks are in place. For example, due to the properties of conditional probabilities, we have that  $P_k(n_k|n_{k-1}) \geq 0$  and  $\sum_{n_k} P_k(n_k|n_{k-1}) = 1$ . Furthermore,

$$P_l(n_l) = \sum_{n_0, \dots, n_{l-1}} P_l(n_l, n_{l-1}, \dots, n_0), \quad (1.13a)$$

$$= \sum_{n_0, \dots, n_{l-1}} P_l(n_l|n_{l-1}) P_{l-1}(n_{l-1}|n_{l-2}) \cdots P_1(n_1|n_0) P_0(n_0), \quad (1.13b)$$

$$= \sum_{n_0, \dots, n_{l-1}} P_l(n_l|n_{l-1}) P_{l-1}(n_{l-1}|n_{l-2}) \cdots P_2(n_2|n_1) P_1(n_1, n_0), \quad (1.13c)$$

$$= \sum_{n_1, \dots, n_{l-1}} P_l(n_l|n_{l-1}) P_{l-1}(n_{l-1}|n_{l-2}) \cdots P_2(n_2|n_1) P_1(n_1), \quad (1.13d)$$

$$= \sum_{n_{l-1}} P_l(n_l|n_{l-1}) P_{l-1}(n_{l-1}). \quad (1.13e)$$

We see then how in Markov processes the transition rates  $P_l(n_l|n_{l-1})$  are important. Hence, we'll describe them in terms of a transition matrix  $T_{nm}$  with the properties that

- $T_{nm} \geq 0$ ,
- $\sum_n T_{nm} = 1$ ,
- $P_l(n) = \sum_m T_{nm} P_{l-1}(m)$ ,

which correspond, respectively, to

- $P_k(n_k|n_{k-1}) \geq 0$ ,
- $\sum_{n_k} P_k(n_k|n_{k-1}) = 1$
- $P_l(n_l) = \sum_{n_{l-1}} P_l(n_l|n_{l-1}) P_{l-1}(n_{l-1})$ .

So far, we've been describing discrete systems: they have both discrete states and discrete time. Continuous states could require, *exempli gratia*, the Langevin equation (see, *exempli gratia*, Salinas 2001; Tomé and M. J. de Oliveira 2014). However, we will now consider the case with discrete states, but continuous time.

Let us suppose the transitions from state  $m$  to  $n$  take place along a time  $\tau \ll 1$ . Then we can represent this in the transition matrix by writing

$$T_{nm} = \delta_{nm} + \tau W_{nm}, \quad (1.14)$$

where  $W_{nm}$  is assumed to remain finite as we take a limit  $\tau \rightarrow 0$  later on.

The normalization condition  $\sum_n T_{nm} = 1$  now becomes  $\sum_n W_{nm} = 0$  (which is possible because the elements of  $W_{nm}$  correspond to transition rates, not probabilities). Notice then that  $W_{nn} = -\sum_{m \neq n} W_{mn}$ . Hence, we find that

$$P_l(n) = \sum_m T_{nm} P_{l-1}(m), \quad (1.15a)$$

$$= \sum_m (\delta_{nm} + \tau W_{nm}) P_{l-1}(m), \quad (1.15b)$$

$$= \tau \sum_{m \neq n} W_{nm} P_{l-1}(m) + (1 + \tau W_{nn}) P_{l-1}(n), \quad (1.15c)$$

$$= \tau \sum_{m \neq n} W_{nm} P_{l-1}(m) + \left( 1 - \tau \sum_{m \neq n} W_{mn} \right) P_{l-1}(n), \quad (1.15d)$$

from which we find

$$\frac{P_l(n) - P_{l-1}(n)}{\tau} = \sum_{m \neq n} [W_{nm} P_{l-1}(m) - W_{mn} P_{l-1}(n)]. \quad (1.16)$$

Notice that the left-hand side of this equation describes the probability evolving. The right-hand side has a term that increases probability ( $W_{nm} P_{l-1}(m)$ ), and one that decreases it ( $W_{mn} P_{l-1}(n)$ ). Notice that they are associated with the fact that  $W_{nm}$  represents the transition rate for a state  $m$  transitioning to  $n$ , while  $W_{mn}$  represents the transition rate for  $n$  to change into  $m$ . This can be seen from our previous definition of  $T_{nm}$  as  $P(n|m)$ .

Let now  $t = (l-1)\tau$  and take the limit as  $\tau \rightarrow 0$ . We then get to

$$\frac{dP_n}{dt} = \sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)], \quad (1.17)$$

which is known as the master equation. Notice how it resembles a continuity equation with current  $J_n = \sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)]$ .

Notice that, due to the fact that  $\sum_n P_n = 1$  (normalization of probability), we have

$$\sum_n \frac{dP_n}{dt} = \frac{d}{dt} \sum_n P_n = 0, \quad (1.18)$$

implying that

$$\sum_n \sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)] = 0. \quad (1.19)$$

This can also be seen by noticing how

$$\frac{dP_n}{dt} = \sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)], \quad (1.20a)$$

$$= \sum_m W_{nm} P_m(t) \quad (1.20b)$$

and from the previously established fact that  $\sum_n W_{nm} = 0$ .

In a steady state, we have  $\frac{dP_n}{dt} = 0$  for all  $n$ . Therefore, we get

$$\sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)] = 0. \quad (1.21)$$



That is, the net current carrying probability around vanishes. However, there are two possibilities: either each term on the sum vanishes independently—which is known as the detailed balance condition—or, or at least some of them do not vanish, but their sum does. In the former case, we have equilibrium. In the latter, non-equilibrium. It can be shown that, for equilibrium, the probability distribution tends towards the Gibbs distribution.

Reference

### 1.3 Entropy and Entropy Production in Stochastic Terms

Our goal is now to reformulate thermodynamics concepts in terms of these stochastic ideas. In equilibrium Statistical Mechanics one has to postulate that entropy is given by

$$S = k_B \log \Omega, \quad (1.22)$$

where  $\Omega$  is the number of accessible microstates of the system. In non-equilibrium Statistical Mechanics, we'll also have to make similar assumptions, that can be motivated, but not proved.

We'll assume that the entropy is given in terms of the probability distribution by

$$S = -k_B \sum_n P_n \log P_n \quad (1.23)$$

(*conferatur* the expressions for Gibbs and Shannon entropy).

We'll also make a postulate about the entropy production, which was first made by Schnakenberg (1976). We define

$$\sigma(t) = \frac{k_B}{2} \sum_{n,m} (W_{nm}P_m - W_{mn}P_n) \log \frac{W_{nm}P_m}{W_{mn}P_n}. \quad (1.24)$$

Notice each term of this expression has the form

$$(x - y) \log \frac{x}{y}, \quad (1.25)$$

which is always non-negative, but vanishes if the detailed balance holds.

If we define

$$X_{mn} = \frac{k_B}{2} \log \frac{W_{nm}P_m}{W_{mn}P_n} \quad (1.26)$$

and

$$J_{mn} = W_{nm}P_m - W_{mn}P_n, \quad (1.27)$$

then we can write the entropy production in the form of a sum of products of thermodynamic forces and currents,

$$\sigma(t) = \sum_{n,m} J_{mn} X_{mn}. \quad (1.28)$$

It is worth pointing out that one can describe the currents on a thermodynamic system in a way analogous to electric currents: in terms of Kirchoff laws. See, *exempli gratia*, Schnakenberg 1976.

We know the time derivative of the entropy and the entropy production are related. It is then interesting to differentiate our prescription for entropy in order to see how exactly they relate. We find

$$\frac{dS}{dt} = -k_B \sum_n \frac{dP_n}{dt} \log P_n - k_B \sum_n \frac{P_n}{P_n} \frac{dP_n}{dt}, \quad (1.29a)$$

$$= -k_B \sum_n \frac{dP_n}{dt} \log P_n - k_B \sum_n \frac{dP_n}{dt}, \quad (1.29b)$$

$$= -k_B \sum_n \frac{dP_n}{dt} \log P_n, \quad (1.29c)$$

$$= -k_B \sum_{n,m} W_{nm} P_m \log P_n, \quad (1.29d)$$

$$= -k_B \sum_{n,m} (W_{nm} P_m - W_{mn} P_n) \log P_n, \quad (1.29e)$$

$$= \frac{k_B}{2} \sum_{n,m} (W_{nm} P_m - W_{mn} P_n) \log \frac{P_m}{P_n}, \quad (1.29f)$$

where we used  $\sum_n P_n = 1$  (a constant) in the third line,  $\sum_m W_{mn} = 0$  in the fifth line, and essentially wrote  $1 = \frac{1}{2} + \frac{1}{2}$  in the last line.

We see then that we can write

$$\frac{dS}{dt} = \sigma(t) - \phi(t), \quad (1.30)$$

where the entropy flux  $\phi(t)$  is given by

$$\phi(t) = -\frac{k_B}{2} \sum_{n,m} (W_{nm} P_m - W_{mn} P_n) \log \frac{W_{mn}}{W_{nm}}. \quad (1.31)$$

This expression makes sense as an entropy flux, because there are situations in which one can define thermodynamic quantities\*—such as temperature and the chemical potential—and in which this expression will reduce to  $\phi(t) = \frac{\dot{Q}}{T}$ , as we'd expect from the Clausius relation.

It is also interesting to notice that we may write

$$\phi(t) = k_B \sum_{n,m} \left\langle W_{mn} \log \frac{W_{mn}}{W_{nm}} \right\rangle, \quad (1.32)$$

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\*We do not refer strictly to equilibrium in here, since in that case the detailed balance would hold and the flux would vanish as a consequence. However, there are situations out of the equilibrium which do admit a thermodynamic description. I think Proesmans and Fiore 2019 discusses examples of such systems.

where the angled brackets denote an ensemble average. The interest in this expression is that we can numerically compute ensemble averages without knowledge of the specific probability distribution, and the transition rates  $W_{nm}$  are assumed to be given in the problem. Hence, we get an easy to use expression for the entropy flux. If we also have  $\frac{dS}{dt} = 0$  (steady state), then  $\phi(t) = \sigma(t)$  and we have an expression for the entropy production.

This construction naturally incorporates the Second Law of Thermodynamics (as stated in terms of the entropy production) in its formalism. However, we still haven't discussed the First Law of Thermodynamics.

The internal energy of a system will be given by

$$U = \sum_n E_n(t) P_n(t). \quad (1.33)$$

If we differentiate this expression with respect to time, we find that there are two distinct terms,

$$\frac{dU}{dt} = \sum_n \frac{dE_n}{dt} P_n + \sum_n E_n \frac{dP_n}{dt}. \quad (1.34)$$

The first term corresponds to changing the energy levels of the system, while keeping the probabilities constant. This can be achieved, for example, by varying parameters of the system, such as an external magnetic field, or the system's pressure, and so on. Hence, we can interpret the first term as representing work per time.

The second term represents the change in energy due to variation on the probability of the state  $n$  being the system's microstate at a given time. Hence, it corresponds to heat per time.

In consistency with the First Law, we then get

$$\frac{dU}{dt} = \dot{W} + \dot{Q}. \quad (1.35)$$

Since we are dealing with stochastic processes, we can actually assign a probability distribution to work. One can show that given a path in phase space, the probabilities for work going forwards and in reverse through such a path will respect

$$\frac{P_F(W)}{P_R(-W)} = e^{W - \Delta F}, \quad (1.36)$$

which is a consequence of the Crooks Fluctuation Theorem\* (Crooks 1999), which we'll discuss on Section 1.4, where  $W$  is the work done along the path and  $\Delta F$  is the difference in free energy along the transformation.

Notice then that we have

$$\langle e^{-W} \rangle = \int_{-\infty}^{+\infty} e^{-W} P_F(W) dW, \quad (1.37a)$$

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\*Prof. Fiore referred to Eq. (1.36) as the “Jarzynski relation”, but I couldn't find references to this. However, Eq. (1.36) seems to be a consequence of what was obtained by Crooks (1999).

$$= \int_{-\infty}^{+\infty} e^{-W} P_R(-W) e^{W-\Delta F} dW, \quad (1.37b)$$

$$= e^{-\Delta F} \int_{-\infty}^{+\infty} P_R(-W) dW, \quad (1.37c)$$

$$= e^{-\Delta F}, \quad (1.37d)$$

which is known as the Jarzynski equality (Jarzynski 1997). Using Jensen's inequality, we have that  $\langle e^{-W} \rangle \geq e^{-\langle W \rangle}$ , from which it follows that

$$\langle W \rangle \geq \Delta F, \quad (1.38)$$

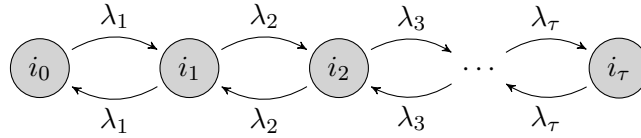
which is a familiar relation from Thermodynamics (see Fermi 1956, Eq. (112), but beware the sign convention on the definition of work).

## 1.4 Crooks Fluctuation Theorem

Since we used the Jarzynski relation, which can be seen as a consequence of the Crooks Fluctuation Theorem, we might as well prove the theorem. The result we'll prove is not the same stated on Eq. (1.36) on the previous page, but a related, stronger one. Notice that in Thermodynamics,  $W - \Delta F$  is a measure of the reversibility of a process (see Fermi 1956, Sec. 17), vanishing when it is reversible and being positive otherwise. This is extremely similar to entropy production. It is, in fact, entropy production in some sense. For further details, see the original work by Crooks (1999).

Which sense?

We'll consider a sequence of microscopic states connected by some protocols. In this way, we have a trajectory defined on state space. Our question will be, at first, to find how the probabilities of this trajectory happening forwards and backwards are related. This is illustrated on Fig. 3.



**Figure 3:** Illustration of the process considered in the Crooks Fluctuation Theorem. Changes from a state  $i_n$  to the next are mediated by some protocol  $\lambda_{n+1}$ . We consider the probabilities of both the forward and backwards trajectory happening.

From each state to the next, there is some difference in energy. We'd like to separately consider the amount due to exchange of heat and the amount due to work. Following our earlier definitions, heat is associated with a change in energy due to change of state, while work is due to a change in protocol. We then define the quantities

$$\Delta W_t \equiv E(i_t, \lambda_{t+1}) - E(i_t, \lambda_t), \quad (1.39)$$

and

$$\Delta Q_t \equiv E(i_{t+1}, \lambda_t) - E(i_t, \lambda_t). \quad (1.40)$$

What exactly is  $E(i, \lambda)$ ? Shouldn't it be  $E(i)$ ?

Notice that  $\Delta W_t + \Delta Q_t = \Delta E_t = E(i_{t+1}, \lambda_{t+1}) - E(i_t, \lambda_t)$ , as we would expect. Summing over the discrete times we get to the work and heat along the entire trajectory,

$$W \equiv \sum_{t=0}^{\tau-1} \Delta W_t \quad \text{and} \quad Q \equiv \sum_{t=0}^{\tau-1} \Delta Q_t, \quad (1.41)$$

which satisfy  $W + Q = E(i_\tau, \lambda_\tau) - E(i_0, \lambda_0)$ . Notice that  $W$  and  $Q$  are odd functions of the trajectory: if we run the trajectory backwards, the work will be  $-W$  and the heat  $-Q$ , in consistency with  $-W - Q = E(i_0, \lambda_0) - E(i_\tau, \lambda_\tau)$ .

Let us then compute the probability of each trajectory happening. Assuming the process is Markovian, we get

$$\frac{P_F(i_0, i_1, \dots, i_\tau)}{P_R(i_\tau, i_{\tau-1}, \dots, i_0)} = \frac{T_{\tau, \tau-1} T_{\tau-1, \tau-2} \cdots T_{1,0} P(i_0)}{T_{\tau-1, \tau} T_{\tau-2, \tau-1} \cdots T_{0,1} P(i_\tau)}, \quad (1.42)$$

where  $T_{nm} = P(i_n | i_m)$  are the elements of the transition matrix. To proceed, we'll also assume that the so-called local detailed balance holds:

$$T_{n, n-1} e^{-\beta E(i_{n-1})} = T_{n-1, n} e^{-\beta E(i_n)}. \quad (1.43)$$

Notice that this resembles the expression for the detailed balance ( $T_{n,m} P_m = T_{m,n} P_n$ , with  $n \neq m$  and no sum implied), apart from the facts that we are using the Gibbs distribution for the probability and we're only assuming it holds for “neighbor” states in the chain. Since both sides of Eq. (1.43) are related to the same protocol  $\lambda_n$ , we can write Eq. (1.43) as

$$\frac{T_{n, n-1}}{T_{n-1, n}} = e^{-\beta(E(i_n, \lambda_n) - E(i_{n-1}, \lambda_n))} = e^{-\beta \Delta Q_{n-1}}, \quad (1.44)$$

where we used our previous definition of the heat exchange when going from one state to the other.

Using Eq. (1.44), Eq. (1.42) becomes

$$\frac{P_F(i_0, i_1, \dots, i_\tau)}{P_R(i_\tau, i_{\tau-1}, \dots, i_0)} = e^{-\beta \Delta Q_{\tau-1}} e^{-\beta \Delta Q_{\tau-2}} \cdots e^{-\beta \Delta Q_0} \frac{P(i_0)}{P(i_\tau)}, \quad (1.45a)$$

$$= e^{-\beta Q} \frac{P(i_0)}{P(i_\tau)}. \quad (1.45b)$$

To proceed, let us now recall that our definition of entropy, Eq. (1.23) on page 8, lets us write\*

$$S = -k_B \sum_n P_n \log P_n = -k_B \langle \log P_n \rangle, \quad (1.46)$$

---

\*Prof. Fiore actually wrote Eq. (1.46) without the Boltzmann constant. Not sure if it was set to one or something else.

which we can interpret as an ensemble average. In particular, it invites us to interpret  $-\log P_n$  as a notion of “microscopic entropy”. Eq. (1.45) on the previous page then becomes

$$\frac{P_F(i_0, i_1, \dots, i_\tau)}{P_R(i_\tau, i_{\tau-1}, \dots, i_0)} = e^{-\beta Q + \log P(i_0) - \log P(i_\tau)}, \quad (1.47a)$$

$$= e^{\Sigma_F}, \quad (1.47b)$$

where  $\Sigma_F$  is the entropy production, here defined in analogy with Eq. (1.30) on page 9, which states the entropy production in the variation in entropy added to the incoming heat flux. Notice that  $\Sigma_F$  is odd in trajectory.

Let us now compute the probability of measuring an entropy production  $\Sigma$  when we let the system evolve for a time  $\tau$ . In the forward trajectory, it will be given by

$$P_F(\Sigma) = \langle \delta(\Sigma - \Sigma_F) \rangle_F, \quad (1.48a)$$

$$= \sum_{i_0, \dots, i_\tau} \delta(\Sigma - \Sigma_F) P_F(i_0, \dots, i_\tau). \quad (1.48b)$$

Similarly,

$$P_R(\Sigma) = \langle \delta(\Sigma - \Sigma_R) \rangle_R, \quad (1.49a)$$

$$= \sum_{i_0, \dots, i_\tau} \delta(\Sigma - \Sigma_R) P_R(i_\tau, \dots, i_0), \quad (1.49b)$$

$$P_R(-\Sigma) = \sum_{i_0, \dots, i_\tau} \delta(\Sigma + \Sigma_R) P_R(i_\tau, \dots, i_0), \quad (1.49c)$$

where we used the fact that the Dirac delta is even. Notice, however, that Eq. (1.47) means these expressions imply

$$P_F(\Sigma) = \sum_{i_0, \dots, i_\tau} \delta(\Sigma - \Sigma_F) P_F(i_0, \dots, i_\tau), \quad (1.50a)$$

$$= \sum_{i_0, \dots, i_\tau} \delta(\Sigma - \Sigma_F) P_R(i_\tau, \dots, i_0) e^{\Sigma_F}, \quad (1.50b)$$

$$= e^\Sigma \sum_{i_0, \dots, i_\tau} \delta(\Sigma - \Sigma_F) P_R(i_\tau, \dots, i_0), \quad (1.50c)$$

$$= e^\Sigma \sum_{i_0, \dots, i_\tau} \delta(\Sigma + \Sigma_R) P_R(i_\tau, \dots, i_0), \quad (1.50d)$$

$$= e^\Sigma P_R(-\Sigma), \quad (1.50e)$$

where Eq. (1.50d) used the fact that the entropy production is odd in trajectory, and hence  $\Sigma_F = -\Sigma_R$ . We have thus arrived at the Crooks Fluctuation Theorem,

$$\frac{P_F(\Sigma)}{P_R(-\Sigma)} = e^\Sigma. \quad (1.51)$$

Notice that it means the probability of measuring a negative microscopic entropy production is not zero, but it is exponentially suppressed. This suppression means that it is difficult to explore these effects experimentally. Nevertheless, we see that a bright side of the result is its generality: we only assumed the system to be Markovian and to satisfy the local detailed balance, with no further assumptions on, *exempli gratia*, being or not in equilibrium.

The Crooks Fluctuation Theorem might seem like a violation of the Second Law of Thermodynamics, but it isn't. Due to the fact that it employs a local form of entropy, the Second Law does not apply. In fact, notice that if we now deal with averages, we find that

$$\langle e^{-\Sigma} \rangle = \int e^{-\Sigma} P_F(\Sigma) d\Sigma, \quad (1.52a)$$

$$= \int e^{-\Sigma} e^{+\Sigma} P_R(\Sigma) d\Sigma, \quad (1.52b)$$

$$= 1. \quad (1.52c)$$

The Jensen inequality then implies that

$$1 = \langle e^{-\Sigma} \rangle \geq e^{-\langle \Sigma \rangle}, \quad (1.53)$$

$$\langle \Sigma \rangle \geq 0, \quad (1.54)$$

meaning the Crooks Fluctuation Theorem doesn't only respect the Second Law, but actually implies it.

## 2 Equilibrium Statistical Mechanics

Now that we know the differences between equilibrium and non-equilibrium, we'll focus firstly on the simpler case of equilibrium Statistical Mechanics. In this scenario, one usually considers a system in thermal contact with a single reservoir, the properties of which do not depend on time.

When working in equilibrium, the notions of transition rates won't be so useful, for we already know the probability distribution in advance: it is the Gibbs distribution,

$$P_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}}. \quad (2.1)$$

If the probability distribution is known, we don't need to solve the master equation, and as a consequence those ideas become unnecessary. Still, they will be useful when we come back to non-equilibrium.

This will be a lighting review of equilibrium Statistical Mechanics. For further details, hit the books (*exempli gratia* Kardar [2007](#); Pathria and Beale [2022](#); Reichl [2016](#); Salinas [2001](#)).

## 2.1 Canonical Ensemble

In the canonical ensemble, we deal with a fixed temperature  $T$ , so the system is assumed to be exchanging heat with a given thermal bath. It is often convenient to define the inverse temperature  $\beta = \frac{1}{k_B T}$ , in terms of which we may write the partition function,

$$Z = \sum_n e^{-\beta E_n}. \quad (2.2)$$

Notice that we may write the mean energy in terms of the partition function as

$$\langle E \rangle = \sum_n E_n P_n, \quad (2.3a)$$

$$= \sum_n E_n \frac{e^{-\beta E_n}}{Z}, \quad (2.3b)$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n}, \quad (2.3c)$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}, \quad (2.3d)$$

$$= -\frac{\partial}{\partial \beta} \log Z, \quad (2.3e)$$

where we employed the Gibbs distribution. Through a similar calculation, we can obtain the second moment of the distribution for the energy by computing

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \quad (2.4)$$

Notice that these formulae imply that

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial^2}{\partial \beta^2} \log Z, \quad (2.5a)$$

$$= -\frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right), \quad (2.5b)$$

$$= \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 - \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}, \quad (2.5c)$$

$$= \langle E \rangle^2 - \langle E^2 \rangle. \quad (2.5d)$$

Our interest in this comes from the fact that the specific heat at constant volume can



be expressed as

$$c_V = \frac{\partial \langle E \rangle}{\partial T}, \quad (2.6a)$$

$$= \frac{d\beta}{dT} \frac{\partial \langle E \rangle}{\partial \beta}, \quad (2.6b)$$

$$= -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta}, \quad (2.6c)$$

$$= \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}. \quad (2.6d)$$

These notions, allied to the hypothesis that the system is extensive (meaning we can write  $\langle E \rangle = Nu$  and  $c_V = N\tilde{c}_V$ , where  $u$  and  $\tilde{c}_V$  are the energy and specific heat per particle, respectively) let us see the connection of the canonical ensemble with thermodynamics. Firstly, we recall the ergodic hypothesis: time averages of the system correspond to ensemble averages. This is widely used in Statistical Mechanics, but still lacks a general proof. Assuming it, we notice that, as time passes, the energy of the system will oscillate about  $\langle E \rangle$ . Nevertheless, the oscillations become negligible in the thermodynamic limit,  $N \rightarrow +\infty$ . Indeed,

$$\lim_{N \rightarrow +\infty} \frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle E \rangle} = \lim_{N \rightarrow +\infty} \frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{\langle E \rangle}, \quad (2.7a)$$

$$= \lim_{N \rightarrow +\infty} \frac{\sqrt{Nk_B T^2 \tilde{c}_V}}{Nu}, \quad (2.7b)$$

$$= 0. \quad (2.7c)$$

Hence, even though in the canonical ensemble the system is continuously trading energy with the thermal bath, in the thermodynamics limit we can understand  $\langle E \rangle$  as the system's internal energy.

## Two Level System

As an example, let us briefly consider a two level system, in which each of  $N$  non-interacting particles might either be in a ground state with 0 energy or in an excited state with  $\epsilon$  energy. Since the particles are non-interacting, the partition function can be written as

$$Z = \zeta_1 \cdot \zeta_2 \cdots \zeta_N = \zeta^N, \quad (2.8)$$

where each  $\zeta$  is understood as a “one-particle partition function”. For this problem, we have

$$\zeta = 1 + e^{-\beta\epsilon}. \quad (2.9)$$

Hence, the probability of finding a given particle in the ground state is

$$P_0 = \frac{e^{-\beta \cdot 0}}{\zeta} = \frac{1}{1 + e^{-\beta\epsilon}}, \quad (2.10)$$

while the excited state has

$$P_1 = \frac{e^{-\beta\epsilon}}{\zeta} = \frac{1}{1 + e^{+\beta\epsilon}}. \quad (2.11)$$

These results resemble, but do not match, the Fermi–Dirac distribution. This is expected, since only one fermion can be in each state at a time.

It is interesting to remark that we are considering localized (*id est*, distinguishable) particles when making this computation. One can also understand this example as a particular case of the Maxwell–Boltzmann distribution (see, *exempli gratia*, Reif 2009, Chap. 9).

Let us then use the partition function to compute physical observables. The internal energy per particle is given by

$$u = -\frac{1}{N} \frac{\partial}{\partial \beta} \log Z, \quad (2.12a)$$

$$= -\frac{\partial}{\partial \beta} \log \zeta, \quad (2.12b)$$

$$= \frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}, \quad (2.12c)$$

$$= \frac{\epsilon}{1 + e^{\beta\epsilon}}. \quad (2.12d)$$

It should be remarked that, in the canonical ensemble, the internal energy is not minimized, the Helmholtz free energy is. This is in accordance with the fact from Thermodynamics that a minimum of Helmholtz free energy corresponds to stable thermal equilibrium (see Fermi 1956, Sec. 17).

The Helmholtz free energy per particle will be given by

$$f = -\frac{k_B T}{N} \log Z, \quad (2.13a)$$

$$= -k_B T \log \zeta, \quad (2.13b)$$

$$= -k_B T \log(1 + e^{-\beta\epsilon}). \quad (2.13c)$$

Therefore, we see that the entropy per particle will be given by

$$s = \frac{u - f}{T}, \quad (2.14a)$$

$$= k_B \beta (u - f), \quad (2.14b)$$

$$= \frac{k_B \beta \epsilon}{1 + e^{\beta\epsilon}} + k_B \log(1 + e^{-\beta\epsilon}). \quad (2.14c)$$

Now that we know  $u$ ,  $f$ , and  $s$ , we are able to compute any quantities we desire.

In order to better understand the system, we should consider a few “remarkable limits”. Namely, how does it behave at low and high temperatures?

The low temperature limit corresponds to picking  $k_B T \ll \epsilon$ , or, equivalently, to  $\beta\epsilon \gg 1$ . In this case, the exponential that occurs on the expression for the partition function leads

Care to explain this comment any further?

to a high suppression, so that high-energy states become less probable. Hence, we expect for all particles to be on the ground state. Eqs. (2.12) to (2.14) on the previous page then lead to

$$\lim_{\beta\epsilon \gg 1} u = 0, \quad \lim_{\beta\epsilon \gg 1} f = 0, \quad \lim_{\beta\epsilon \gg 1} s = 0. \quad (2.15)$$

The high temperature limit means  $k_B T \gg \epsilon$ , which is equivalent to  $\beta\epsilon \ll 1$ . In this case, there is essentially no suppression on the exponential that goes into the partition function, and hence all states become equally likely. Eqs. (2.12) to (2.14) on the preceding page now imply

$$\lim_{\beta\epsilon \ll 1} u = \frac{\epsilon}{2}, \quad \lim_{\beta\epsilon \ll 1} f = -k_B T \log 2, \quad \lim_{\beta\epsilon \ll 1} s = k_B \log 2. \quad (2.16)$$

Notice that these results means we have essentially  $\frac{N}{2}$  in each of the two states. Furthermore, we recover the Boltzmann entropy formula for each particle, since each particle can be in two possible states with equal probabilities.

It is also instructive for us to plot the expressions for the internal energy, entropy, and specific heat as functions of the temperature. These are shown in Fig. 4 on the next page. Notice that the specific heat is given by

$$c = \frac{\partial u}{\partial T}, \quad (2.17a)$$

$$= -k_B \beta^2 \frac{\partial u}{\partial \beta}, \quad (2.17b)$$

$$= \frac{k_B \beta^2 \epsilon^2 e^{\beta\epsilon}}{(1 + e^{\beta\epsilon})^2}. \quad (2.17c)$$

It is particularly interesting that the specific heat attains a finite maximum. This feature is a general property of systems with finitely many discrete states and it is known as the Schottky anomaly.

## Quantum Harmonic Oscillators

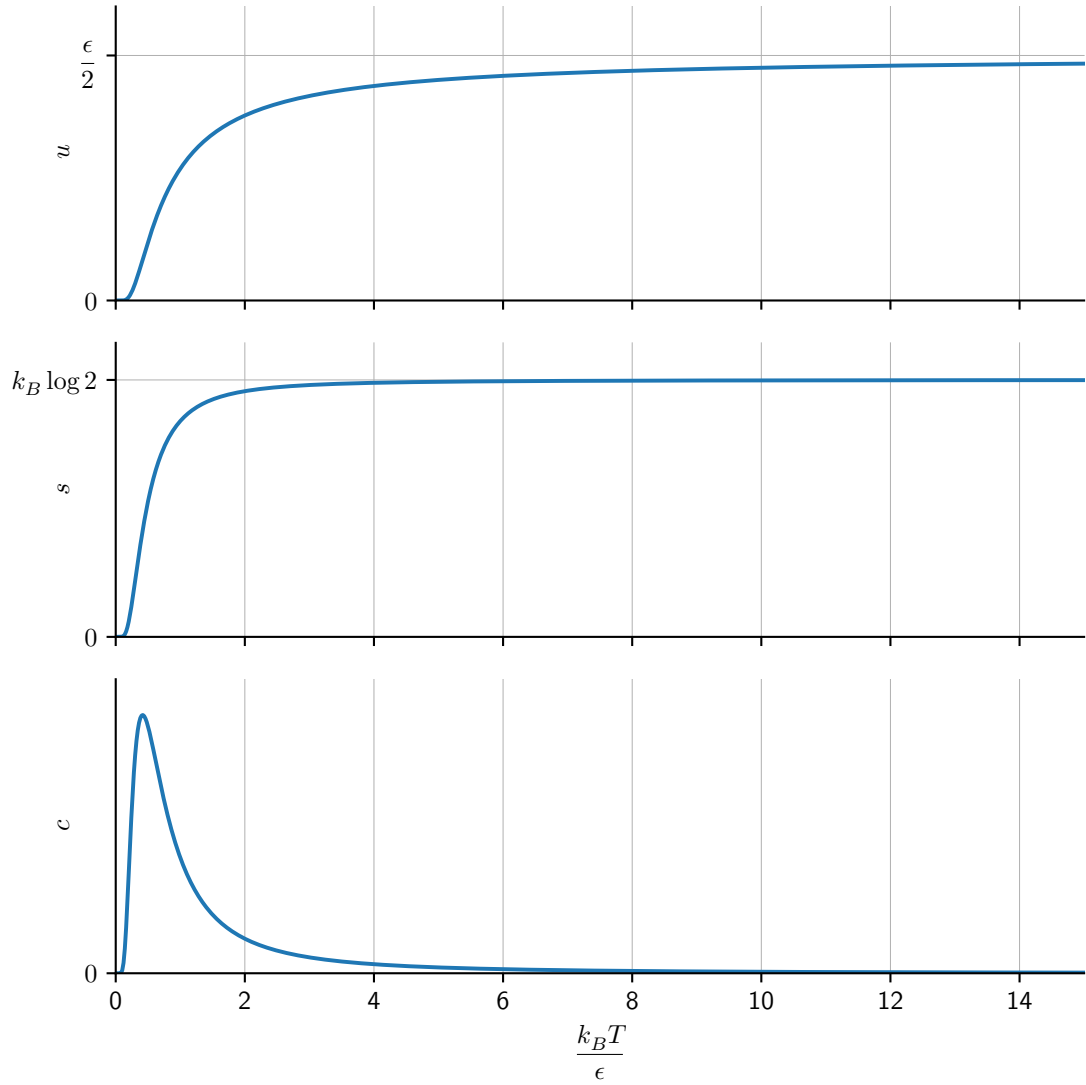
Let us next study the case of  $N$  quantum harmonic oscillators subject to a thermal bath at inverse temperature  $\beta = \frac{1}{k_B T}$ . For a single oscillator, we have the energy

$$\epsilon_n = \hbar\omega_0 \left( n + \frac{1}{2} \right), \quad (2.18)$$

where  $n$  is a non-negative integer. The partition function is then given by

$$Z = \sum_{\{\text{states}\}} e^{-\beta \sum_{i=0}^N \epsilon_i}, \quad (2.19a)$$

$$= \left( \sum_{\{i\}} e^{-\beta \epsilon_i} \right)^N, \quad (2.19b)$$



**Figure 4:** Internal energy per particle  $u$ , entropy per particle  $s$ , and specific heat per particle  $c$  as functions of temperature for the two-level system. Notice that the specific heat attains a finite maximum. This is a general feature of systems with finitely many discrete levels and is known as the Schottky anomaly.

where we used the assumption that the different oscillators do not interact<sup>\*</sup>.

We can then obtain the partition function by dealing with a one-particle partition function  $\zeta$ . It will be given by

$$\zeta = \sum_{n=0}^{+\infty} e^{-\beta \hbar \omega_0 (n + \frac{1}{2})}, \quad (2.20a)$$

$$= \frac{e^{-\frac{\beta \hbar \omega_0}{2}}}{1 - e^{-\beta \hbar \omega_0}}. \quad (2.20b)$$

Therefore,

$$Z = \left( \frac{e^{-\frac{\beta \hbar \omega_0}{2}}}{1 - e^{-\beta \hbar \omega_0}} \right)^N. \quad (2.21)$$

From the partition function we can obtain the internal energy, the Helmholtz free energy, and the entropy just as before. Their expressions per particle will be given by

$$u = \frac{\hbar \omega_0}{2} + \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}, \quad (2.22)$$

$$f = \frac{\hbar \omega_0}{2} + k_B T \log(1 - e^{-\beta \hbar \omega_0}), \quad (2.23)$$

and

$$s = \frac{\hbar \omega_0}{T(e^{\beta \hbar \omega_0} - 1)} - k_B \log(1 - e^{-\beta \hbar \omega_0}). \quad (2.24)$$

For low temperatures ( $k_B T \ll \hbar \omega_0$  or  $\beta \hbar \omega_0 \gg 1$ ), Eqs. (2.22) to (2.24) lead to the limiting behaviour

$$\lim_{\beta \hbar \omega_0 \gg 1} u = \frac{\hbar \omega_0}{2}, \quad \lim_{\beta \hbar \omega_0 \gg 1} f = \frac{\hbar \omega_0}{2}, \quad \lim_{\beta \hbar \omega_0 \gg 1} s = 0, \quad (2.25)$$

which matches our expectation that all oscillators should be at the ground state.

The specific heat is given by

$$c = \frac{k_B \beta^2 \hbar^2 \omega_0^2 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2}, \quad (2.26)$$

which implies

$$\lim_{\beta \hbar \omega_0 \gg 1} c = k_B \beta^2 \hbar^2 \omega_0^2 e^{-\beta \hbar \omega_0}. \quad (2.27)$$

This model was originally proposed by Einstein to explain how the specific heat of solids vanishes at low temperatures, and hence we see there is a qualitative agreement between experiment and theory. Nevertheless, there is a quantitative disagreement with

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<sup>\*</sup>Interacting systems are more difficult to deal with. Later in the course, we'll learn for example about the transfer matrix approach to deal with them.

experiment, since the correct behaviour at low temperatures should be  $\sim T^3$  instead of an exponential decay. This was later corrected by Debye by introducing interactions in the model (for a more detailed account, see Kardar 2007, Sec. 6.2; Pathria and Beale 2022, Sec. 7.4).

At high temperatures ( $k_B T \gg \hbar \omega_0$  or  $\beta \hbar \omega_0 \ll 1$ ), Eqs. (2.22) to (2.24) on the previous page imply

$$\lim_{\beta \hbar \omega_0 \ll 1} u = k_B T, \quad \lim_{\beta \hbar \omega_0 \ll 1} f = k_B T \log(\beta \hbar \omega_0), \quad \lim_{\beta \hbar \omega_0 \ll 1} s = k_B \left( 1 + \log \left( \frac{k_B T}{\hbar \omega_0} \right) \right), \quad (2.28)$$

while Eq. (2.26) on the preceding page leads to the specific heat at high temperatures

$$\lim_{\beta \hbar \omega_0 \ll 1} c = k_B, \quad (2.29)$$

in accordance with the Dulong–Petit law, that states the specific heat of a solid at high temperatures should tend to a constant (this can be understood under the light of the equipartition theorem, which is discussed, *exempli gratia*, in Pathria and Beale 2022, Sec. 3.7; Salinas 2001, Sec. 6.3).

It is remarkable that, in Eq. (2.28), the expressions for the entropy and Helmholtz free energy still involve  $\hbar$ , since the high temperature limit corresponds to the classical limit. The occurrence of  $\hbar$ , however, is a necessity already in classical statistical mechanics in order to ensure that it is recovered by the quantum mechanical calculations.

The plots for  $u$ ,  $s$ , and  $c$  for the system of harmonic oscillators are shown in Fig. 5 on the following page.

Perhaps discuss this in greater detail

## 2.2 Classical Statistical Physics

Motivated by the weird occurrence of an  $\hbar$  in an expression that should be classical (Eq. (2.28)), let us take a moment to discuss classical statistical physics.

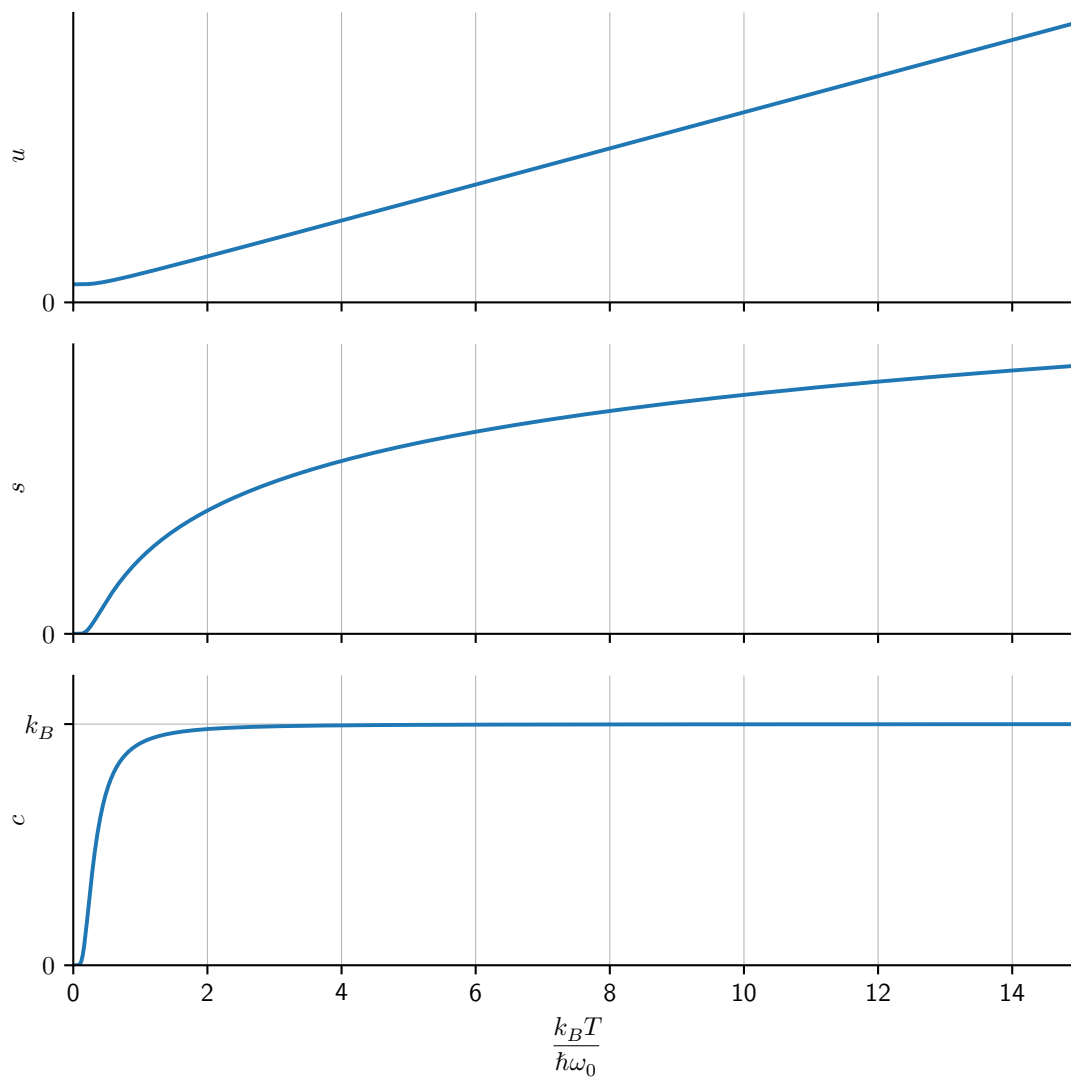
In classical systems, the states live in the phase space, which can be described in terms of generalized coordinates and their conjugate momenta,  $q$  and  $p$ , respectively. The partition function for a system with Hamiltonian  $\mathcal{H}$  can then be in principle be written as

$$Z = \sum_{\{\sigma\}} e^{-\beta \mathcal{H}(\sigma)} \stackrel{?}{=} \int e^{-\beta \mathcal{H}(q,p)} d^N q d^N p, \quad (2.30)$$

where  $\sigma$  denotes an arbitrary state and denote  $q = (q^1, q^2, \dots, q^N)$  and  $p = (p_1, p_2, \dots, p_N)$ , so that our notation allows for an arbitrary number of degrees of freedom. The question mark is in there because there is still an issue: the units on Eq. (2.30) do not match, since the measure of the integral has its own units.

To solve this issue, we'll introduce an arbitrary constant  $h$  with dimensions of action such that we can now write

$$Z = \int e^{-\beta \mathcal{H}(q,p)} \frac{d^N q d^N p}{h^N}. \quad (2.31)$$



**Figure 5:** Internal energy per particle  $u$ , entropy per particle  $s$ , and specific heat per particle  $c$  as functions of temperature for a system of  $N$  non-interacting quantum harmonic oscillators. As the temperature gets larger, the specific heat tends to a constant, in accordance with the Dulong–Petit law. It also vanishes for small temperatures, in qualitative agreement with experiment.

This constant can then be fixed by matching the classical predictions with the high temperature limits of the quantum predictions. As the notation suggests, it will indeed be Planck's constant.

A way of interpreting this is that  $h$  gives us a measure of “granularity” of phase space in the sense that it converts the volume of phase space and the actual number of states.

Let us now consider a couple of examples.

### Classical Harmonic Oscillators

Let us begin with a system of  $N$  classical harmonic oscillators, which we'll then expect to reproduce the high energy behavior of our quantum calculation. The Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{m\omega_0^2 q_i^2}{2}. \quad (2.32)$$

Therefore, the partition function becomes

$$Z = \int \exp\left(-\beta\left(\sum_{i=1}^N \frac{p_i^2}{2m} + \frac{m\omega_0^2 q_i^2}{2}\right)\right) \frac{d^N q d^N p}{h^N}, \quad (2.33a)$$

$$= \left( \int \exp\left(-\beta\left(\frac{p^2}{2m} + \frac{m\omega_0^2 q^2}{2}\right)\right) \frac{dq dp}{h} \right)^N, \quad (2.33b)$$

$$= \left( \frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{\beta m \omega_0^2}} \right)^N, \quad (2.33c)$$

$$= \left( \frac{2\pi}{\beta \hbar \omega_0} \right)^N, \quad (2.33d)$$

$$= \frac{1}{\beta^N \hbar^N \omega_0^N}, \quad (2.33e)$$

which leads to

$$u = k_B T, \quad (2.34)$$

$$f = k_B T \log(\beta \hbar \omega_0), \quad (2.35)$$

and

$$s = k_B \left( 1 + \log\left(\frac{k_B T}{\hbar \omega_0}\right) \right), \quad (2.36)$$

which match Eq. (2.28) on page 21.

### Classical Ideal Gas

A particularly interesting example for us to consider is that of a classical ideal gas. There are two main reasons for that:



- i. we'll be able to recover the we'll known equations of state, and hence understand how to derive them from first principles;
- ii. our initial approach will lead to a wrong expression for the entropy that will need to be corrected, hence paving the way for further discussion.

We'll be dealing with a gas comprised of  $N$  particles which are assumed not to interact. Furthermore, we assume it to be isotropic (hence, we're ignoring effects due to gravity, for example). The Hamiltonian is then given by

$$\mathcal{H} = \sum_{i=1}^N \frac{p_{x,i}^2}{2m} + \frac{p_{y,i}^2}{2m} + \frac{p_{z,i}^2}{2m} = \frac{1}{2m} \sum_{i=1}^N \|\mathbf{p}_i\|^2. \quad (2.37)$$

Let us begin with the naïve computation. The partition function would then be given by

$$Z = \int \exp\left(-\frac{\beta}{2m} \sum_{i=1}^N \|\mathbf{p}_i\|^2\right) \frac{d^{3N}q d^{3N}p}{h^{3N}}, \quad (2.38a)$$

$$= \frac{1}{h^{3N}} \left[ \int \exp\left(-\frac{\beta \|\mathbf{p}\|^2}{2m}\right) d^3q d^3p \right]^N, \quad (2.38b)$$

$$= \frac{V^N}{h^{3N}} \left[ \int \exp\left(-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}\right) dp_x dp_y dp_z \right]^N, \quad (2.38c)$$

$$= \frac{V^N}{h^{3N}} \left[ \frac{2\pi m}{\beta} \right]^{\frac{3N}{2}}. \quad (2.38d)$$

Using this wrong partition function, we get to the correct internal energy  $U$ ,

$$U = -\frac{\partial}{\partial \beta} \log Z = \frac{3}{2} N k_B T. \quad (2.39)$$

Nevertheless, it leads us to the wrong Helmholtz free energy  $F$ . In spite of this, we can get to the correct expression for the pressure by doing

$$p = \left( \frac{\partial F}{\partial V} \right)_T, \quad (2.40a)$$

$$= k_B T \frac{\partial}{\partial V} \log Z, \quad (2.40b)$$

$$= \frac{N k_B T}{V}. \quad (2.40c)$$

We can see the issue arising by explicitly computing the Helmholtz free energy, which leads us to

$$F = -k_B T \log Z, \quad (2.41a)$$

$$= -Nk_B T \left[ \log \left( \frac{V}{h^3} \right) + \frac{3}{2} \log \left( \frac{2\pi m}{\beta} \right) \right], \quad (2.41b)$$

which is not extensive in  $V$ . Hence, we're doing something wrong.

It is particularly curious that we did get two equations of state correctly, as we can see on Eqs. (2.39) and (2.40) on the preceding page. From Thermodynamics, we know this is enough to characterize the system completely. One may then wonder whether the issue in here lies in Statistical Mechanics or was already there in Thermodynamics, putting in risk our model of an ideal gas. Thermodynamics is safe, though: the result that two equations of state are sufficient to characterize a system follows from the assumption that entropy is extensive, and hence it does not hold in our case. If we decide to compute the free energy per unit particle from our equations of state and then assume extensivity explicitly, we'll be able to obtain the correct expression known from thermodynamics. The question is then: why isn't our expression as taken directly from the partition function matching the correct expression?

Eq. (2.38) on the previous page shows us that we're currently considering the partition function

$$Z = \zeta^N, \quad (2.42)$$

where the one-particle partition function  $\zeta$  is given by

$$\zeta = \frac{V}{h^3} \left[ \frac{2\pi m}{\beta} \right]^{\frac{3}{2}}. \quad (2.43)$$

We'll make an *ad hoc* assumption: the partition function is actually given by

$$Z = \frac{\zeta^N}{N!} = \frac{V^N}{N!} \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3N}{2}}. \quad (2.44)$$

There are justification for this assumption. For example, it is necessary to recover the classical results from the quantum mechanical results (see Pathria and Beale 2022, Sec. 3.5 and references therein). Another point of view is that it must be introduced to account for the indistinguishability of the gas' particles\*. At last, we can simply justify it in an *ad hoc* manner: it is needed because without it the result is wrong.

Using this new expression for the partition function, we get to<sup>†</sup>

$$\log Z = N \log \zeta - \log N!, \quad (2.45a)$$

$$= N \log \zeta - N \log N + N \mathcal{O}(\log N), \quad (2.45b)$$

$$\approx N \left[ \log \frac{\zeta}{N} + 1 \right], \quad (2.45c)$$

---

\*Prof. Fiore disagrees with this justification since we can always distinguish classical particles by following their trajectories. Caticha (2019) argues that it doesn't matter whether the particles are or not distinguishable, but rather if their distinguishability interests us.

<sup>†</sup>It is curious that in the case of finite  $N$  the results will lead to a non-extensive entropy, due to the remaining terms in the Stirling approximation. In the literature, there seems to be at least one claim that entropy will actually not be exactly extensive (see Peters 2014).

where we employed Stirling's approximation on Eq. (2.45b) on the preceding page. As a consequence, the Helmholtz free energy now reads

$$F = -Nk_B T \left[ \log \frac{\zeta}{N} + 1 \right], \quad (2.46a)$$

$$= -Nk_B T \left[ \log \left( \frac{V}{N} \frac{1}{h^3} \left( \frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \right) + 1 \right], \quad (2.46b)$$

$$= -Nk_B T \left[ \log \left( \frac{V}{N} \frac{1}{\lambda^3} \right) + 1 \right], \quad (2.46c)$$

where in the last line we defined the thermal wavelength  $\lambda$  by

$$\lambda = h \left( \frac{\beta}{2\pi m} \right)^{\frac{1}{2}} \quad (2.47)$$

Notice that Eq. (2.46) is indeed extensive on volume and number of particles, as it should be.

We may then compute the entropy for an ideal gas. It will be given by

$$S = \frac{U - F}{T}, \quad (2.48a)$$

$$= \frac{3}{2} Nk_B + Nk_B \left[ \log \left( \frac{V}{N\lambda^3} \right) + 1 \right], \quad (2.48b)$$

$$= Nk_B \left[ \log \left( \frac{V}{N\lambda^3} \right) + \frac{5}{2} \right], \quad (2.48c)$$

$$= Nk_B \left[ \log \frac{V}{N} + \log \frac{1}{h^3} + \frac{3}{2} \log(2\pi m k_B T) + \frac{5}{2} \right], \quad (2.48d)$$

$$= Nk_B \left[ \frac{3}{2} \log k_B T + \log \frac{V}{N} - 3 \log h + \frac{3}{2} \log(2\pi m) + \frac{5}{2} \right]. \quad (2.48e)$$

Let us now perform the same calculation with the equations of state we previously obtained, Eqs. (2.39) and (2.40) on page 24. They yield

$$\frac{1}{T} = \frac{3Nk_B}{2U} = \frac{3k_B}{2u} = \left( \frac{\partial s}{\partial u} \right)_v, \quad (2.49a)$$

$$\frac{p}{T} = \frac{Nk_B}{V} = \frac{k_B}{v} = \left( \frac{\partial s}{\partial v} \right)_u, \quad (2.49b)$$

which can be integrated to obtain

$$s(u, v) = \frac{3}{2} k_B \log u + k_B \log v + s_0, \quad (2.50)$$

where  $s_0$  is some integration constant. If we explicitly impose extensivity of entropy, we'll obtain

$$S(U, V, N) = Ns(u, v), \quad (2.51a)$$

$$= \frac{3}{2} N k_B \log \frac{U}{N} + N k_B \log \frac{V}{N} + N s_0, \quad (2.51b)$$

$$= N k_B \left[ \frac{3}{2} \log \left( \frac{3}{2} k_B T \right) + \log \frac{V}{N} + \frac{s_0}{k_B} \right], \quad (2.51c)$$

$$= N k_B \left[ \frac{3}{2} \log k_B T + \log \frac{V}{N} + \log \frac{3}{2} + \frac{s_0}{k_B} \right]. \quad (2.51d)$$

## 2.3 Gases with Diatomic Molecules

### Classical Theory

For classical systems, the mean energy always has the form\*

$$U = \frac{f}{2} N k_B T, \quad (2.52)$$

where  $f$  is the number of quadratic terms on the Hamiltonian (*id est*, essentially the number of degrees of freedom). Hence, for harmonic oscillators, we have  $U = N k_B T$ . For a monoatomic ideal gas,  $U = \frac{3}{2} N k_B T$ . For an ideal gas made of rigid diatomic molecules,  $U = \frac{5}{2} N k_B T$ . If the molecules of this diatomic ideal gas can vibrate,  $U = \frac{7}{2} N k_B T$ .

For all ideal gases, however, the pressure is the same: since they are non-interacting by definition, the dependence on the positional degrees of freedom is the same, so the volume appears on the calculation in the same way it did for the monoatomic gas. Since the pressure is deduced from the volume dependency, the equation of state for the pressure is the same for all ideal gases. We'll later consider interactions among different molecules in the van der Waals gas, which will lead to a different expression for the pressure.

Cross reference

To figure out the thermodynamic properties of the diatomic gas, let us start by noticing the kinetic energy of a single molecule is given by

$$K = \frac{m_1 \|\dot{\mathbf{r}}_1\|^2}{2} + \frac{m_2 \|\dot{\mathbf{r}}_2\|^2}{2}, \quad (2.53)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the positions of the atoms composing the molecule as measured from the laboratory reference frame. We may then define the position of the center of mass,  $\mathbf{R}$ , and the separation between the particles,  $\mathbf{r}$ , by

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \quad \text{and} \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \quad (2.54)$$

In terms of these variables the kinetic energy can be written as

$$K = \frac{M \|\dot{\mathbf{R}}\|^2}{2} + \frac{\mu \|\dot{\mathbf{r}}\|^2}{2}, \quad (2.55)$$

where we also defined

$$M = m_1 + m_2 \quad \text{and} \quad \mu = \frac{m_1 m_2}{M}. \quad (2.56)$$

---

\*This is known as the equipartition theorem, discussed, *exempli gratia*, by Pathria and Beale (2022, Sec. 3.7) and Salinas (2001, Sec. 6.3).

It is convenient to express the terms related to  $\mathbf{r}$  in spherical coordinates. We then get

$$\frac{\mu r^2}{2} = \frac{\mu}{2} (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2), \quad (2.57)$$

and find the Lagrangian

$$L = K - V, \quad (2.58a)$$

$$= \frac{M \|\dot{\mathbf{R}}\|^2}{2} + \frac{\mu}{2} (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2) - V, \quad (2.58b)$$

where  $V$  is some potential that might later model the oscillations of the molecule. Notice that the first term of Eq. (2.58b) corresponds to the translational degrees of freedom, while the three following terms correspond to rotational and vibrational degrees of freedom. Translation is already present for monoatomic gases, but rotations and vibrations are a new feature.

The Hamiltonian for a single molecule is then

$$H = \frac{\|\mathbf{p}_R\|^2}{2M} + \frac{p_r^2}{2\mu} + \frac{p_\theta^2}{2\mu r^2} + \frac{p_\phi^2}{2\mu r^2 \sin^2 \theta} + V. \quad (2.59)$$

For a rigid molecule, similar to a dumbbell, we'll have  $p_r = 0$  and  $V = 0$  (non-interacting gas, no internal interactions). Let us denote the fixed distance between the two atoms by  $b$ . In this case, the Hamiltonian simplifies to

$$H = \frac{\|\mathbf{p}_R\|^2}{2M} + \frac{p_\theta^2}{2\mu b^2} + \frac{p_\phi^2}{2\mu b^2 \sin^2 \theta}, \quad (2.60)$$

meaning it has five quadratic terms. As a consequence, the internal energy will be

$$U = \frac{5}{2} N k_B T. \quad (2.61)$$

For a vibrating molecule, the potential has to be that of a harmonic oscillator, so we'll have  $p_r \neq 0$  and  $V \propto r^2$ . This time, the Hamiltonian becomes

$$H = \frac{\|\mathbf{p}_R\|^2}{2M} + \frac{p_r^2}{2\mu} + \frac{p_\theta^2}{2\mu r^2} + \frac{p_\phi^2}{2\mu r^2 \sin^2 \theta} + \frac{m\omega^2 r^2}{2}, \quad (2.62)$$

with seven quadratic terms. Therefore, the internal energy is

$$U = \frac{7}{2} N k_B T. \quad (2.63)$$

For completeness, let us compute the partition function for the rigid, dumbbell-like molecule. It will be given by

$$Z = \frac{\zeta^N}{N!}, \quad (2.64)$$

where the one-molecule partition function  $\zeta$  is given by

$$\zeta = \int e^{-\beta H} \frac{d^3 R d^3 p_R d\theta dp_\theta d\phi dp_\phi}{h^5}, \quad (2.65a)$$

$$= \frac{V}{h^5} \int e^{-\beta \left[ \frac{\|\mathbf{p}_R\|^2}{2M} + \frac{p_\theta^2}{2\mu b^2} + \frac{p_\phi^2}{2\mu b^2 \sin^2 \theta} \right]} d^3 p_R d\theta dp_\theta d\phi dp_\phi, \quad (2.65b)$$

$$= \frac{V}{h^5} \int \left( \frac{2\pi M}{\beta} \right)^{\frac{3}{2}} \left( \frac{2\pi \mu b^2}{\beta} \right)^{\frac{1}{2}} \left( \frac{2\pi \mu b^2 \sin^2 \theta}{\beta} \right)^{\frac{1}{2}} d\theta d\phi, \quad (2.65c)$$

$$= \frac{(2\pi)^{\frac{7}{2}} V}{h^5 \beta^{\frac{5}{2}}} M^{\frac{3}{2}} \mu b^2 \int_0^\pi \sin \theta d\theta, \quad (2.65d)$$

$$= \frac{2(2\pi)^{\frac{7}{2}} V}{h^5 \beta^{\frac{5}{2}}} M^{\frac{3}{2}} \mu b^2 \int_0^\pi, \quad (2.65e)$$

$$= \frac{4\pi V}{h^5 \beta^{\frac{5}{2}}} (2\pi M)^{\frac{3}{2}} (2\pi \mu b^2). \quad (2.65f)$$

Do notice that on Eq. (2.65a) the integral is being taken in phase space, so there is no Jacobian due to the choice of spherical coordinates.

From Eq. (2.65), it is then straightforward to obtain that

$$U = \frac{5}{2} N k_B T, \quad (2.66)$$

$$c_V = \frac{5}{2} N k_B, \quad (2.67)$$

$$pV = N k_B T, \quad (2.68)$$

as previously claimed.

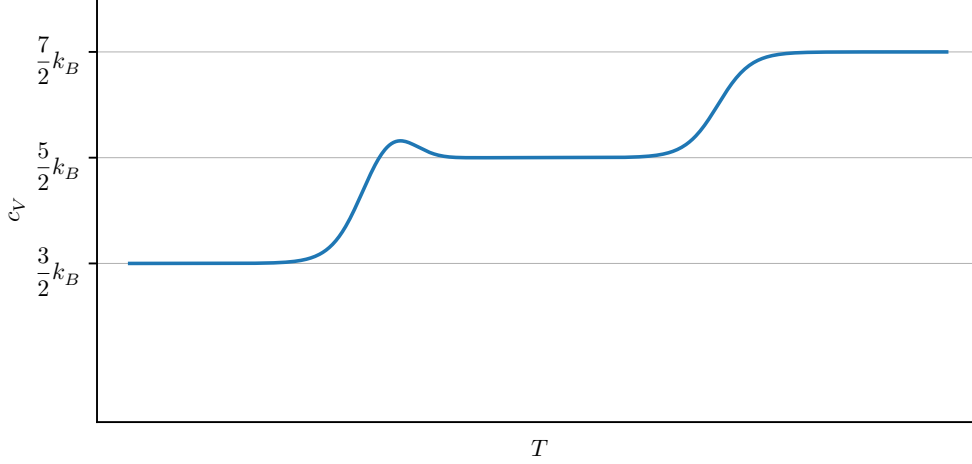
## Quantum Theory

Eq. (2.67), obtained with the classical theory, claims that the specific heat of a gas of diatomic molecules is constant. However, that is not true. Experimentally, a minimum amount of energy is needed to activate the rotational and vibrational degrees of freedom, which leads to the graph of specific heat as a function of temperature having a few plateaus, corresponding to the temperatures in which the new degrees of freedom become relevant (for graphs and experimental data, see Pathria and Beale 2022, Sec. 6.5.B; Salinas 2001, Sec. 8.4; Wannier 1987, Chap. 11). The temperature dependency of the specific heat is sketched on Fig. 6 on the next page.

While classical theory fails to explain why the diatomic gas behaves as if it was monoatomic, quantum theory succeeds. To understand how, let us analyse the rotational degrees of freedom in particular. This is possible because the partition function can be decomposed as a product of simpler partition functions, (see Salinas 2001, Sec. 8.4).

Quantum mechanically, the rotational Hamiltonian of a single molecule will be

$$\hat{H}_{\text{rot}} = \frac{\hat{J}^2}{2I}, \quad (2.69)$$



**Figure 6:** Sketch of the specific heat per molecule of a diatomic ideal gas of heteromolecules (id est, each molecule is composed of two different nuclei). The characteristic bump before the specific heat reaches  $\frac{5}{2}k_B$  is typical of diatomic gases composed of heteromolecules. As higher temperatures are achieved, new degrees of freedom get activated and the specific heat increases. The figure is adapted from the figures given by Chabay and Sherwood (2015, Sec. 12.9), Pathria and Beale (2022, Sec. 6.5.B), Salinas (2001, Sec. 8.4), and Wannier (1987, Chap. 11)

where  $I$  is the molecule's moment of inertia. We know that  $\hat{J}^2$  has the eigenstates

$$\hat{J}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle, \quad (2.70)$$

where  $l \in \mathbb{N}_0$ ,  $-l \leq m \leq l$ , and each energy level has a  $(2l+1)$ -fold degeneracy. Therefore, the “one-molecule rotational partition function” is

$$\zeta_{\text{rot}} = \sum_{l=0}^{+\infty} \sum_{m=-l}^l e^{-\frac{\beta \hbar^2 l(l+1)}{2I}}, \quad (2.71a)$$

$$= \sum_{l=0}^{+\infty} (2l+1) e^{-\frac{\beta \hbar^2 l(l+1)}{2I}}. \quad (2.71b)$$

This expression can be computed numerically, but not analytically. In spite of this difficulty, we can obtain analytical expressions for the remarkable limits of high and low temperatures.

At low temperatures, we have  $\frac{\beta \hbar^2}{2I} \gg 1$ , so rotational energy is much lower than thermal energy. As a consequence, high values of  $l$  are suppressed and we can approximate  $\zeta_{\text{rot}}$  by the first two terms of the sum. We get

$$\zeta_{\text{rot}} \approx \sum_{l=0}^1 (2l+1) e^{-\frac{\beta \hbar^2 l(l+1)}{2I}}, \quad (2.72a)$$

$$= 1 + 3e^{-\frac{\beta\hbar^2}{I}}. \quad (2.72b)$$

From Eq. (2.72) on the preceding page, we see the “rotational Helmholtz free energy per molecule” is given by

$$f_{\text{rot}} = -k_B T \log \zeta_{\text{rot}}, \quad (2.73a)$$

$$= -k_B T \log \left( 1 + 3e^{-\frac{\beta\hbar^2}{I}} \right), \quad (2.73b)$$

$$\approx -3k_B T e^{-\frac{\beta\hbar^2}{I}}. \quad (2.73c)$$

Eq. (2.72) on the previous page also leads to

$$u_{\text{rot}} = -\frac{\partial}{\partial \beta} \log \zeta_{\text{rot}}, \quad (2.74a)$$

$$\approx \frac{3\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}}, \quad (2.74b)$$

and hence

$$c_{\text{rot}} = \frac{\partial u}{\partial T} \approx 3k_B \left( \frac{\beta\hbar^2}{I} \right)^2 e^{-\frac{\beta\hbar^2}{I}}, \quad (2.75)$$

which tends to zero for temperatures much smaller than the “rotational temperature”  $T_R = \frac{\hbar^2}{2k_B I}$ , showing the rotational degrees of freedom “freeze” at low temperatures. The rotational (and vibrational) temperatures for some gases are shown on Table 1.

**Table 1:** *Rotational and vibrational temperatures for some diatomic gases. Taken from Salinas 2001, p. 156.*

Gas	$T_R$ (K)	$T_V$ ( $10^3$ K)
H <sub>2</sub>	85.4	6.10
N <sub>2</sub>	2.86	3.34
O <sub>2</sub>	2.07	2.23
CO	2.77	3.07
NO	2.42	2.69
HCl	15.2	4.14

For high temperatures ( $\frac{\beta\hbar^2}{2I} \ll 1$ ), there is a very small spacing between different energy levels, which allows us to approximate the sum on Eq. (2.71) on the previous page



by an integral, which leads us to

$$\zeta_{\text{rot}} = \sum_{l=0}^{+\infty} (2l+1) e^{-\frac{\beta \hbar^2 l(l+1)}{2I}}, \quad (2.76a)$$

$$= \int_0^{+\infty} (2\xi+1) e^{-\frac{\beta \hbar^2 \xi(\xi+1)}{2I}} d\xi, \quad (2.76b)$$

$$= \int_0^{+\infty} e^{-\frac{\beta \hbar^2 u}{2I}} du, \quad (2.76c)$$

$$= \frac{2k_B T I}{\hbar^2}, \quad (2.76d)$$

where on Eq. (2.76c) we performed the substitution  $u = \xi(\xi+1)$ .

Notice that Eq. (2.76) will then lead to the conclusion that  $c_{\text{rot}} = k_B$ , corresponding to all rotational degrees of freedom being activated and matching the classical prediction, as expected.

Instead of just approximating the sum by an integral on Eq. (2.76), we could be careful and use the Euler–MacLaurin expansion formula (see Abramowitz and Stegun 1972; Arfken, Weber, and Harris 2013, Sec. 12.3), as Salinas (2001, Sec. 8.4) does, to get the asymptotic expression

$$\zeta_{\text{rot}} = \frac{T}{T_R} \left[ 1 + \frac{1}{3} \left( \frac{T_R}{T} \right) + \frac{1}{15} \left( \frac{T_R}{T} \right)^2 + \dots \right], \quad (2.77)$$

which leads to the specific heat

$$c_{\text{rot}} = k_B \left[ 1 + \frac{1}{45} \left( \frac{T_R}{T} \right)^2 + \dots \right], \quad (2.78)$$

from which we can see that the specific heat will tend to  $k_B$  for  $T \gg T_R$ . For heteromolecules, the dots on Eq. (2.78) predict the bump of Fig. 6 on page 30, matching experiment.

A similar analysis can be carried out for the vibrational degree of freedom, which can be modeled as a harmonic oscillator. We'll get a similar result that the degree of freedom “freezes” at low temperatures. The specific heat will be given by Eq. (2.26) on page 20, which we previously obtained when studying an ensemble of harmonic oscillators.

Our main lesson is then that, in polyatomic molecules, we are often able to deal with each degree of freedom separately. For some more details on polyatomic molecules, Pathria and Beale (see 2022, Sec. 6.5.C).

## 2.4 Interactions and the Virial Expansion

So far, we have only considered non-interacting systems, which, albeit simple, are not realistic. We won't be able to deal exactly with interactions, but it is possible to obtain approximate expressions. In this section, we'll see one such method and illustrate it with

the van der Waals gas, the most famous model of a “real” gas. For some more information, one can see, *exempli gratia*, the texts by Kardar (2007, Chap. 5), Pathria and Beale (2022, Chap. 10), and Salinas (2001, Sec. 6.4).

For an ideal gas, the equation of state for pressure reads

$$\frac{p}{k_B T} = \frac{1}{v}, \quad (2.79)$$

and we have  $p = p(T, v)$  in general. Hence, it is reasonable to expect we can write the equation of state for more real gases in the form

$$\frac{p}{k_B T} = \frac{1}{v} + \frac{A(T)}{v^2} + \frac{B(T)}{v^3} + \dots, \quad (2.80)$$

which is known as the virial expansion. We’d like then to compute the virial coefficients  $A$ ,  $B$ , and so on from first principles. We’ll focus on only the first coefficient,  $A$ .

The actual equation of state we’ll try to understand from first principles is that of a van der Waals gas,

$$p = \frac{k_B T}{v - b} - \frac{a}{v^2}, \quad (2.81)$$

where  $a$  and  $b$  are constants. As we shall see, we can interpret  $b$  as representing the finite volume of the gas’ molecules and  $a$  as representing the intermolecular interactions, which are assumed to behave as hard spheres with a small attractive potential. As illustrated in Fig. 7 on the following page, this model provides a simplified version of the Lennard-Jones potential, which is the typical potential for intermolecular interactions, but is harder to treat.

We’ll begin with a general approach and impose the hard sphere potential only at the end, so we’ll also derive a more general expression that applies to a wide class of interactions.

We assume the interaction potential to depend solely on the distances between molecules,  $V = V(\|\mathbf{r}_i - \mathbf{r}_j\|)$ . This time, we can’t use a one-particle partition function, so we write  $Z$  as

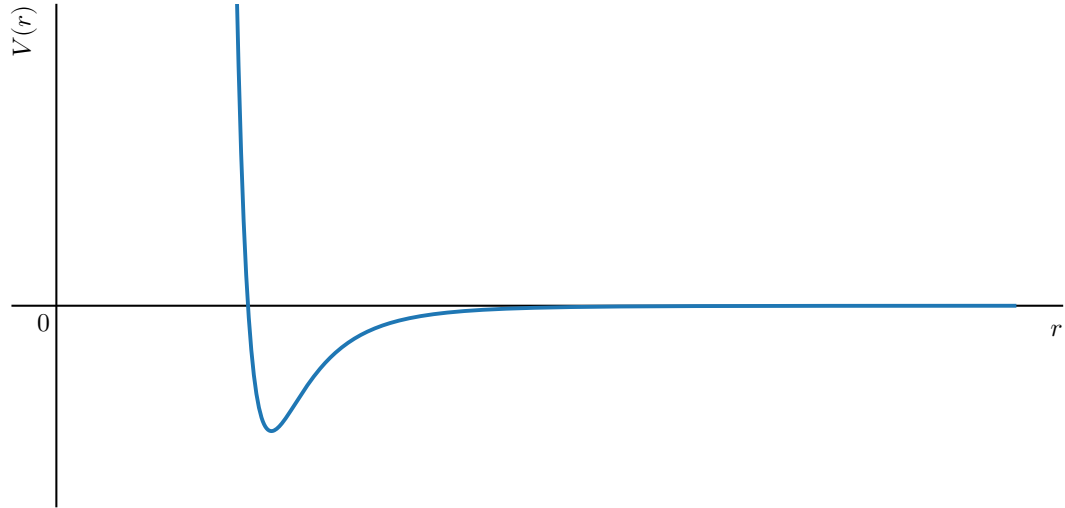
$$Z = \frac{1}{N!} \int e^{-\beta H(q,p)} \frac{d^{3N}q d^{3N}p}{h^{3N}}, \quad (2.82a)$$

$$= \frac{1}{N!} \int e^{-\beta \left( \sum_{i=1}^N \frac{\|\mathbf{p}_i\|^2}{2m} + \sum_{i < j} V(\|\mathbf{r}_i - \mathbf{r}_j\|) \right)} \frac{d^{3N}q d^{3N}p}{h^{3N}}, \quad (2.82b)$$

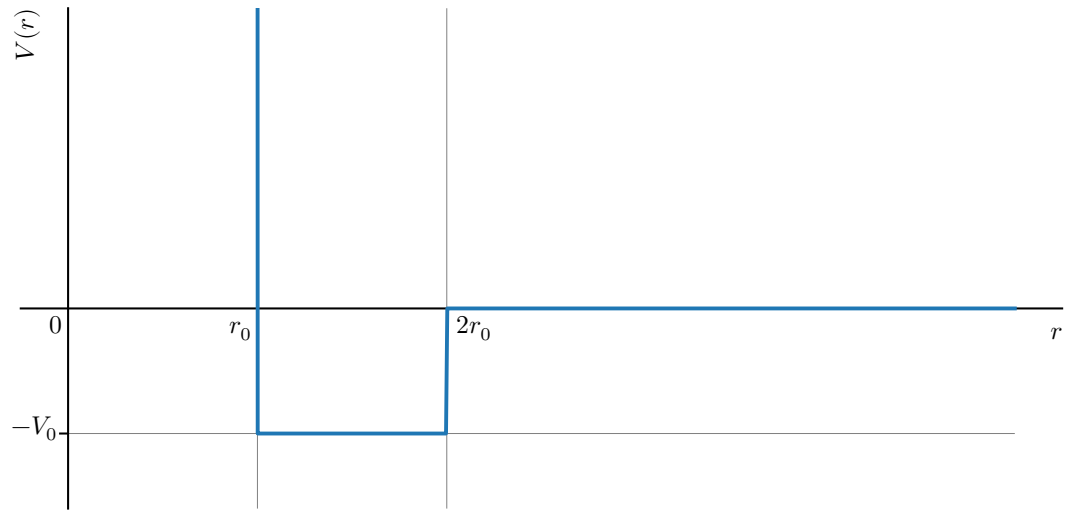
where the sum over  $i$  and  $j$  with the condition  $i < j$  prevents us from overcounting the interactions. While the integrals over generalized coordinates got more complicated, the integrals over momenta work just like the ideal gas, leading us to

$$Z = \frac{1}{N! h^{3N}} \left( \frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \int e^{-\beta \sum_{i < j} V(\|\mathbf{r}_i - \mathbf{r}_j\|)} d^{3N}q, \quad (2.83a)$$

$$= \frac{1}{N! h^{3N}} \left( \frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} Q_N, \quad (2.83b)$$

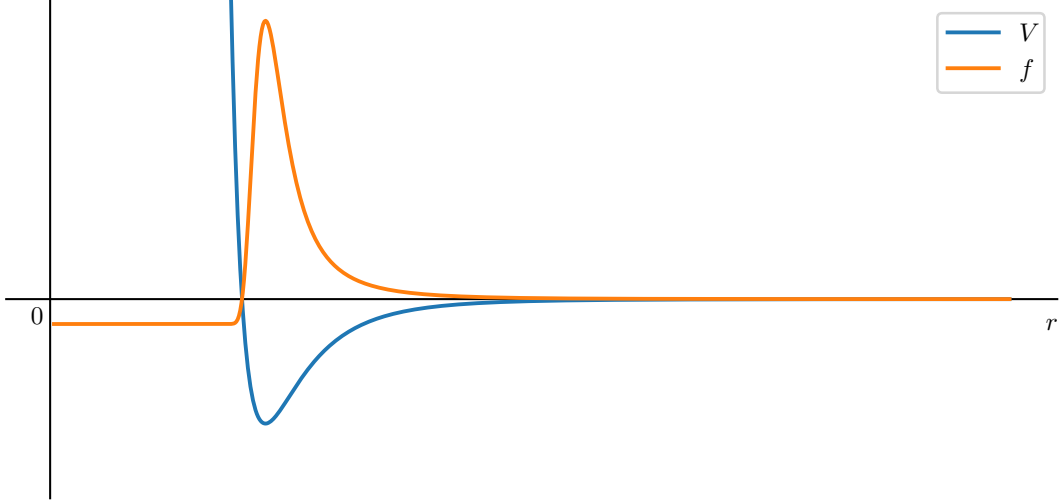


(a) Lennard-Jones potential. Typical shape of the potential for intermolecular interactions.



(b) Potential for hard sphere scattering with a small attraction.

**Figure 7:** A simplification of the Lennard-Jones potential is a potential for hard sphere scattering with a small attractive region.



**Figure 8:** While the Lennard-Jones potential diverges at the origin, the function  $f$  defined by Eq. (2.85) is well-behaved everywhere.

where  $Q_N$  is given by

$$Q_N \equiv \int e^{-\beta \sum_{i < j} V(\|\mathbf{r}_i - \mathbf{r}_j\|)} d^{3N}q, \quad (2.84a)$$

$$= \int \prod_{i < j} e^{-\beta V(\|\mathbf{r}_i - \mathbf{r}_j\|)} \prod_{k=1}^N d^3r_k. \quad (2.84b)$$

For simplicity, let us denote  $V_{ij} \equiv V(\|\mathbf{r}_i - \mathbf{r}_j\|)$ . It will also be convenient to define

$$f_{ij} = e^{-\beta V_{ij}} - 1, \quad (2.85)$$

for  $f_{ij}$  will remain finite when  $V_{ij}$  diverges (see Fig. 8) and overall make the calculations simpler.

In terms of this new function, we can write  $Q_N$  as

$$Q_N = \int \prod_{i < j} (1 + f_{ij}) \prod_{k=1}^N d^3r_k. \quad (2.86)$$

Notice that the product  $\prod_{i < j} (1 + f_{ij})$  has the form

$$\prod_{i < j} (1 + f_{ij}) = (1 + f_{12})(1 + f_{13})(1 + f_{14}) \cdots (1 + f_{1N})(1 + f_{23}) \cdots (1 + f_{N-1,N}), \quad (2.87a)$$

$$= 1 + \sum_{i < j} f_{ij} + \cdots, \quad (2.87b)$$

where the dots include terms quadratic or higher on the  $f_{ij}$ . Our first approximation will consist on neglecting such terms. Hence, we'll write

$$\prod_{i < j} (1 + f_{ij}) \approx 1 + \sum_{i < j} f_{ij}. \quad (2.88)$$

With this approximation,  $Q_N$  can be written as

$$Q_N = \int (1 + \sum_{i < j} f_{ij}) \prod_{k=1}^N d^3 r_k, \quad (2.89a)$$

$$= \int \prod_{k=1}^N d^3 r_k + \sum_{i < j} \int f_{ij} \prod_{k=1}^N d^3 r_k, \quad (2.89b)$$

$$= V^N + \sum_{i < j} \int f_{ij} d^3 r_i d^3 r_j \prod_{k \neq i, j} d^3 r_k, \quad (2.89c)$$

$$= V^N + V^{N-2} \sum_{i < j} \int f_{ij} d^3 r_i d^3 r_j, \quad (2.89d)$$

$$= V^N + \frac{V^{N-2} N(N-1)}{2} \int f_{12} d^3 r_1 d^3 r_2, \quad (2.89e)$$

where we used the fact that, since we're integrating over  $\mathbf{r}_i$  and  $\mathbf{r}_j$ , all terms in the sum are equal. If we now introduce coordinates  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  and\*  $\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2$ , the integral becomes

$$Q_N = V^N + \frac{V^{N-2} N(N-1)}{2} \int f(r) d^3 R d^3 r, \quad (2.90a)$$

$$= V^N + \frac{V^{N-1} N(N-1)}{2} \int f(r) d^3 r, \quad (2.90b)$$

$$= V^N + 2\pi V^{N-1} N(N-1) \int f(r) r^2 dr, \quad (2.90c)$$

where in the last step we chose to work in spherical coordinates and used the assumption that the interaction depends only on the distance between the molecules, and hence it is isotropic.

To compute thermodynamics quantities we'll ultimately be interested in  $\log Z$ . Hence, we notice now that Eq. (2.90) leads us to

$$\log Q_N = N \log V + \log \left[ 1 + \frac{2\pi N(N-1)}{V} \int f(r) r^2 dr \right]. \quad (2.91)$$

---

\*One could choose  $\mathbf{R}$  to be the position of the center of mass. I'm using  $\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2$  to avoid having to think about the Jacobians that go into the integral, but either choice should work out equally well.

Now comes our second approximation: we'll assume  $\frac{N}{V} \ll 1$ , *id est*, that the gas is in a low density regime\*. Under this hypothesis, we can write

$$\log Q_N \approx N \log V + \frac{2\pi N(N-1)}{V} \int f(r)r^2 dr. \quad (2.92)$$

Using Eqs. (2.83) and (2.92) on page 33 and on the current page we get to

$$\frac{1}{N} \log Z = -\frac{1}{N} \log N! + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \frac{1}{N} \log Q_N, \quad (2.93a)$$

$$\approx -\log N + 1 + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \log V + \frac{2\pi(N-1)}{V} \int f(r)r^2 dr, \quad (2.93b)$$

$$\approx -\log N + 1 + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \log V + \frac{2\pi N}{V} \int f(r)r^2 dr, \quad (2.93c)$$

$$= \log \frac{V}{N} + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \frac{2\pi N}{V} \int f(r)r^2 dr + 1, \quad (2.93d)$$

$$= \log v + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \frac{2\pi}{v} \int f(r)r^2 dr + 1. \quad (2.93e)$$

With Eq. (2.93) we can now compute thermodynamic quantities. The Helmholtz free energy per molecule, for example, is given by

$$f(T, v) = -\frac{1}{\beta N} \log Z, \quad (2.94a)$$

$$= -\frac{1}{\beta} \left[ \log v + \frac{3}{2} \log \frac{2\pi m}{\beta h^2} + \frac{2\pi}{v} \int f(r)r^2 dr + 1 \right]. \quad (2.94b)$$

Therefore, the pressure is given by

$$p(T, v) = -\left( \frac{\partial f}{\partial v} \right)_T, \quad (2.95a)$$

$$= \frac{k_B T}{v} - \frac{2\pi k_B T}{v^2} \int f(r)r^2 dr. \quad (2.95b)$$

By comparing Eqs. (2.80) and (2.95) on page 33 and on this page, we see we've found the first virial term to be

$$A(T) = -2\pi \int_0^{+\infty} f(r)r^2 dr. \quad (2.96)$$

---

\*  $\frac{N}{V} \ll 1$  is not dimensionally correct, but it should be understood in comparison with the terms that go along with it on Eq. (2.91) on the previous page.

Let us now consider the specific case of the van der Waals gas. We go back to the hard sphere potential of Fig. 7b on page 34 and notice that it leads us to

$$A(T) = -2\pi \left[ \int_0^{r_0} f(r)r^2 dr + \int_{r_0}^{2r_0} f(r)r^2 dr + \int_{2r_0}^{+\infty} f(r)r^2 dr \right], \quad (2.97a)$$

$$= -2\pi \left[ -\int_0^{r_0} r^2 dr + \int_{r_0}^{2r_0} (e^{\beta V_0} - 1)r^2 dr + 0 \right], \quad (2.97b)$$

$$= -2\pi \left[ -\frac{r_0^3}{3} + \frac{7r_0^3}{3}(e^{\beta V_0} - 1) \right], \quad (2.97c)$$

$$= \frac{2\pi r_0^3}{3} - \frac{14\pi r_0^3}{3}(e^{\beta V_0} - 1). \quad (2.97d)$$

For a weakly attractive potential, in which  $V_0$  can be assumed to be very small, we can then write

$$A(T) = \frac{2\pi r_0^3}{3} - \frac{14\pi r_0^3 V_0}{3k_B T}. \quad (2.98)$$

If we now recall the equation of state for the van der Waals gas, Eq. (2.81) on page 33, we can see that

$$\frac{p}{k_B T} = \frac{1}{v - b} - \frac{a}{k_B T v^2}, \quad (2.99a)$$

$$= \frac{1}{v(1 - \frac{b}{v})} - \frac{a}{k_B T v^2}, \quad (2.99b)$$

$$= \frac{1}{v} + \frac{b}{v^2} + \frac{b^2}{v^3} + \dots - \frac{a}{k_B T v^2}, \quad (2.99c)$$

$$= \frac{1}{v} + \left( b - \frac{a}{k_B T} \right) \frac{1}{v^2} + \frac{b^2}{v^3} + \dots. \quad (2.99d)$$

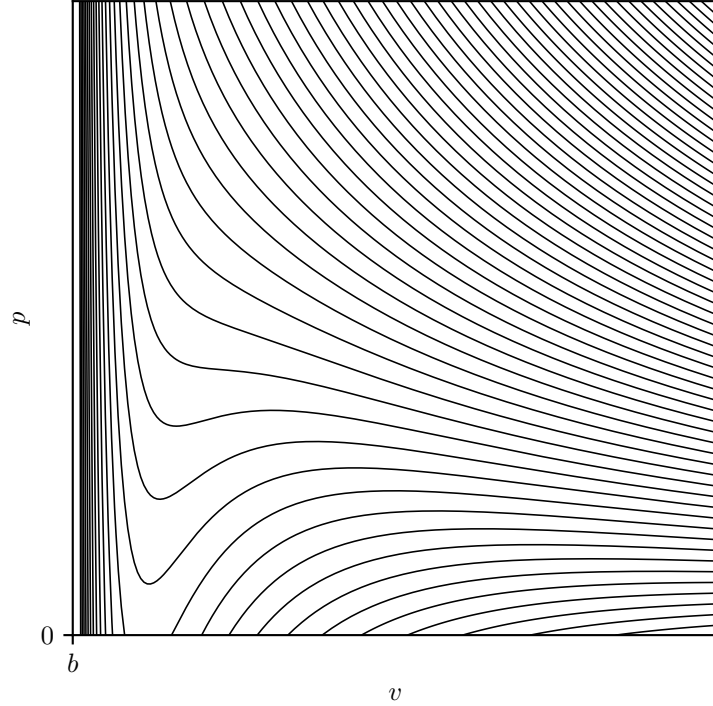
Comparing Eqs. (2.98) and (2.99) lets us identify

$$a = \frac{14\pi r_0^3 V_0}{3} \quad \text{and} \quad b = \frac{2\pi r_0^3}{3}, \quad (2.100)$$

which justifies interpreting the van der Waals gas as a gas of weakly attractive hard spheres. For further discussion on the van der Waals equation see, *exempli gratia*, the text by Kardar (2007, Sec. 5.3).

As last, it is worth mentioning that for high temperatures the van der Waals gas behaves just like an ideal gas, as depicted on Fig. 9 on the following page. However, for small temperatures, the isotherms do not match experiment and there's even the presence of thermodynamic instabilities ( $(\frac{\partial p}{\partial v})_T > 0$ ). Later, we'll take a close look at these issues and notice there is a phase transition happening with the same critical exponents of the Ising model (for now, you might want to check Salinas 2001, Sec. 12.1).

Cross reference



**Figure 9:**  $p$ - $v$  diagram for the van der Waals gas. Each line is an isotherm. Notice that for high temperatures, we recover the behavior of an ideal gas, while small temperatures present new, problematic behaviors that hint at what we'll later learn to be a phase transition.

## 2.5 Grand Canonical Ensemble

The canonical ensemble is frequently useful, but the canonical partition function doesn't factorize for quantum gases due to particle indistinguishability. For these cases, it will be useful to use the grand canonical ensemble.

Let us begin by discussing when to use the different ensembles. While we overlooked the microcanonical ensemble at jumped straight at the canonical ensemble, a traditional way of deriving the canonical partition function is by considering the physical situation corresponding to each ensemble.

The so-called microcanonical ensemble (discussed, *exempli gratia*, by Kardar [2007](#), Sec. 4.2; Pathria and Beale [2022](#), Sec. 2.3; Salinas [2001](#), Chap. 4) corresponds to an isolated system, which means we hold the internal energy  $U$ , the volume  $V$ , and the number of particles  $N$  fixed. In this situation, the fundamental principle of Statistical Mechanics states that all microstates are equally likely and, as a consequence, the problem boils down to counting the number of accessible microstates. Denoting said number of microstates by  $\Omega(U, V, N)$ , the entropy is obtained through Boltzmann's formula  $S(U, V, N) = k_B \log \Omega(U, V, N)$ , from which we can obtain all other thermodynamic properties.

The canonical ensemble corresponds to a different physical situation. When using it,



we assume to be describing a subsystem  $S$  of an isolated system.  $S$  itself is not isolated, but rather is subject to a thermal bath  $R$  at temperature  $T$ . Under these conditions, one can show (see, *exempli gratia*, Salinas 2001, Chap. 5), that the probability distribution for the microstates of the subsystem will be given by the Gibbs distribution,

$$p_j = \frac{e^{-\beta E_j}}{Z}. \quad (2.101)$$

Notice, in particular, that  $Z$  is a function of temperature, volume, and number of particles. Hence, the system and bath exchange energy in order to keep the temperature fixed, but the volume and number of particles of the subsystem remain fixed.

The canonical ensemble is one of the most used ones. Computing the number of microstates in the microcanonical ensemble is often a cumbersome task, while computing the canonical partition function is typically fair easier.

In spite of that, there are physical situations in which the canonical ensemble is not convenient. In some of these, the grand canonical ensemble might be a better choice. It corresponds to the situation in which the subsystem  $S$  is subject not only to a thermal bath, but also to a particle bath. Hence, volume is held fixed, but energy and number of particles are not. Instead, temperature and chemical potential are kept constant while energy and number of particles fluctuate.

In this last physical situation, using the facts known from the microcanonical ensemble and the hypothesis that the energy and number of particles of the subsystem are much less than those of the composite system involving the bath, one can show (Salinas 2001, Sec. 7.2) that the probability distribution for the microstates of the subsystem will be

$$p_j = \frac{e^{-\beta E_j + \beta \mu N_j}}{\sum_i e^{-\beta E_i + \beta \mu N_i}}, \quad (2.102)$$

where  $\beta$  is the (fixed) inverse temperature,  $\mu$  is the (fixed) chemical potential, and the sum is carried over states of fixed temperature and chemical potential. We define

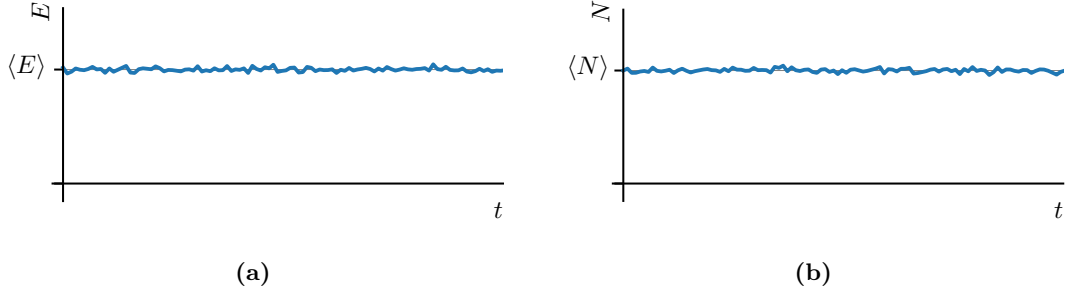
$$\Xi(T, V, \mu) = \sum_i e^{-\beta E_i + \beta \mu N_i} \quad (2.103)$$

to be the grand canonical partition function.

The fact that we are dealing with systems in equilibrium means, in this context, that while the energy and number of particles of the subsystem do fluctuate with time, they fluctuate about average values, as illustrated on Fig. 10 on the next page. In the thermodynamic limit, these fluctuations will die off and become negligible, just like we had in the canonical ensemble.

One then might inquire about how we'll compute the grand canonical partition function. There are two main approaches:

- i. our first option is to list all states, their respective energies  $E_i$  and particle numbers  $N_i$ , and then perform the sum on Eq. (2.103);



**Figure 10:** *In the grand canonical ensemble, the energy and number of particles on the subsystem under consideration fluctuate about an average. In the thermodynamic limit, these fluctuations become negligible.*

- ii. an alternative, but equivalent, approach is to regroup the sum in terms of fixed values of  $N$ , writing

$$\Xi(T, V, \mu) = \sum_{N=0}^{+\infty} e^{\beta\mu N} \sum_i e^{-\beta E_i(N)}, \quad (2.104a)$$

$$= \sum_{N=0}^{+\infty} e^{\beta\mu N} Z(T, V, N), \quad (2.104b)$$

where  $E_i(N)$  denotes the energy of state  $i$  at fixed  $N$ .

Notice that the second method allows us to understand the grand canonical partition function in terms of the more familiar canonical partition function.

We are able to relate partition functions to thermodynamic potentials. For example, for the canonical partition function we have

$$Z(T, V, N) = e^{-\beta F(T, V, N)}, \quad (2.105)$$

where  $F(T, V, N)$  is the Helmholtz free energy. To find out the expression for the grand canonical partition function, we begin by noticing that

$$\Xi(T, V, \mu) = \sum_{N=0}^{+\infty} e^{\beta\mu N - \beta F(T, V, N)}, \quad (2.106a)$$

$$= \sum_{N=0}^{+\infty} e^{-\beta[F(T, V, N) - \mu N]}. \quad (2.106b)$$

To make the connection with thermodynamics, we may then approximate this sum by its maximum term, which is the one that dominates in the thermodynamic limit. In this situation, we'll get to

$$\Xi(T, V, \mu) \approx e^{-\beta \min_N \{F(T, V, N) - \mu N\}}, \quad (2.107a)$$

$$= e^{-\beta \Phi(T, V, \mu)}, \quad (2.107b)$$

where we used the fact that  $\min_N \{F(T, V, N) - \mu N\}$  is just a Legendre transformation from the Helmholtz free energy to the grand potential\*  $\Phi$ . Therefore, we can write

$$\Phi(T, V, \mu) = -k_B T \log \Xi(T, V, \mu). \quad (2.108)$$

Our next step is then to compute the ensemble averages, with particular interest on the expressions for the mean energy and mean number of particles. For the mean number of particles we have

$$\langle N \rangle = \sum_i N_i p_i, \quad (2.109a)$$

$$= \frac{1}{\Xi} \sum_i N_i e^{-\beta E_i + \beta \mu E_i}, \quad (2.109b)$$

$$= \frac{1}{\beta \Xi} \frac{\partial}{\partial \mu} \sum_i e^{-\beta E_i + \beta \mu E_i}, \quad (2.109c)$$

$$= \frac{1}{\beta \Xi} \frac{\partial \Xi}{\partial \mu}, \quad (2.109d)$$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \Xi. \quad (2.109e)$$

Notice next that

$$-\frac{1}{\Xi} \frac{\partial \Xi}{\partial \beta} = -\frac{1}{\Xi} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i + \beta \mu E_i}, \quad (2.110a)$$

$$= -\frac{1}{\Xi} \sum_i (E_i - \mu N_i) e^{-\beta E_i + \beta \mu E_i}, \quad (2.110b)$$

$$= -\sum_i (E_i - \mu N_i) p_i, \quad (2.110c)$$

$$= -\langle E \rangle + \mu \langle N \rangle. \quad (2.110d)$$

Eqs. (2.109) and (2.110) imply that

$$\langle E \rangle = -\frac{1}{\Xi} \frac{\partial \Xi}{\partial \beta} - \mu \langle N \rangle, \quad (2.111a)$$

$$= -\frac{\partial}{\partial \beta} \log \Xi - \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \log \Xi. \quad (2.111b)$$

To simplify this expression for  $\langle E \rangle$ , we can introduce the fugacity<sup>†</sup>,

$$z = e^{\beta \mu}, \quad (2.112)$$

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\*Kardar (2007, Sec. 119)[Sec. 3.5.5]reichl2016ModernCourseStatistical call it grand potential. Salinas (2001, p. 52) calls it “grand thermodynamic potential”. Pathria and Beale (2022, Sec. 4.3) prefers “ $q$ -potential”. Prof. Fiore referred to it as “grand canonical potential”.

<sup>†</sup>Salinas (2001, p. 130) mentions the fugacity is sometimes called the “activity”.

in terms of which we may write

$$p_i = \frac{z^{N_i} e^{-\beta E_i}}{\Xi} \quad (2.113)$$

and

$$\Xi(T, V, z) = \sum_{N=0}^{+\infty} z^N Z(T, V, N). \quad (2.114)$$

In terms of the fugacity, the mean energy can be written as

$$\langle E \rangle = \frac{1}{\Xi} \sum_i E_i z^{N_i} e^{-\beta E_i}, \quad (2.115a)$$

$$= -\frac{1}{\Xi} \left( \frac{\partial}{\partial \beta} \sum_i z^{N_i} e^{-\beta E_i} \right)_z, \quad (2.115b)$$

$$= - \left( \frac{\partial}{\partial \beta} \log \Xi \right)_z. \quad (2.115c)$$

Eqs. (2.111) and (2.115) on the preceding page and on the current page are consistent with each other because different variables are kept constant in each of them.

As for the number of particles, we have

$$\langle N \rangle = \frac{1}{\Xi} \sum_i N_i z^{N_i} e^{-\beta E_i}, \quad (2.116a)$$

$$= \frac{z}{\Xi} \left( \frac{\partial \Xi}{\partial \beta} \right)_\beta, \quad (2.116b)$$

$$= z \left( \frac{\partial}{\partial \beta} \log \Xi \right)_\beta. \quad (2.116c)$$

Using reduction of derivatives (see Callen 1985, Sec. 7.3) one can show that, for some quantity  $q$ ,

$$\left( \frac{\partial q}{\partial \beta} \right)_z = \left( \frac{\partial q}{\partial \beta} \right)_\mu + \left( \frac{\partial q}{\partial \mu} \right)_\beta \left( \frac{\partial \mu}{\partial \beta} \right)_z, \quad (2.117a)$$

$$= \left( \frac{\partial q}{\partial \beta} \right)_\mu - \frac{\mu}{\beta} \left( \frac{\partial q}{\partial \mu} \right)_\beta, \quad (2.117b)$$

where we computed  $\left( \frac{\partial \mu}{\partial \beta} \right)_z = -\frac{\mu}{\beta}$  from  $z = e^{\beta \mu}$ . Notice Eq. (2.117) is precisely the relation necessary for consistency between Eqs. (2.111) and (2.115) on the previous page and on this page, as one can see from plugging in  $q = -\log \Xi$  into Eq. (2.117).

It remains for us to study the quantity

$$\langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2, \quad (2.118)$$

which will be relevant to the grand canonical ensemble for a couple of reasons.

- i.  $\langle (N - \langle N \rangle)^2 \rangle$  is related to  $\frac{\partial \langle N \rangle}{\partial \mu}$ , and hence the positivity of one will imply the positivity of the other, ensuring that the number of particles increases with the chemical potential.
- ii. This will allow us to notice that the fluctuations of the number of particles about the expected value become negligible in the thermodynamic limit, with the expected value matching the fixed value of  $N$  one would get from the canonical ensemble, hence showing the ensembles are equivalent.

Through the usual arguments, one can show that

$$\langle N^2 \rangle = \frac{1}{\Xi} \frac{1}{\beta^2} \frac{\partial^2 \Xi}{\partial \mu^2}. \quad (2.119)$$

A calculation analogous to the one we did in Eq. (2.5) on page 15 also lets us see that

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \log \Xi, \quad (2.120a)$$

$$= \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu}. \quad (2.120b)$$

Since  $\langle N^2 \rangle - \langle N \rangle^2 \geq 0$  and  $\beta > 0$ , we conclude  $\frac{\partial \langle N \rangle}{\partial \mu} \geq 0$ .

In some situations, when dealing with phase transitions, one might get  $\frac{\partial \langle N \rangle}{\partial \mu} < 0$ . This is an incorrect result and must be fixed, but it might also be used as a hint of the occurrence of a phase transition.

To deal with the fluctuations, we notice that the thermodynamic number of particles  $N$  is the expected value  $\langle N \rangle$ . One can then show that (Salinas 2001, Sec. 7.2B)

$$\frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle} = \frac{1}{N} \sqrt{\frac{N^2 \kappa_T}{\beta V}}, \quad (2.121a)$$

$$= \left( \frac{k_B T \kappa_T}{v} \right)^{\frac{1}{2}} \frac{1}{\sqrt{N}}, \quad (2.121b)$$

$$\rightarrow 0, \quad (2.121c)$$

where in the last line we took the thermodynamic limit and  $\kappa_T$  is the isothermal compressibility. Hence, we see that in the thermodynamic limit the fluctuations will vanish. This is in fact what allows us to understand the ensemble average  $\langle N \rangle$  as the actual thermodynamic number of particles  $N$ , leading us also to an equivalence of the canonical and grand canonical ensembles.

We typically expect ensembles to be equivalent in the thermodynamic limit for homogeneous systems with short-range interactions. Near phase transitions, this might fail, as we can have  $\kappa_T \rightarrow +\infty$ , which renders the previous argument inconsistent (Eq. (2.121c) only holds if the coefficient on Eq. (2.121b) remains finite in the thermodynamic limit).

For long-range interactions, there is no consensus in the literature on whether there is equivalence of ensembles.

Maybe add diverging references?

### Monoatomic Ideal Gas

As an example of how the grand canonical potential works, let us consider the monoatomic ideal gas one more time.

From Eq. (2.44) on page 25 we know the canonical partition function for the ideal gas is given by

$$Z(T, V, N) = \frac{V^N}{N!} \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3N}{2}}. \quad (2.122)$$

Therefore, the grand canonical partition function will be

$$\Xi(T, V, \mu) = \sum_{N=0}^{+\infty} z^N Z(T, V, N), \quad (2.123a)$$

$$= \sum_{N=0}^{+\infty} \frac{1}{N!} \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3N}{2}} z^N V^N, \quad (2.123b)$$

$$= \exp \left( \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3}{2}} z V \right). \quad (2.123c)$$

Hence, the internal energy as a function of fugacity (not number of particles) is given by

$$U(T, V, z) = \langle E \rangle, \quad (2.124a)$$

$$= -\frac{\partial}{\partial \beta} \log \Xi(T, V, z), \quad (2.124b)$$

$$= \frac{3}{2} \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3}{2}} \frac{zV}{\beta}. \quad (2.124c)$$

As for the expected number of particles, we get

$$N(T, V, z) = \langle N \rangle, \quad (2.125a)$$

$$= z \frac{\partial}{\partial z} \log \Xi(T, V, z), \quad (2.125b)$$


$$= \left[ \frac{2\pi m}{\beta h^2} \right]^{\frac{3}{2}} z V. \quad (2.125c)$$




Notice that Eqs. (2.124) and (2.125) imply





$$\frac{\langle E \rangle}{\langle N \rangle} = \frac{3}{2} k_B T, \quad (2.126)$$

in agreement with the canonical ensemble.

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