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Chapter 3

Elements of classical statistical physics

3.1 Elements of classical mechanics and probability theory

3.1.1 Phase spaces and classical mechanics

We start by discussing elements of classical mechanics, in order to lay out the formalism for classical statistical physics. This is surely a meaningful starting point, as many phenomena can be explained in a classical description. Others cannot. We consider a system of N particles, confined to a region $\Omega \subset \mathbb{R}^3$. The phase space of each particle consists hence of the pair (\mathbf{q}, \mathbf{p}) with $\mathbf{p} \in \mathbb{R}^3$ and $\mathbf{q} \in \Omega$. The total phase space of all particles is the cartesian product.

Phase space of N particles:

$$\Gamma = (\mathbb{R}^3 \times \Omega)^N. \quad (3.1)$$

Points in phase space are often written as γ . The complete description of a classical system is given by $\gamma \in \Gamma$, as then we know all positions and momenta of all particles. The equations of motion of these particles are determined by the Hamiltonian function $H : \Gamma \rightarrow \mathbb{R}$. We take them of the form

$$H(\gamma) = \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} + V_1(\mathbf{q}_i) \right) + \sum_{i \neq j} V_2(\mathbf{q}_i - \mathbf{q}_j), \quad (3.2)$$

where V_1 is a single particle potential and V_2 is an interaction between the particles. To simplify the notation, we have taken all particles to be the same,

with the same mass m . It is often convenient to consider the collection of all positions and all momenta as vectors,

$$\mathbf{p} = (p_{1,1}, p_{1,2}, \dots, p_{N,3}) = (p_1, \dots, p_{3N}), \quad (3.3)$$

and similarly for \mathbf{q} . In this way, the Hamiltonian equations of motion become

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad (3.4)$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \quad (3.5)$$

At this point, maybe a comment is in order how we treat boundaries here. We assume that the boundary of Ω is reflecting, in that when a particle with $(\mathbf{q}_i, \mathbf{p}_i)$ hits the boundary, then \mathbf{q}_i remains the same but with \mathbf{p}_i being mirrored at the tangential plane.

Solutions of the equations of motion exist for all times. For times $t \in \mathbb{R}$ one hence arrives at a map $\mathcal{F}_t : \Gamma \rightarrow \Gamma$ such that $t \mapsto \mathcal{F}_t(\gamma)$ is the solution of the problem with initial state γ . We have $\mathcal{F}_0(\gamma) = \gamma$ and also, since the Hamiltonian is assumed not to be time dependent,

$$\mathcal{F}_t \circ \mathcal{F}_s = \mathcal{F}_{t+s}, \quad (3.6)$$

for all $s, t \in \mathbb{R}$. The family of such functions \mathcal{F}_t is called the flow in phase space.

Two features are important here. The first one is that the energy is conserved. In our new language, this means that

$$H(\mathcal{F}_t(\gamma)) = H(\gamma). \quad (3.7)$$

The second one is that the volume is preserved under dynamics. The volume is measured in the Liouville measure, written as

$$d\gamma = dp_1 dq_1 \dots dq_{3N} = d^{3N} p d^{3N} q. \quad (3.8)$$

Preservation of volume means that

$$\int d\gamma f(\mathcal{F}_t(\gamma)) = \int d\gamma f(\gamma). \quad (3.9)$$

If $f = \chi_S$ is the indicator function of an arbitrary set $S \subset \Gamma$, then the right hand side is the volume of S , whereas the left is the volume of the transformed set $\mathcal{F}_t^{-1}(S) = \{\gamma : \mathcal{F}_t(\gamma) \in S\}$.

An important role will be played by the energy shell. Consider for some energy value E the energy surface.

Energy surface: For any E in the image of H , define the energy surface

$$\{\gamma : H(\gamma) = E\}. \quad (3.10)$$

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It has dimension $6N - 1$. Therefore, subsets of this set will have Liouville measure zero. We can still introduce a meaningful surface measure as follows: For energy E and $\epsilon > 0$, consider the set

$$\{\gamma : E - \epsilon \leq H(\gamma) \leq E\}. \quad (3.11)$$

The integral of a function $f : \Gamma \rightarrow \mathbb{R}$ over the energy surface is then

$$\begin{aligned} \int d\gamma \delta(H(\gamma) - E) f(\gamma) &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \int_{E-\epsilon \leq H(\gamma) \leq E} d\gamma f(\gamma) \\ &= \frac{d}{dE} \int_{H(\gamma) \leq E} d\gamma f(\gamma). \end{aligned} \quad (3.12)$$

So far, we have assumed that we knew the positions and momenta of all particles precisely. As pointed out several times before, this is neither possible nor needed. We hence always have to include a certain degree of randomness in our description. This motivates the next subsection on elements of probability theory.

3.1.2 Distributions and moments

In this subsection, we will be brief and focused. Let us consider systems described by the laws of classical mechanics. The state of the system is then $\gamma \in \Gamma$. We assume Γ to be the above phase space, but the same notion also makes sense for finite state spaces. A common experiment amounts to not exactly preparing γ , but rather a distribution of a set of possible states. We introduce a density ρ , such that $\rho(\gamma)$ is the probability density of having prepared the state γ . From the probability interpretation we have that

$$\rho(\gamma) \geq 0, \quad (3.13)$$

$$\int d\gamma \rho(\gamma) = 1. \quad (3.14)$$

One can interpret this quantity as grasping relative frequencies in a statistical preparation of a state.

Observables, expectation value and variance: An observable is a function $f : \Gamma \rightarrow \mathbb{R}$ that determines the outcome $f(\gamma)$ if a system is in the state γ . The expectation value (or first moment) is given by

$$\langle f \rangle_\rho = \int d\gamma \rho(\gamma) f(\gamma). \quad (3.15)$$

The variance is

$$\langle (f - \langle f \rangle_\rho)^2 \rangle_\rho = \langle f^2 \rangle_\rho - \langle f \rangle_\rho^2. \quad (3.16)$$

The expected mean of outcomes in measurements is just the expectation value. If we repeat many measurements, the mean of the outcomes will converge to this value. The variance is the expected deviation from the mean. These are first and second moments, but similarly, higher moments can also be defined.

3.1.3 Composite classical systems

We will a lot be concerned with composite systems, the phase space of which is of the form $\Gamma = \Gamma_1 \times \Gamma_2$. Densities of the joint state will then depend on the pair $(\gamma_1, \gamma_2) \in \Gamma_1 \times \Gamma_2$. Often, we are interested in observables that act only in one state. For functions that depend on γ_1 only (but not on γ_2), we can write

$$\int d\gamma_1 d\gamma_2 \rho(\gamma_1, \gamma_2) f(\gamma_1) = \int d\gamma_1 (R_1 \rho)(\gamma_1) f(\gamma_1), \quad (3.17)$$

where

$$(R_1 \rho)(\gamma_1) = \int d\gamma_2 \rho(\gamma_1, \gamma_2). \quad (3.18)$$

This distribution is called reduced distribution, or marginal distribution.

Say, take a density ρ in the $6N$ -dimensional phase space of N particles. We are interested in an observable f that depends only on the coordinates of the first particle. Then

$$\langle f \rangle_\rho = \int d^3 p d^3 q (R_1 \rho)(\mathbf{p}, \mathbf{q}) f(\mathbf{p}, \mathbf{q}), \quad (3.19)$$

with

$$(R_1 \rho)(\mathbf{p}_1, \mathbf{q}_1) = \int d^3 p_2 \dots d^3 p_N d^3 q_2 \dots d^3 q_N \rho(\mathbf{p}_1, \dots, \mathbf{q}_N). \quad (3.20)$$

We will now assume that the density does not depend on the numbering of the particles, that is, for every permutation π of $\{1, \dots, N\}$ we have that

$$\rho(\mathbf{p}_{\pi(1)}, \dots, \mathbf{p}_{\pi(N)}) = \rho(\mathbf{p}_1, \dots, \mathbf{q}_N). \quad (3.21)$$

Then all density functions of ρ are the same. The expectation of the kinetic energy is hence

$$\left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right\rangle = N \int d^3 p d^3 q (R_1 \rho)(\mathbf{p}, \mathbf{q}) \frac{\mathbf{p}^2}{2m}. \quad (3.22)$$

In order to compute the variance of the kinetic energy, or the expectation value of the interaction energy, it is no longer sufficient to know the marginal distribution. In order to compute these quantities, we need to know the marginal distribution over two particles.

In case of a composite system $\Gamma = \Gamma_1 \times \Gamma_2$ the density $\rho(\gamma_1, \gamma_2)$ contains in general more information than both marginal distributions $R_i \rho$ together. The exception are product distributions. If

$$\rho(\gamma_1, \gamma_2) = \rho_1(\gamma_1) \rho_2(\gamma_2), \quad (3.23)$$

then the parts are called statistically independent. To prepare statistically independent distributions is particularly easy: One merely needs to keep the parts separate. Two observables f and g are called independent, if for any functions $F, G : \mathbb{R} \rightarrow \mathbb{R}$ it is true that

$$\langle F(f)G(g) \rangle_\rho = \langle F(f) \rangle_\rho \langle G(g) \rangle_\rho. \quad (3.24)$$

In statistical mechanics, one usually considers in addition to acts of preparation discussed here the evolution under Hamiltonian dynamics, captured by \mathcal{F}_t . From the equations of motion for position and momentum one gets for $\rho_t = \rho \circ \mathcal{F}_{-t}$ that

$$\frac{d}{dt}\rho_t = \sum_{i=1}^{3N} \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i}, \quad (3.25)$$

an expression that is also called Poisson-bracket.

Even if parts have been prepared in a statistically independent fashion, they will not remain independent under time evolution in general. That is,

$$\rho(\mathcal{F}_{-t}(\gamma_1, \gamma_2)) \neq \rho_{1,t}(\gamma_1)\rho_{2,t}(\gamma_2). \quad (3.26)$$

An exception is the case where the flow itself remains factoring. This is exactly the case if the Hamiltonian is a sum of Hamiltonians of each parts, so in an entirely non-interacting situation.

3.2 Microcanonical ensemble

3.2.1 Conceptual issues

We have stated several times that the aim of statistical mechanics is to derive or make plausible the phenomenological findings to thermodynamics. This means that we have to establish some sort of translation table, translating concepts of statistical mechanics to those of thermodynamics. Some of them we have just encountered. The container holding some material corresponds to Γ which restricts all position coordinates. The number of particles N has an obvious equivalent in thermodynamics. Also, there is a correspondence between the inner energy and the energy $H(\gamma)$.

This translation is less straightforward in case of entropy, temperature and other thermodynamical functions. These functions were used to grasp thermodynamical equilibria after all. In thermodynamics these equilibrium conditions were defined as those that are established automatically, if one allows a system to relax. In classical dynamics, we also have a notion of time evolution: The flow \mathcal{F}_t describes how a system evolves in time. So one may be tempted to look for those states in classical mechanics that are always reached by themselves, via Hamiltonian dynamics.

This approach is, however, doomed to failure. We have seen that under time evolution, the volume in phase space is preserved. There is no set S of

a non-zero volume that $\mathcal{F}_t(S)$ becomes a point later. We have to look for the emergence of equilibria elsewhere.

The second attempt is based on the – in principle correct – assumption that we are not interested in all observables, but only in some special observables that are related to small number of “macroscopic” features. For such macroscopic observables f_i we would like to compute their expectation value, or better even

$$\lim_{t \rightarrow \infty} f(\mathcal{F}_t(\gamma)) \quad (3.27)$$

The previous argument of preservation of volume is no longer valid. Still, also this attempt does not work, as arguments show that have already been discussed around the turn of the 19th to the 20th century.

The first is the Umkehrwand (I think the German word is used here). There is a time reversal symmetry in classical mechanics, under the map

$$\theta : (\mathbf{p}, \mathbf{q}) \mapsto (-\mathbf{p}, \mathbf{q}) \quad (3.28)$$

that reverses all momenta. It is clear that this time reversal symmetry is not respected in the approach to equilibrium.

The second is the Wiederkehrwand. There is a theorem that shows that for every initial state, the evolution confined to the energy shell will become arbitrarily close to the initial state for a suitable later time. So again, accompanying a tendency to approach equilibrium, there must be a tendency to go out of it again. But this is not what is observed: Already pretty small systems go to equilibrium and stay there.

We can largely resolve these issues, however. The first thing is that the recurrence times in the Wiederkehrwand are ridiculously large, much larger than any feature that one is commonly interested in. So in any numerical simulation, say, roundoff errors will have become much more important before this recurrence is observed. We can hence safely ignore that.

One can argue similarly with the other argument: Indeed, if one numerically simulates the time evolution of a model, and at some point performs a time reversal, then the system will indeed go back for some time. But this is extremely fragile to numerical errors. If the numerics is done very precisely, then one can indeed observe that the system goes back to the initial state. Otherwise, the simulation detours from the exact reverse trajectory and again goes to equilibrium.

If one considers an initial set $S \subset \Gamma$ of states we start with, then we can have a look how this set evolves in time. We already know that its volume is conserved. But this does not mean that its shape is conserved. It will become wobbly, and then develop “fingers” and will look more and more complicated in time. Soon, the entire phase space is spread out with structures way too fine to resolve. So “typically”, a system will converge to a situation that is indistinguishable from the uniform distribution.

3.2.2 Definition of the ensemble

What does typical mean here? It is clear that the entire dynamics can only happen on the energy shell,

$$H(\mathcal{F}_t(\gamma)) = E. \quad (3.29)$$

If there are no obvious symmetries in the problem, usually such systems have no further constants of motion. Such systems, which have no further constants of motion, are called ergodic. If a system is ergodic, hence there exists only one distribution that is stationary in time. We write expectation values as follows:

Expectation values in the micro canonical ensemble:

$$\begin{aligned} \langle f \rangle_E &= \frac{\int d\gamma \delta(H(\gamma) - E) f(\gamma)}{\int d\gamma \delta(H(\gamma) - E)} \\ &= Z(E)^{-1} \int d\gamma \delta(H(\gamma) - E) f(\gamma). \end{aligned} \quad (3.30)$$

The denominator is determined by $\langle 1 \rangle_E = 1$. The value $\langle f \rangle_E$ is called the micro-canonical expectation value of the observable f , and

$$\rho(E) = Z(E)^{-1} \delta(H(\gamma) - E) \quad (3.31)$$

the micro-canonical ensemble. The normalisation is the micro-canonical partition function.

For ergodic systems, for almost all initial states the time average of all observables exists. Since this mean is by definition time-independent, it has to be identical with the micro canonical expectation value,

$$\lim_{t \rightarrow \infty} \frac{1}{T} \int_0^T dt f(\mathcal{F}_t(\gamma)) = \langle f \rangle_E, \quad (3.32)$$

for almost all γ with $H(\gamma) = E$. The micro-canonical ensemble is hence the accurate description of this final situation of a homogeneous looking phase space picture. Of course, also in a thermodynamic description one can think of time averages. But since all measurement outcomes converge to the equilibrium values, all time averages are just the same as the equilibrium values. Hence, at least for ergodic systems, we have made great progress in identifying thermodynamical equilibrium properties for particle number N , inner energy E , and volume Ω and microscopic descriptions in the framework of classical mechanics.

The fine print, of course, is to find out whether a system is ergodic in the first place. This is mathematically often exceedingly hard to prove. There are classic results on billiards in two dimensions are ergodic – in a proof that fills a couple of hundred pages. Still, people believe that this is merely a technicality, and that essentially all “natural” systems are ergodic.

3.3 Canonical ensemble

3.3.1 Definition of the canonical ensemble

So we have made progress understanding what energy, volume and particle number correspond to. Still, we are lacking an understanding of temperature and entropy. After all, temperature is the notion that defines an equilibrium state. We hence bring a system into contact with a heat bath and will assume that the joint system – so the system plus the heat bath – are described by a micro canonical ensemble. The Hamiltonian function of the composite system is

$$H(\gamma, \gamma_B) = H(\gamma) + H_B(\gamma_B) + V(\gamma, \gamma_B), \quad (3.33)$$

with the obvious interpretation of the terms. The interaction term V allows for an exchange of energy, macroscopically speaking for an exchange of heat. But it is sufficient to allow for very small perturbations of the operator $H + H_B$. We expect also from thermostatics that the equilibrium value does not depend on the specifics of how the heat contact has been made. When computing the micro canonical ensemble, we hence set – in an approximation – just

$$V = 0. \quad (3.34)$$

This is surely an approximation, as the system becomes clearly non-ergodic when the two parts are not in contact with one another. But it should be clear that one can think of sequences of systems, which are coupled less and less, each of which being ergodic. So this approximation is less ridiculous as one might think at first (besides, it is not so easy to overcome this. In quantum theory, we have just published new work in the Physical Review Letters on perturbed systems, in 2012).

For observables that do not depend on the coordinates of the heat bath, we hence get

$$\begin{aligned} \langle f \rangle_E &= Z^{-1} \int d\gamma d\gamma_B \delta(H(\gamma) + H_B(\gamma_B) - E) f(\gamma) \\ &= Z^{-1} \int d\gamma f(\gamma) d\gamma_B \delta(H_B(\gamma_B) - (E - H(\gamma))) \\ &= Z^{-1} \int d\gamma f(\gamma) \omega_B(E - H(\gamma)), \end{aligned} \quad (3.35)$$

where Z stands for the same expression as above, with f replaced by 1. Also

$$\omega_B(E_B) = \int d\gamma_B \delta(H_B(\gamma_B) - E_B) \quad (3.36)$$

is the micro-canonical density of states of the bath. We therefore find that expectation values are determined by a density that is no longer concentrated on an energy surface alone.

We note another thing: The only property of the heat bath that matters is the micro-canonical density of states. If we take the heat bath to be an ideal

gas, so in this statistical description N independent particles of mass m in a container Ω with volume V), we can explicitly determine this quantity. We have

$$\begin{aligned}\omega_B(E - H(\gamma)) &= \int d\gamma_B \delta(H_B(\gamma_B) - (E - H(\gamma))) \\ &= \int_{\Omega} d^{3N}q \int d^{3N}p \delta\left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} - (E - H(\gamma))\right).\end{aligned}\quad (3.37)$$

The first integral gives V , the second the surface of a $3N$ -dimension hyper ball with radius

$$(2m(E - H(\gamma)))^{1/2}.\quad (3.38)$$

Calling $\nu_d R^{d-1}$ the surface of a d -dimensional ball of radius R , we get

$$\begin{aligned}\omega_B(E - H(\gamma)) &= (2m)^{3N/2-1} V^N \nu_{3N} (E - H(\gamma))^{3N/2-1} \\ &= c(E - H(\gamma))^{3N/2-1},\end{aligned}\quad (3.39)$$

with a suitable constant $c > 0$. For very small N , this will hardly be a heat bath, so we have to consider the limit of large particle numbers. We therefore consider $N \rightarrow \infty$ and let the energy E of the system and bath proportionally grow with N , so $E = NE_1$. For large N , the energy of the small system itself will be negligible anyway, and we want to keep a finite energy density for the bath.

From thermodynamical considerations on the ideal gas we know that $U_B = fRT/2$, where here $f = 3$ (which originates from the three degrees of freedom of movement). The particle number N is here the actual particle number, and not an abstract ‘‘Stoffmenge’’ as is common in thermodynamics. The unit $k = R/\text{mol}$ is then the Boltzmann constant. We will come back to that later. So we get

$$E_1 = U_B/N = \frac{3}{2}kT\quad (3.40)$$

$$\begin{aligned}\langle f \rangle_E &= Z^{-1} \int d\gamma f(\gamma) c(E - H(\gamma))^{3N/2-1} \\ &= Z^{-1} \int d\gamma f(\gamma) \left(1 - \frac{H(\gamma)}{NE_1}\right)^{3N/2-1}.\end{aligned}\quad (3.41)$$

Since we know that

$$e^{-x} = \lim_{n \rightarrow \infty} \left(1 - \frac{x}{n}\right)^n,\quad (3.42)$$

for $N \rightarrow \infty$, we get

$$\begin{aligned}\langle f \rangle_{\beta} &:= \lim_{N \rightarrow \infty} \langle f \rangle_{NE_1} = Z^{-1} \int d\gamma f(\gamma) e^{-\frac{3H(\gamma)}{2E_1}} \\ &= Z^{-1} \int d\gamma f(\gamma) e^{-\beta H(\gamma)},\end{aligned}\quad (3.43)$$

with

$$\beta = \frac{3}{2E_1} = \frac{1}{kT}. \quad (3.44)$$

This is important enough to deserve a box:

Canonical ensemble: The canonical expectation value of f at the inverse temperature $\beta > 0$ is given by

$$\langle f \rangle_\beta = \int d\gamma \rho_\beta(\gamma) f(\gamma), \quad (3.45)$$

with the canonical ensemble being the distribution

$$\rho_\beta(\gamma) = Z^{-1} e^{-\beta H(\gamma)}. \quad (3.46)$$

The normalisation is provided by the canonical partition function defined as

$$Z = \int d\gamma e^{-\beta H(\gamma)}. \quad (3.47)$$

3.3.2 Equivalence of ensembles

At this point, we have a good reason to be confused: We have just derived two different ensembles, apparently quite different ones, that claim to describe equilibrium situations well. This seems a paradoxical situation. Which one is the correct one? After all, from thermodynamics we know that temperature is defined by the property that the state of two systems is not changed when bringing two bodies at the same temperature together.

At the same time, it is also clear that the two ensembles must be different: Note that the canonical distribution is nowhere zero in phase space, whereas the micro-canonical one is zero except on the energy shell.

This paradox can be resolved by acknowledging that in the regime where the two situations described here are supposed to capture thermodynamical systems in equilibrium, they are practically identical anyway. This observation is called the equivalence of ensembles. This becomes a mathematical statement if one formulates a precise thermodynamic limit of $N \rightarrow \infty$ and $V \rightarrow \infty$ at E/N being fixed or β being fixed. The actual rigorous proofs that are available are actually quite hairy, however, and the ones commonly stated in text books not quite satisfactory and sometimes even wrong.

For this course, we take a pragmatic approach and rather show that for large systems, the canonical distribution is very much concentrated around an energy surface. This is an instance of the effect known in mathematics as concentration of measure. Let us be specific and look at the variance of energy observables in

the canonical ensemble, i.e.,

$$\begin{aligned}\langle H^2 \rangle_\beta - \langle H \rangle_\beta^2 &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right).\end{aligned}\quad (3.48)$$

Note, after all, that

$$U = \langle H \rangle_\beta. \quad (3.49)$$

This gives

$$\begin{aligned}\langle H^2 \rangle_\beta - \langle H \rangle_\beta^2 &= -\frac{\partial U}{\partial \beta} = kT^2 \frac{\partial U}{\partial T} = kT^3 \frac{\partial S}{\partial U} \frac{\partial U}{\partial T} \\ &= kT^3 \frac{\partial S}{\partial T} \\ &= kT^2 C_V,\end{aligned}\quad (3.50)$$

where all derivatives are done at fixed V, \mathbf{N}, \dots . Now C_V is an extensive quantity, linear in the particle number N . The variance hence diverges as $N \rightarrow \infty$. However, this is not the interesting quantity, but rather the energy density per particle. For this, we get for its variance

$$\left(\left\langle \left(\frac{H}{N} \right)^2 \right\rangle_\beta - \left\langle \frac{H}{N} \right\rangle_\beta^2 \right)^{1/2} = \left(\frac{kT^2 C_V}{N^2} \right)^{1/2} \sim \frac{1}{\sqrt{N}}, \quad (3.51)$$

for large N . The relative deviations of the energy density hence converges to zero for large N . The fluctuations of the order $N^{-1/2}$ is also characteristic for fluctuations in central limit theorems, where independent random variables are being added. The value of the energy per particle is the canonical energy expectation value $\langle H \rangle_\beta$: Hence, since fluctuations can be neglected for large N , the canonical ensemble of inverse temperature β is equivalent with the micro canonical ensemble with energy $U = \langle H \rangle_\beta$.

3.3.3 Revisiting thermodynamic potentials

We have already been doing a good job with refining our “dictionary” for translating statistical concepts into thermodynamical ones. The volume V was easy, this is pretty much the same in thermodynamics as in statistical physics. The energy was a bit trickier, but we now get in what way E and U are the same thing. The temperature T is more subtle, but we have just looked at that.

We are not quite there yet, however. In order to have complete knowledge about a thermodynamical system, we have to know a thermodynamic potential, as we have learned earlier in the course. We know how to compute the inner energy as a function of T, V , and N , from the formula $U = \langle H \rangle_\beta$. After all, V and N are already parameters of the Hamiltonian function. Still, as we surely

remember, $U(T, V, N)$ is not quite a thermodynamic potential: It depends on the wrong variables.

A thermodynamic potential that depends on just these variables, however, is the free energy. We know that, on the one hand,

$$\begin{aligned} U &= F + TS = F - T \frac{\partial F}{\partial T} \\ &= F + \beta \frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta} (\beta F). \end{aligned} \quad (3.52)$$

On the other hand, exploiting our new knowledge on statistical physics,

$$\begin{aligned} \langle H \rangle_\beta &= \frac{\int d\gamma H e^{-\beta H(\gamma)}}{\int d\gamma e^{-\beta H(\gamma)}} \\ &= \frac{\partial}{\partial \beta} \ln \int d\gamma e^{-\beta H(\gamma)} \\ &= -\frac{\partial}{\partial \beta} \ln Z(\beta, V, N). \end{aligned} \quad (3.53)$$

If we are to identify the left hand sides of the two sets of equations, we have to set

$$F(T, V, N) = -kT \ln \int d\gamma e^{-\frac{H(\gamma)}{kT}} + c_0(V, N), \quad (3.54)$$

where the additional term c_0 does not depend on the temperature T . In order to understand this term better, let us compare F for the ideal gas with the expression for $\ln Z$. This gives

$$\begin{aligned} Z &= \left(\int_{\mathbf{q}_i \in \Omega} d^{3N} q \right) \left(\int d^{3N} p e^{-\frac{\beta}{2m} \sum_{i=1}^{3N} p_i^2} \right) \\ &= V^N \left(\int dp e^{-\frac{\beta}{2m} p^2} \right)^{3N} \\ &= V^N \left(\frac{2\pi m}{\beta} \right)^{3N/2}. \end{aligned} \quad (3.55)$$

That is to say,

$$-\frac{1}{\beta} \ln Z = NkT \left(-\frac{3}{2} \ln T - \ln V + \text{const} \right). \quad (3.56)$$

This we can compare with our expression known from thermodynamics,

$$F(T, V, N) = NRT \left(-\frac{f}{2} \ln T - \ln V + \ln N + \text{const}' \right). \quad (3.57)$$

Here, we have taken for simplicity logarithms of dimensionless expressions, hence the constants still depend on our choice of units. The prefactors are again the

same, identifying again N with the “Stoffmenge” in the above way, and setting $f = 3$.

So, meditating over this, we see that the dependence in temperature is correct, after having set $f = 3$. The dependence on the volume is also fine. But, in the expression derived from statistical physics, the term $\ln N$ is lacking. We can hence set

$$c_0 = c_0(N) = -N \ln N \sim -\ln(N!). \quad (3.58)$$

This is perfectly acceptable, given that the above term c_0 does not depend on the temperature. Still, it is a bit of an ad hoc insertion, identifying expressions in statistical physics and thermodynamics. Frankly, classical statistical physics is unable to give a satisfactory explanation to this. In this framework, we simply have to add it in order to render the free energy an extensive function of V and N . Therefore, it comes as no surprise that it was already added by Gibbs in the early descriptions of the field. We will come back to this and will properly derive this in the framework of quantum statistical mechanics.

Now we are essentially there. The other thermodynamic functions we get from this. For example, we have

$$S = -\frac{\partial F}{\partial T} = k\beta^2 \frac{\partial}{\partial \beta} \left(-\frac{1}{\beta} \ln Z \right), \quad (3.59)$$

but it should be clear that once we have access to a thermodynamical potential, we can derive any thermodynamic quantity of the system.

3.4 Remarks on the ensembles of classical statistical mechanics

3.4.1 Gibbs’ variational principle

Remember that we had defined the free energy as the Legendre transform of the inner energy, i.e., as $\inf\{U - T_B S\}$, where T_B was treated as a parameter. The infimum was supposed to be taken at all equilibrium values for given values of the control parameters. In the last subsection, we have both derived the inner energy as well as the entropy as functionals over the canonical density ρ_β .

But surely, it also makes sense to think of a corresponding expression in which the infimum is not taken over all macroscopic equilibrium states, but rather over all microscopic states, i.e., all densities ρ . We therefore consider

$$\hat{f}(H) := \inf \left\{ \int d\gamma \rho(\gamma) H(\gamma) - \frac{1}{\beta} \hat{S}(\rho) \right\}, \quad (3.60)$$

$$\hat{S}(\rho) := \int d\gamma \hat{s}(\rho(\gamma)), \quad (3.61)$$

where the infimum is taken over all positive integrable functions $\rho : \Gamma \rightarrow \mathbb{R}$ with

$$\int d\gamma \rho(\gamma) = 1, \quad (3.62)$$

and the function \hat{s} is given by the function

$$\hat{s}(t) = \begin{cases} -t \ln t & \text{for } t > 0, \\ 0 & \text{for } t = 0, \\ -\infty & \text{for } t < 0. \end{cases} \quad (3.63)$$

Here, we have left out the Boltzmann constant in the definition, so

$$S = k\hat{S}(\rho_\beta). \quad (3.64)$$

If we insert ρ for the canonical ensemble ρ_β , then the above expression just becomes $F(T, V, N)$ again. Indeed, we again have a Legendre transform: The set of density functions forms an infinite dimensional vector space, in which concepts like convexity of sets and functions are defined as before. In this sense, the functional

$$H \mapsto -\hat{F} \quad (3.65)$$

is the Legendre transform of the functional

$$\rho \mapsto \hat{S}(\rho). \quad (3.66)$$

Surely, $-\hat{F}$ is convex, and hence \hat{F} is concave.

Let us now try to find the actual infimum in Eq. (3.60). To start with, we have

$$\begin{aligned} & \lambda\hat{S}(\rho_1) + (1 - \lambda)\hat{S}(\rho_2) - \hat{S}(\lambda\rho_1 + (1 - \lambda)\rho_2) \\ &= \int d\gamma (\lambda\hat{s}(\rho_1(\gamma)) + (1 - \lambda)\hat{s}(\rho_2(\gamma)) - \hat{s}(\lambda\rho_1(\gamma) + (1 - \lambda)\rho_2(\gamma))) \geq 0, \end{aligned} \quad (3.67)$$

because of the concavity of \hat{s} . That is to say, \hat{S} is concave. In fact, it is even strictly concave (since \hat{s} is strictly concave, the integral can be zero only if for almost all γ we have that $\rho_1(\gamma) = \rho_2(\gamma)$). Since the first integral is affine in ρ , we have to find the infimum over a strictly concave function. This means that this infimum can be attained at most in a single point. In order to identify this point, we make use of differential calculus. We consider curves $\epsilon \mapsto \rho_\epsilon$ for an ϵ in a small region around the origin, and assume that ρ_0 is the extremum of the expression

$$\int d\gamma \rho_\epsilon H - \beta^{-1} \hat{S}(\rho_\epsilon) \quad (3.68)$$

That means that the first derivative to ϵ must disappear at $\epsilon = 0$, so

$$\begin{aligned} 0 &= \int d\gamma \rho'_0(\gamma) H(\gamma) - \beta^{-1} \int d\gamma \hat{s}'(\rho(\gamma)) \rho'_0(\gamma) \\ &= \int d\gamma \rho'_0(\gamma) \left(H(\gamma) + \frac{1}{\beta} \ln \rho_0(\gamma) + \frac{1}{\beta} \right). \end{aligned} \quad (3.69)$$

Here,

$$\rho'_\epsilon = \frac{\partial \rho}{\partial \epsilon}, \quad (3.70)$$

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and ρ'_0 is except from the condition

$$\int d\gamma \rho'_0(\gamma) = \frac{d}{d\epsilon} \int d\gamma \rho_\epsilon(\gamma) = 0 \quad (3.71)$$

an arbitrary integrable function. Hence, the expression in the bracket of Eq. (3.69) has to be a constant function. For the point ρ_0 of the extremum one gets the condition

$$\rho_0(\gamma) = ce^{-\beta H(\gamma)}, \quad (3.72)$$

with some constant c that is to be determined by

$$\int d\gamma \rho_0(\gamma) = 1. \quad (3.73)$$

Canonical ensemble as minimiser of the free energy: The unique infimum of the free energy is taken at the canonical ensemble ρ_β .

We have seen a similar statement before, needless to say. But now we have extended this result to an infimum over all densities allowed by a microscopic classical theory, and not merely about thermodynamic properties. The minimum free energy is assumed for the micro canonical ensemble, quite a remarkable result.

3.4.2 Equipartition theorem

Let $f : \Gamma \rightarrow \mathbb{R}$ be an arbitrary differentiable function. We first have a look at

$$\tilde{f}(\gamma) = f(\gamma)e^{-\beta H(\gamma)} \quad (3.74)$$

as a function of the momentum coordinates $\{p_j\}$. If we assume that f does not grow for $p_j \rightarrow \pm\infty$ not so fast that it compensates the exponential factor, then we get

$$\int d\gamma \frac{\partial}{\partial p_j} \left(f(\gamma)e^{-\beta H(\gamma)} \right) = \int d\gamma' \left(\tilde{f}_{p_j \rightarrow \infty} - \tilde{f}_{p_j \rightarrow -\infty} \right) = 0, \quad (3.75)$$

where $d\gamma'$ denotes the integration over all variables except p_j . After division by the partition function Z , we get

$$0 = Z^{-1} \int d\gamma \left(\frac{\partial f}{\partial p_j} - \beta f \frac{\partial H}{\partial p_j} \right) e^{-\beta H} = \left\langle \frac{\partial f}{\partial p_j} \right\rangle_\beta - \beta \left\langle f \frac{\partial H}{\partial p_j} \right\rangle_\beta. \quad (3.76)$$

A convenient, but by now means the only, choice is to take for f simple another momentum coordinate p_i . Then we have the following statement:

Equipartition theorem:

$$\left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle_\beta = \frac{1}{\beta} \delta_{i,j}. \quad (3.77)$$

Usually, the Hamiltonian is of the form

$$H(p, q) = \sum_{i=1}^N \left(\frac{1}{2m_i} p_i^2 + V(q) \right). \quad (3.78)$$

Then

$$\frac{1}{2} p_i \frac{\partial H}{\partial p_i} \quad (3.79)$$

is just the i -th contribution in the sum leading to the kinetic energy. We can hence conclude the following. This result specifically is often referred to as equipartition theorem.

Equipartition theorem applied to the expectation value of the kinetic energy: Each of the n degrees of freedom contributes $kT/2$ to the canonical expectation value of the kinetic energy.

Having this insight in mind, we can give the inner energy of the ideal gas without any calculation: Since the particles do not interact, the expectation value of the Hamiltonian is just the expectation value of the kinetic energy itself. For each particle, three momentum coordinates contribute. That is to say,

$$\langle H \rangle_\beta = \frac{3}{2} NkT. \quad (3.80)$$

So we have finally found a good reason for the choice of $f = 3$ that was possibly more mysterious before.

But we can go much further than that. We can say something even on the inner energy of gases consisting of particles having some structure. Let us consider a gas made out of molecules that are shaped like an O_2 molecule. The specifics are not so important: But rather the fact that two angular momentum angles contribute (but not a third, from the symmetry of the molecule). This means that per molecule, we have $3 + 2 = 5$ degrees of freedom. This gives us the inner energy

$$\langle H \rangle_\beta = \frac{5}{2} NkT. \quad (3.81)$$

It should be clear from this that this is a simple, but quite powerful insight. For a molecule for which the constituents are not in aligned on a line, such as a H_2O water molecule, we have

$$\langle H \rangle_\beta = \frac{6}{2} NkT, \quad (3.82)$$

and so on. In general, we have for f degrees of freedom

$$\langle H \rangle_\beta = \frac{f}{2} NkT, \quad (3.83)$$

which is exactly the formula encountered before.

3.4.3 Virial expansion

For ideal gases, we could always compute the partition functions: This is, needless to say, due to the fact that particles do not interact. If the Hamiltonian is of the form

$$H(\gamma) = \sum_{j=1}^N h(\gamma_j), \quad (3.84)$$

where γ_j denotes the phase space coordinates of the j -th particle, then, say, the canonical partition function is just the N -th power of the partition function of each particle. This is a radical simplification, to say the least. The free energy, for example, can in this way computed to be

$$F = -NkT \log \int d\gamma_1 e^{-\beta H(\gamma_1)}. \quad (3.85)$$

This trick, however, no longer works for particles that interact. Unfortunately, this is the generic situation: All particles interact to some extent. Fortunately, in turn, we can go a long way in case this interaction is weak.

Let us consider a gas with two-particle interaction potential Φ , so the Hamiltonian is given by

$$H(\gamma) = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + \sum_{i<j} \Phi(|\mathbf{q}_i - \mathbf{q}_j|). \quad (3.86)$$

This potential Φ we get from a microscopic model. A good model for interactions between molecules constitutes the Lennard Jones potential: It is given by

$$\Phi(r) = \frac{c_1}{r^{12}} - \frac{c_2}{r^6} \quad (3.87)$$

for $r > 0$. The r^{-6} comes from induced dipole-dipole attractive interactions, whereas the r^{-12} reflects a sharp repulsion. This is no typo: There is really a power of 12 in the denominator.

The canonical partition function becomes

$$\begin{aligned} Z &= \int d^{3N} p e^{-\sum_{j=1}^N \beta \mathbf{p}_j^2 / (2m)} \int_{\mathbf{q}_j \in \Omega} d^{3N} q e^{-\beta \sum_{i<j} \Phi(|\mathbf{q}_i - \mathbf{q}_j|)} \\ &= Z_{\text{ideal}} \left(\frac{1}{V^N} \int d^{3N} q \prod_{i<j} e^{-\beta \Phi(|\mathbf{q}_i - \mathbf{q}_j|)} \right) \\ &= Z_{\text{ideal}} Z_{\text{pot}}. \end{aligned} \quad (3.88)$$

Here, Z_{ideal} is the corresponding expression for the ideal gas, the one we would get for $\Phi = 0$. Z_{pot} reflects the term arising from the potential energy.

Of course, all the misery and trouble is now in computing this additional term Z_{pot} , as we already know how to compute the former. It is clear that the product runs over $\binom{N}{2}$ terms. Now, each of these terms is almost exactly equal to one – unless the particles are really close to each other. Remember that we are thinking of macroscopic containers here, so the typical distance between particles is of that order of magnitude, whereas the above deviation from unity becomes relevant only in case the particles become as close as 10^{-10}m . So there are many orders of magnitude between these scales.

To reflect this insight, let us write

$$f(r) = e^{-\beta\Phi(r)} - 1. \quad (3.89)$$

In this way, we get

$$Z_{\text{pot}} = \frac{1}{V^N} \int d^{3N}q \prod_{i<j} (1 + f(|\mathbf{q}_i - \mathbf{q}_j|)) \quad (3.90)$$

If we expand this product, we get the irritating number of $2^{N(N-1)/2}$ terms. Each term is essentially characterised by the knowledge whether for a given pair (i, j) the number 1 contributes, or a factor $f(|\mathbf{q}_i - \mathbf{q}_j|)$.

If the interaction is weak, and very dilute, then it is a good approximation to neglect this potential altogether, and we are back to the ideal gas. This corresponds to $Z_{\text{pot}} = 1$.

- In the next best approximation, we assume that at each instance in time, at most two particles interact with each other. This is often still a remarkably good approximation, since the probability for three-body collisions can be neglected. Of these terms, we have $\binom{N}{2}$ many, and each contributes

$$V^{-N+(N-2)} \int d^{3N}\mathbf{q}_1 d^{3N}\mathbf{q}_2 f(|\mathbf{q}_1 - \mathbf{q}_2|). \quad (3.91)$$

In the double integral, we substitute

$$\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2, \quad (3.92)$$

$$\mathbf{Q} = (\mathbf{q}_1 + \mathbf{q}_2)/2, \quad (3.93)$$

- Now, since, in integration only terms contribute for which $\mathbf{q}_1 \approx \mathbf{q}_2$, we hardly make an error by integrating \mathbf{Q} over the entire volume.
- Similarly, we can integrate \mathbf{q} over \mathbb{R}^3 .
- Then, we can set $N(N-1) \approx N^2$.

The sum of terms containing f then becomes

$$\frac{N^2}{2V} \int d\mathbf{q} f(|\mathbf{q}|). \quad (3.94)$$

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This quantity we treat as a small quantity. In this approximation, we hence get

$$\begin{aligned}
 F &= -\frac{1}{\beta} \log Z \\
 &\approx F_{\text{ideal}} - \frac{1}{\beta} \log \left(1 + \frac{N^2}{2V} \int d\mathbf{q} f(|\mathbf{q}|) \right) \\
 &\approx F_{\text{ideal}} - \frac{N^2}{2\beta V} \int d\mathbf{q} f(|\mathbf{q}|).
 \end{aligned} \tag{3.95}$$

Defining

$$B(T) = \frac{1}{2} \int d\mathbf{q} f(|\mathbf{q}|) = \frac{1}{2} \int d\mathbf{q} \left(e^{-\beta\Phi(|\mathbf{q}|)} - 1 \right), \tag{3.96}$$

we finally get the following expression for the pressure.

Pressure in virial expansion:

$$\begin{aligned}
 p &= -\frac{\partial F}{\partial V} \approx \frac{NkT}{V} + \frac{N^2 kT}{V^2} B(T) \\
 &= \frac{NkT}{V} \left(1 + \frac{N}{V} B(T) \right).
 \end{aligned} \tag{3.97}$$

Since N/V is just the particle density, this is the beginning of an expansion of the pressure in terms of powers of the particle density. $B(T)$ is in this light also called second virial coefficient. The first virial coefficient is then simply 1. Since one can easily measure the pressure as a function of the particle density and the temperature, one can easily determine $B(T)$ also experimentally. More elaborate derivations also produce higher order terms in this expansion.