

# Foundations of statistical mechanics

## 1 Macrostate vs. microstates

Consider an *isolated* system, for example our typical thermodynamic system, shown in Fig. 1 – a certain amount of gas enclosed in a given volume. We assume it has reached its equilibrium state. From a *macroscopic* point of view, we characterize this equilibrium state – let us call it the *macrostate* – with a few macroscopic variables, namely the internal energy  $U$  (or  $E$ ), the volume  $V$  and the number of particles  $N$ . As we already discussed, we expect/want to be able to express all other macroscopic quantities  $S, p, T, \mu, \dots$  in terms of these.

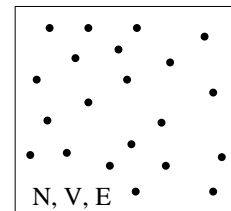


Fig 1. Typical system of interest: atoms or molecules in a gas phase, in an enclosure.

Note that there are some error bars on all these quantities. In principle, we could probably count  $N$  exactly, and measure the volume  $V$  to very high accuracy, but  $E$  is certainly only defined within a  $\delta E$  interval, since the atoms collide with the walls and therefore some energy is exchanged back and forth between the gas and the wall. Or, since we are looking at it, it means that some photons have bounced off these atoms and then entered our eyes, so again some small energy fluctuations have occurred – in general, every time we try to measure some quantity related to the system, we perturb it a bit and allow its energy to vary somewhat. We expect this fluctuation  $\delta E$  to be very small,  $\delta E \ll E$ . In this limit, the final results we derive should be independent of  $\delta E$ .

Let us assume that the gas is made from classical, non-interacting atoms. Then, from a *microscopic* point of view, we can describe its state – let us call it the *microstate* – by specifying the  $3N$  positions  $(x_i, y_i, z_i)$ ,  $i = 1, N$ , and  $3N$  momenta  $(p_{x,i}, p_{y,i}, p_{z,i})$ ,  $i = 1, N$ , of the atoms. However, these values are not unique: there are very many ways in which we can arrange the positions and the momenta of the atoms so that they are consistent with the macrostate (i.e. the  $N$  atoms are all inside volume  $V$ , and their total energy is  $E$ ); and even if we choose one of these microstates as the “initial condition”, it will keep changing in time as atoms move around, changing their  $\vec{r}_i$ , collide with each other and the walls, changing their  $\vec{p}_i$ , etc. We call the number of distinct microstates compatible with a given macrostate the *multiplicity* of that macrostate. We will denote it by  $\Omega(E, \delta E, N, V)$ , where I wrote the  $\delta E$  explicitly to remind ourselves that there is a certain variation allowed for the energy  $E$ .

We would like to be able to count this multiplicity (we will see soon why we need it). Let me show first how we do this for a very simple system, with  $N = 1$ . To make things even simpler, let's assume that our atom moves in only one dimension, along the  $x$  axis, not in a 3D box. Of course, this is not a thermodynamic system since 1 is a small number, but after we understand this, we can generalize to many atoms and 3D. The Hamiltonian of our 1D particle is:

$$\mathcal{H}(x, p) = \frac{p_x^2}{2m} + U(x) \quad (1)$$

where  $U(x) = 0$ , if  $0 < x < L$ , and  $U(x) = \infty$  otherwise. In other words, this potential keeps our particle inside the “volume”  $L$ . The microstate of this particle is represented by the pair  $(x, p)$  of its position and its momentum, i.e. by a point in the *phase-space* of the system. We know that in time, this point moves around ( $x(t)$  and  $p(t)$  change their values) according to Hamilton's equations:

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial p_x} = \frac{p_x}{m}; \dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = -\frac{dU}{dx}$$

We can solve these equations of motion quite easily. First, the Hamiltonian does not depend explicitly on time – as a result, we know that the energy of the system is conserved. So the particle will have

whatever energy  $E$  it had initially, and moreover its momentum must satisfy  $p_x^2/2m = E \rightarrow p_x = \pm\sqrt{2mE}$ , with the sign changing everytime the particle hits a wall. Indeed, when the particle is away from the walls,  $dU/dx = 0 \rightarrow p_x = \text{const.}$

The microstate of the particle thus describes a trajectory in the phase space, as shown in Fig. 2. For a given energy  $E$  and length  $L$ , the particle can be in any of the microstates on the directed line shown  $\rightarrow$ . If, say, at the initial time it has a positive momentum  $p_x = p(E) = \sqrt{2mE}$  and a position  $x = L/3$ , (the black dot), then it will move towards right with constant momentum until it hits the wall; at this time its momentum reverses sign and the particle starts moving towards the left until it hits the left wall, and so on and so forth. So if we wait long enough, the particle will go through all the possible microstates associated with the macrostate  $E, L$ . Now the question is how to count the number of microstates – how can one count the number of points on a line?!

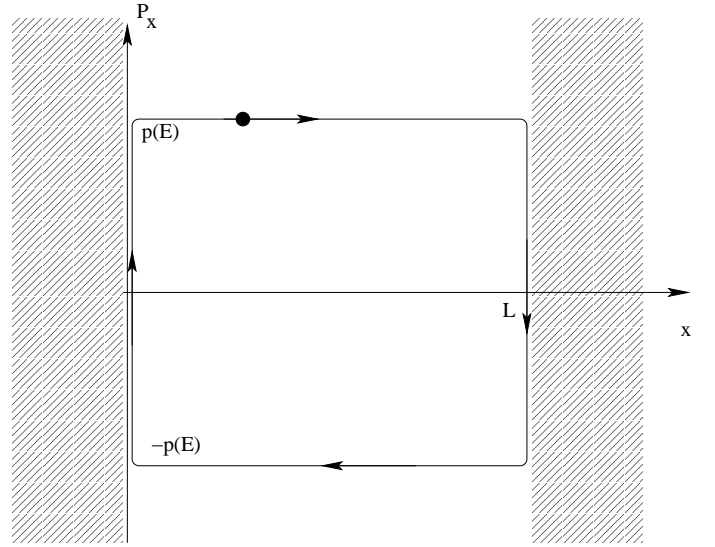


Fig 2. Trajectory in the phase-space of the microstate of a 1D particle enclosed between walls, if its energy is  $E$  and the “volume” is  $L$ .

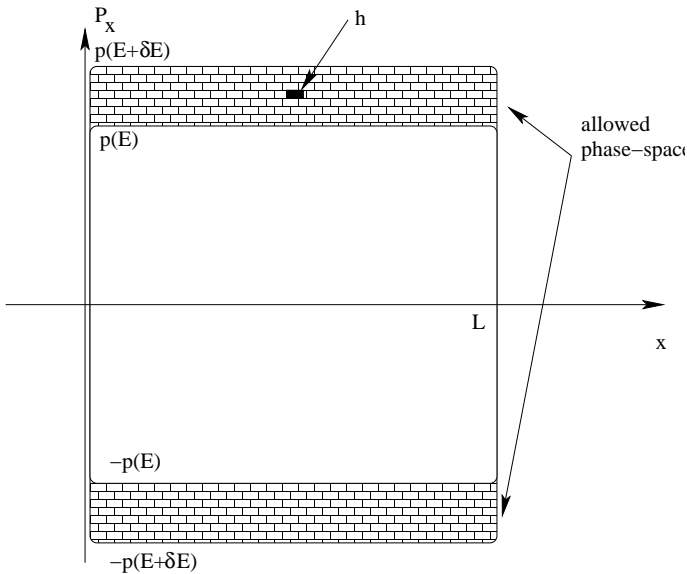


Fig 3. Multiplicity of a macrostate specified by  $E, \delta E$  and  $L$ , given by how many microstates, each covering an area  $h$ , we can fit in the allowed phase-space.

The answer is that the multiplicity is the ratio of the “volume” of the allowed phase-space (all phase-space volume enclosed between  $E$  and  $E + \delta E$  trajectories) and the “volume”  $h$  occupied by each distinguishable microstate. For this problem, we therefore have:

$$\Omega(E, \delta E, L) = \frac{2L[\sqrt{2m(E + \delta E)} - \sqrt{2mE}]}{h} \approx \frac{L}{h} \sqrt{\frac{2m}{E}} \delta E$$

At this point we should remember that our world is in fact quantum, and that classical mechanics is but an approximation. Quantum mechanics tells us that we cannot specify, simultaneously, both the position and the momentum of an object with infinite accuracy; we always have  $\Delta x \cdot \Delta p_x > h$ . As a result, two microstates that are closer to one another than this are simply not “different”. Also, as I said, the energy is never fully fixed, there is always a little variation  $\delta E$ . So the proper question is, how many microstates that are separated from one another by more than  $\Delta x \cdot \Delta p_x \sim h$  can we fit in between the phase trajectories corresponding to energies  $E$  and  $E + \delta E$ ? This is illustrated in Fig. 3.

if we use a Taylor expansion and remember that  $\delta E \ll E$ . Some of this looks reasonable – we expect to have more microstates if the “volume”  $L$  is larger. Also, we expect the number of microstates to be proportional to the small variation  $\delta E$ . What is strange, is that this diverges as  $E \rightarrow 0$ . The explanation for this is that at very low energies, we should use quantum mechanics to solve the problem properly. We know that the allowed energy levels are in fact discrete, and this simple classical calculation does not hold at low energies, comparable to the spacing between consecutive allowed eigenenergies. This classical calculation should be ok at very large energies, far from the ground-state, where the spacing between allowed levels is much much smaller than  $E$ , so that we can pretend that  $E$  is a continuous variable (which is what we do in classical mechanics).

So before generalizing this calculation to many classical particles, let us also do it for a quantum particle. We do this for several reasons – we would like to see that indeed, at large energies the two results agree; we would also like to see that  $h$  (and not  $\hbar/2$ , or some other combination) is what we should use as the “volume” occupied by a distinguishable microstate; and finally, we will study quantum systems as well, so we may as well start now.

The allowed eigenstates for a particle described by the Hamiltonian of Eq. (1) satisfy the Schrödinger equation, which, for  $0 < x < L$ , is:

$$\mathcal{H}\phi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) = E\phi(x)$$

with the boundary conditions  $\phi(0) = \phi(L) = 0$ , because of the infinite-energy walls. We know that the eigensolutions are indexed by an integer quantum number  $n \geq 1$ :

$$\phi_n(x) = A \sin\left(\frac{n\pi x}{L}\right); E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = \frac{h^2}{8mL^2} n^2 \quad (2)$$

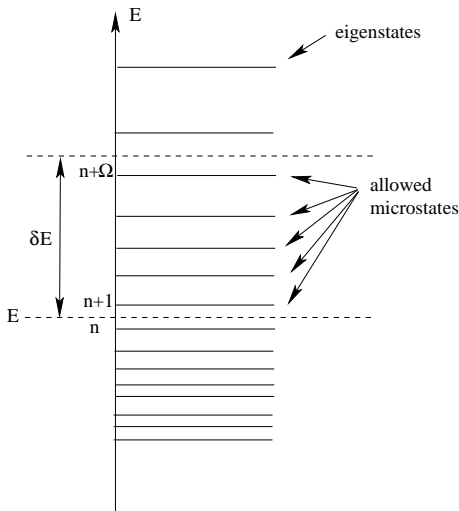


Fig 4. Multiplicity of a macrostate specified by  $E$ ,  $\delta E$ , and  $L$  for a quantum system.

where  $A$  is some normalization constant. Now, if we ask how many microstates are between  $E$  and  $E + \delta E$ , the answer is the number of distinct eigenstates with energies  $E \leq E_n \leq E + \delta E$ , since the particle could be in any of these (note: this means we have to count degeneracies as well, but in this case we know that the eigenstates are non-degenerate). It follows that if the energy interval  $\delta E$  is very narrow, we might have zero, or maybe just one microstate allowed. Let us assume that  $\delta E$  is large enough that we have a few eigenstates in there. As suggested in Fig. 4, we can then calculate the multiplicity  $\Omega$  by requesting that

$$E \leq E_{n+1}; E + \delta E \geq E_{n+\Omega} \rightarrow$$

$$E \approx E_{n+1} = \frac{h^2}{8mL^2} (n+1)^2 \rightarrow n \approx \sqrt{E \frac{8mL^2}{h^2}} - 1$$

$$\delta E \approx E_{n+\Omega} - E_n = \frac{\hbar^2 \pi^2}{2mL^2} [(n+\Omega)^2 - (n+1)^2] = \frac{h^2}{8mL^2} (2n(\Omega-1) + \Omega^2 - 1)$$

Combining these equations, we can find  $\Omega$  as a function of  $E$ ,  $\delta E$  and  $L$ . What we were interested in, was to check the result at large  $E$ . In this case,  $n \sim \sqrt{E}$  is a large number, much larger than

$\Omega$ , especially if  $\delta E$  is fairly narrow. If  $\delta E$  is not too narrow, we expect  $\Omega$  also to be quite a bit larger than 1 (remember that in the classical limit we perceive energy as a continuous variable, so we expect many level within a reasonable  $\delta E$ ). As a result, for  $n \gg \Omega \gg 1$ , we can approximate  $2n(\Omega - 1) + \Omega^2 - 1 \approx 2n\Omega \approx 2\Omega\sqrt{E\frac{8mL^2}{h^2}}$ , and we have:

$$\delta E \approx \frac{h^2}{8mL^2} 2\Omega\sqrt{E\frac{8mL^2}{h^2}} \rightarrow \Omega \approx \frac{L}{h}\sqrt{\frac{2m}{E}}\delta E$$

Alright! So indeed, at high energies this agrees with the classical calculation, showing that we did it properly. Notice that this quantum calculation removes the problem with the  $1/\sqrt{E}$  divergence. First, we cannot set  $E = 0$ , since the lowest possible energy of the system is its ground-state energy  $E_1 = h^2/(8mL^2)$ . Moreover, because at low  $E$  we no longer can expect that  $n \gg \Omega \gg 1$ , we actually have to solve the equations above exactly, and we will find that  $\Omega$  is a small number, as little as 1 if a single eigenstate fits in between  $E, E + \delta E$ . So there is no singularity, that came from trying to apply the classical result in the limit of low energies where it is not valid.

Now we can generalize. Let us do it first for a classical system that contains  $N$  identical microsystems ( $N$  atoms of the same species, in our typical example). Let us assume that each microsystem has  $2f$  degrees of freedom, described by  $f$  generalized coordinates  $q_1, \dots, q_f$  and  $f$  generalized momenta,  $p_1, \dots, p_f$ . For simple atoms in 3D  $f = 3$ , as already discussed. If we deal with molecules, for instance, then there are more degrees of freedom. We can use 3 positions and 3 momenta to describe the position and momentum of the center-of-mass of the molecule, but we need extra coordinates to characterize the location of the atoms in the molecule with respect to one another (a “relative” distance and its associated momentum, and some angles and their associated angular momenta to characterize spatial orientation of the molecule). A different type of classical system that we will consider is a magnetic system, where we have spins arranged in a lattice. If we treat it classically, a spin is like a small magnetic moment that can point in any direction. Because the atoms are frozen at their lattice positions and cannot move, their only degrees of freedom describe the orientations of their spins, so  $f = 2$  and we have two angles  $\theta, \phi$  and two angular momenta  $p_\theta, p_\phi$  per spin. Etc.

So the first step for a given classical system is to identify the  $2Nf$  microscopic degrees of freedom,  $(\mathbf{q}, \mathbf{p})$ , and the Hamiltonian describing the system,  $\mathcal{H}(\mathbf{q}, \mathbf{p})$  (from now on, I will use  $\mathbf{q}$  as a shorthand notation for all  $q_1, \dots, q_{Nf}$ , and similarly for  $\mathbf{p}$ ). The microstate of the system is now a point  $(\mathbf{q}(\mathbf{t}), \mathbf{p}(\mathbf{t}))$  in the  $2Nf$ -dimensional phase-space whose axes are all the generalized coordinates and momenta (we obviously cannot plot this if  $Nf > 1$ , but we can think of it). As the system evolves in time according to Hamilton’s equations:

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \quad \forall i = 1, \dots, Nf$$

the microstate describes a trajectory in the phase-space. Since the system is isolated, the energy  $E$  is conserved, so we expect all allowed microstates to be located in the “volume” described by the condition  $E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E$ . A distinguishable microstate occupies a volume  $h^{Nf}$ , since for each degree of freedom we must have  $\Delta q_i \Delta p_i > h$ . It follows that the number of microstates is:

$$\Omega(E, \delta E, N, \dots) = \frac{1}{\mathcal{G}_N h^{Nf}} \int_{E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E} d\mathbf{q}d\mathbf{p} \quad (3)$$

i.e. the allowed phase space “volume” divided by the “volume” occupied by a distinct microstate ( $d\mathbf{q}d\mathbf{p} = dq_1 \dots dq_{Nf} dp_1 \dots dp_{Nf}$  is the infinitesimal phase-space volume).  $\mathcal{G}_N$  is a number whose

meaning and value we will discuss in a second. Before doing that, let me define the phase-space volume containing all points with energy less than  $E$ :

$$\omega(E, N, \dots) = \int_{\mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E} d\mathbf{q}d\mathbf{p} = \int d\mathbf{q}d\mathbf{p} \Theta(E - \mathcal{H}(\mathbf{q}, \mathbf{p})) \quad (4)$$

It follows that the desired multiplicity is:

$$\Omega(E, \delta E, N, \dots) = \frac{1}{\mathcal{G}_N h^{Nf}} [\omega(E + \delta E, N, \dots) - \omega(E, N, \dots)] \approx \frac{1}{\mathcal{G}_N h^{Nf}} \frac{\partial \omega(E, N, \dots)}{\partial E} \delta E \quad (5)$$

if  $\delta E \ll E$ . In other words, if we are able to estimate  $\omega(E, N, \dots)$  from Eq. (4), then we get  $\Omega(E, \delta E, \dots)$  immediately from Eq. (5).

The factor  $\mathcal{G}_N$  is called the *Gibbs coefficient*, and it is equal to:

$$\mathcal{G}_N = \begin{cases} N! & \text{if the microsystems have translational degrees of freedom} \\ 1 & \text{if the microsystems are frozen in a lattice} \end{cases} \quad (6)$$

Let us try to understand where this is coming from. Let us use again first a simple example, with say two 1D atoms, so that  $N = 2$ ,  $f = 1$ . This system has translational degrees of freedom – the atoms move around. The microstate is described by  $(x_1, p_{x,1})$  for the first atom, and  $(x_2, p_{x,2})$  for the second atom, so it is represented by a point  $(x_1, x_2, p_{x,1}, p_{x,2})$  in the 4D phase-space. When we want to count the microstates for this system, we have a problem. The microstate  $(x_1, x_2, p_{x,1}, p_{x,2})$  seems to be different from the microstate  $(x_2, x_1, p_{x,2}, p_{x,1})$  (i.e., we just exchange locations and momenta for the two particles) since they are distinct points in the phase-space. On the other hand, if our atoms are truly identical, they are *indistinguishable*. It follows that these two microstates are in fact one, since all we can say is that one particle is at  $(x_1, p_{x,1})$  and the other one at  $(x_2, p_{x,2})$ , but we cannot distinguish which is which, so we cannot claim that there are two distinct microstates. As a result, to find the true multiplicity of this system we have to divide by 2, to eliminate this redundancy. Of course, if we have  $N$  identical microsystems that can move around and interchange their positions, we have to divide the total number of microstates by  $N!$ , since this is how many of the microstates differ only through a permutation of the individual coordinates and momenta of the  $N$  particles, and therefore are not distinct.

Initially physicists did not include this  $N!$  factor for classical calculations, because in our classical world different objects are distinguishable, even if they are very similar. For instance, consider white billiard balls on a perfect billiard table where there is no friction so that the energy of the system is conserved (as a classical analog of an isolated 2D gas). Even if the billiard balls are perfectly identical, we can still distinguish them, for instance by filming their motion for awhile and tracing where each one of them went. As a result, we are able to distinguish two states which differ only through a permutation on the balls, because we can figure out which ball is which, and we would not divide by  $N!$ . In fact, the evolution of the system will be the same if we just label each ball with 1, 2, ... which makes them into distinguishable objects so that instead of  $N$  identical objects, we actually have 1 object of species 1 (= ball labelled with “1”), 1 object of species 2 (= ball labelled with “2”), etc. We cannot do this for quantum objects, though. We certainly cannot “label” atoms. We can keep track of which is which as long as they are separated from one another by more than a de Broglie wavelength  $\lambda$ . This is why, if they are arranged in a lattice and cannot move around and get too close to each other, we set  $\mathcal{G}_N = 1$ . But if they can move around, every so often two of them will collide. At such an event, we “see” a probability “blob” of size  $\lambda$  unite with another “blob” of size  $\lambda$  to create a bigger “blob” for a short time, which then divides into two new “blobs”

as the collision ends. At this point we cannot say anymore which atom is which. After a short while, enough collisions take place that we cannot identify any particular atom in the system – moving identical quantum objects are truly indistinguishable, and we have to divide by the  $N!$  Gibbs factor. Of course, if we have several different types of microsystems, e.g.  $N_1$  molecules of species 1 (say,  $O_2$ ) and  $N_2$  molecules of species 2 (say  $H_2O$ ), then the Gibbs factor will be  $N_1!N_2!$ , *not*  $(N_1 + N_2)!$ . In this case, we can distinguish any  $O_2$  from any  $H_2O$  without problems, we just cannot distinguish the  $O_2$  amongst themselves and the  $H_2O$  amongst themselves.

The absence of the  $N!$  from the initial classical calculations led to some serious problems with the results, which are known as the “Gibbs’s paradox”. We will discuss this a bit later, but let me just say here that if  $\mathcal{G}_N$  is properly included, this paradox is solved. The fact that  $\mathcal{G}_N$  is needed (which is only the case for truly indistinguishable objects, true of quantum, but not for classical objects) and that  $h$  appears in a “classical” formula, are clear manifestations of the fact that classical mechanics is only a high-energy approximation of quantum mechanics.

Let us see an example: we assume we have  $N$  identical atoms in a 3D box of volume  $V$ , the total energy of the isolated system is between  $E$ ,  $E + \delta E$ , and we want to find the number of allowed microstates  $\Omega(E, \delta E, N, V)$ . For this system, the generalized coordinates and momenta are simply the positions  $\vec{r}_i$  and the momenta  $\vec{p}_i$ ,  $i = 1, N$  of the atoms,  $f = 3$ . Moreover, as long as all  $\vec{r}_i \in V$ , the Hamiltonian is simply:

$$\mathcal{H}(\mathbf{p}) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

where  $m$  is the mass of an atom. The atoms are not allowed outside of  $V$  (the potential energy becomes infinite in that case). According to the rules we just discussed, we need first to calculate:

$$\omega(E, V, N) = \int d\vec{r}_1 \dots \int d\vec{r}_N \int d\vec{p}_1 \dots \int d\vec{p}_N \Theta(E - \mathcal{H}(\mathbf{p}))$$

where the Heaviside function  $\Theta$  just enforces the condition that we only count microstates with total energy less than  $E$ . The spatial integrals are straightforward,  $\int d\vec{r}_i = V, \forall i = 1, \dots, N$  since if any particle is located outside  $V$ , the total energy becomes infinite and the  $\Theta$ -function becomes zero. Using this and the expression of the Hamiltonian, we have:

$$\omega(E, V, N) = V^N \int d\vec{p}_1 \dots \int d\vec{p}_N \Theta \left( E - \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right) = V^N \int d\vec{p}_1 \dots \int d\vec{p}_N \Theta \left( 2mE - \sum_{i=1}^N \vec{p}_i^2 \right)$$

since  $2m > 0$  so multiplying by it leaves the value of the  $\Theta$  unchanged. But the  $3N$  integrals we have ( $N$  momenta, each with three components if we are in 3D) represent precisely the volume of a  $3N$ -dimensional hypersphere of radius  $R = \sqrt{2mE}$ , i.e.  $V_{3N}(\sqrt{2mE})$ . In the math review, we showed that  $V_n(R) = R^n \pi^{\frac{n}{2}} / \Gamma(\frac{n+2}{2})$ . It follows that:

$$\omega(E, V, N) = V^N (2mE)^{\frac{3N}{2}} \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N+2}{2}\right)}$$

The atoms have translational degrees of freedom so  $\mathcal{G}_N = N!$ , and therefore:

$$\Omega(E, \delta E, N, V) = \frac{1}{N!h^{3N}} \frac{d\omega(E, V, N)}{dE} \delta E = \frac{1}{N!\Gamma\left(\frac{3N}{2}\right)} V^N E^{\frac{3N}{2}-1} \left(\frac{2m\pi}{h^2}\right)^{\frac{3N}{2}} \delta E \quad (7)$$

We will discuss more examples in class, and several other ones are worked out in the textbook.

Now that we know how to calculate the multiplicity  $\Omega(E, \delta E, N, \dots)$  of a given macrostate, let us see why do we need it.

## 2 Postulates of the classical statistical mechanics

Each macroscopic variable  $A_{macro}$  that we wish to express as a function of  $E, V, N$  (if we go back to our usual example) can be thought of as the average of some microscopic quantity which depends on the microstate of the system. For instance, to find the pressure (macroscopic variable) we have to see how many atoms hit a certain area of the wall, and what is the total variation per unit time in their momenta, which defines the force imparted to that area of the wall – so we have to average over some length of time the average momentum variation, per unit area and unit time. This of course depends on the microscopic variables  $(\mathbf{q}, \mathbf{p})$ . Similarly,  $T$  is related to the average energy of each particle, so to measure it we need to average another microscopic function of  $(\mathbf{q}, \mathbf{p})$  over some length of time. So in general, we postulate (postulate no. 1) that for any  $A_{macro}$  variable of interest, there is some microscopic function  $A(\mathbf{q}, \mathbf{p})$  so that:

$$A_{macro} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt A(\mathbf{q}(t), \mathbf{p}(t)) \quad (8)$$

where the integral is just the time average over a certain “measurement time”  $\tau$ . The limit  $\tau \rightarrow \infty$  does not mean that we really measure for an infinite amount of time; it is just a reflection of the fact that the microstate of the system changes very fast, on a characteristic time-scale  $\tau_{micro} \ll \tau$ . This  $\tau_{micro}$  could be, for instance, the average time between two collisions. This depends on various parameters, but is usually many orders of magnitude less than a second. So if the measuring time is of the order of minutes, this is so much larger than  $\tau_{micro}$ , that we can replace it with  $\infty$ .

The problem with Eq. (8) is that in order to calculate this average, we need to be able to solve the equations of motion so as to know how the generalized coordinates and momenta vary in time. As we’ve already discussed, this is an impossible task, so we have to approach the problem differently.

Gibbs, following work done by Boltzmann, introduced the idea of *statistical ensemble* and replaced the time integral with an *ensemble average*. Here is how this works. Suppose, as a thought experiment, that instead of just one thermodynamic system, we actually have a *statistical ensemble* of  $\mathcal{N}$  (which has nothing to do with  $N$ ) identical copies of the system, all in the same macrostate. At any given time, these copies will all be in different possible microstates, and if  $\mathcal{N} \gg 1$ , they will actually “sample” all allowed phase-space, meaning that if we take a snapshot of the microstates of all systems in the ensemble, there will be at least one system in any of the allowed microstates. Of course, more likely microstates will have more systems in that microstate. Let  $\rho(\mathbf{q}, \mathbf{p})$  be the density of probability to find a system of the ensemble in the microstate  $(\mathbf{q}, \mathbf{p})$  (this is zero for microstates which belong to a different macrostate, for instance by having too large an energy). We then define the *ensemble average* of the microscopic function  $A(\mathbf{q}, \mathbf{p})$  as:

$$\langle A \rangle = \int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho(\mathbf{q}, \mathbf{p}) A(\mathbf{q}, \mathbf{p}) \quad (9)$$

In other words, we calculate what is the average value of  $A$ , *at a given instance of time*, if we average over the values it has amongst all members of the statistical ensemble.  $\mathcal{G}_N$  is included because we do not want to overcount the contribution of microstates which are in fact identical, and we include  $h^{Nf}$  for cosmetic purposes, so that  $d\Gamma = \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}}$  is dimensionless. Of course, the probability density must be normalized:

$$\int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho(\mathbf{q}, \mathbf{p}) = 1$$

The second postulate is that:

$$A_{macro} = \langle A \rangle \quad (10)$$

i.e. that we can replace the time average over the time evolution of a single system (which we cannot perform), with an instantaneous average over the distribution of microstates of a large enough ensemble of  $\mathcal{N}$  copies of the system (which average we can do, if we can figure out what is  $\rho(\mathbf{q}, \mathbf{p})$ ). This idea (see sketch in Fig. 5) came about from Boltzmann's *ergodic hypothesis*, which is that if we wait long enough, the trajectory of the single system will pass through all allowed microstates. If this is true, the two averages are obviously equal if  $\rho(\mathbf{q}, \mathbf{p})$  simply records in which parts of the phase-space does the system stay longer. Very simple mechanical systems satisfy the ergodic hypothesis, as shown by our 1D example of Fig. 2. In that case, if we wait long enough, the particle goes at least once through each allowed microstate. We can also see that in that case, the density of probability  $\rho(\mathbf{q}, \mathbf{p}) = C$  is equal for all allowed microstates (none is more likely than any other one, since the particle goes in "order" through all of them), and zero for microstates which are not allowed. The constant  $C$  can be found from the normalization condition, and we are done! (By the way, can you now start to see why we bothered learning how to count the number of distinct allowed microstates?)

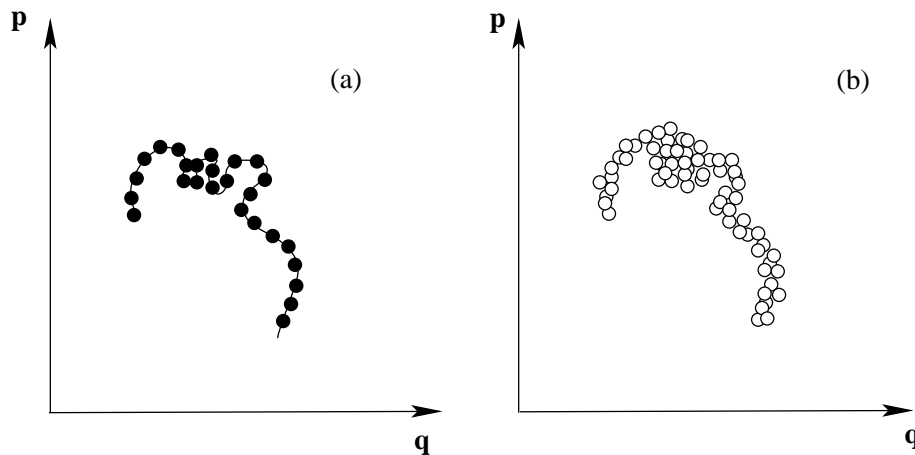


Fig 5. (a) Sketch of the phase-space trajectory of a given thermodynamic system, which we watch for some length of time. The black dots mark the microstates of the system at different moments of time. (b) Instantaneous snapshot of the microstates in which the members of a statistical ensemble are found at a given time. Here, each dot corresponds to the microstate of a different system, at that particular time.

Of course, the problem is that statistical mechanics is needed for much more complicated systems, with  $N \gg 1$ . In this case, it can actually be demonstrated that the ergodic hypothesis fails, meaning that if the system starts in a certain initial microstate, there will be some allowed microstates which will never be reached. It turns out that the second postulate would still be demonstrably true if a relaxed condition, which is called the *quasi-ergodic hypothesis*, holds. This assumes only that the phase-space trajectory passes by close enough to any allowed microstate, not necessarily through it. Even this cannot be demonstrated to be true for all thermodynamic systems – this is why we take Eq. (10) as a postulate, not a theorem. As always with physics, we can verify the results of calculations based on this postulate against experiments, to check its validity. So far, so good.

There is one more technical aspect to this discussion, which is that the result of the ensemble average should not depend on the particular instant of time when we do the ensemble average. This requires that

$$\frac{d}{dt}\rho(\mathbf{q}, \mathbf{p}) = 0$$



which is not apriorily obvious, since as the time goes by, the microstate of each member of the ensemble changes, and so it is possible that this probability density changes in time, making  $\langle A \rangle$  a function of time. In that case,  $\langle A \rangle$  certainly cannot be the answer for a quantity characterizing an equilibrium state, which is time-independent by definition. Fortunately, Liouville's theorem (page 145 of the textbook) shows that indeed  $d\rho/dt = 0$ , so things are consistent – it does not matter at what time we perform the ensemble average, the result  $\langle A \rangle$  is always the same.

Finally, we have a third postulate which says that for a system in equilibrium, and in the absence of any information regarding its state (with the exception of the few macroscopic variables such as  $E, V, N$  defining the macrostate), all allowed microstates are equally likely. This is also reasonable: if we do not know anything about the state of the system, there is no reason to believe that some microstates might be more likely than others.

### 3 The microcanonical ensemble and the statistical definition of entropy

We would like now to see how we can use these postulates to understand how to calculate the entropy  $S(E, V, N)$  of an isolated system. From our review of thermodynamics, we know that once this is known, its various partial derivatives will give us  $T, p, \mu, \dots$  as functions of  $E, V, N$ , and Maxwell relations will give us all the other possible relationships between the macroscopic variables.

Let us consider a statistical ensemble of isolated systems, each of them in the same macrostate with energy between  $E, E+\delta E$ , each containing  $N$  atoms, each of total volume  $V$ , but with various systems in various allowed microstates. Such a statistical ensemble is called a *microcanonical ensemble*.

We know that in equilibrium, the atoms are homogeneously distributed throughout the volume  $V$ . However, there are many allowed microstates for which this is not true. For example, to continue a discussion we started when reviewing the 2nd law of thermodynamics, there are many microstates in which all particles are located in a small volume  $v$ , say in the upper left corner of the container, with no atoms in the rest of the container. In fact we can count precisely how many such allowed microstates are, and the answer is  $\Omega(E, \delta E, N, v)$  as given by Eq. (7), but with  $V^N$  replaced by  $v^N$ . So this is a large number. Moreover, from the 3rd postulate, we know that each one of these highly inhomogeneous allowed microstates has the same probability of being realized as each of the homogeneous microstates. So why is it that we never see an isolated system in equilibrium going spontaneously into one of these inhomogeneous but allowed microstates? The answer is: because the number of inhomogeneous allowed microstates, although large, is so much much smaller than the number of homogeneous allowed microstates, that the probability to be in an inhomogeneous microstate is vanishingly small. In fact, since each microstate is equally likely, we estimate:

$$p_{inhom}(v) = \frac{\Omega(E, \delta E, N, v)}{\Omega(E, \delta E, N, V)} = \frac{v^N}{V^N}$$

Let's get a feel for the numbers. Let's assume  $v = V/2$ , so all we ask for is what is the probability to find all atoms spontaneously congregate in the left half of the container. If we have  $N = 10^{23}$  atoms, we find that  $p_{inhom}(V/2) \approx 1/10^{3 \cdot 10^{22}}$ . Now,  $10^{3 \cdot 10^{22}}$  is such an incredibly big number, that  $p_{inhom}$  is basically zero. The same is true for any other ratio  $v/V < 1$ . In other words, the overwhelming majority of the allowed microstates are homogeneous, and therefore the system will spend virtually all its time in homogeneous microstates, with atoms filling the whole volume. Even if it was initially prepared in an inhomogeneous microstate, it will very quickly become homogeneous, after which, from a macroscopic point of view, we say that the system has reached its equilibrium because the probability to have it become inhomogeneous again is effectively zero.

Before going on, let us calculate  $p_{inhom}$  by another method. The question we ask is: knowing that the probability to find any one atom inside  $v$  is  $v/V$ , what is the probability to find precisely  $n$  atoms inside  $v$ , and the rest outside  $v$ ? From the Bernoulli distribution, we know that this is:

$$P_N(n) = \frac{N!}{n!(N-n)!} \left(\frac{v}{V}\right)^n \left(1 - \frac{v}{V}\right)^{N-n}$$

The probability to find all atoms inside  $v$  is  $P_N(N) = \left(\frac{v}{V}\right)^N \rightarrow 0$  for any value  $v < V$ , simply because  $N$  is so large. In fact, we also know that the most likely (the average) number of atoms inside  $v$  is  $\langle n \rangle = pN = vN/V$ , i.e. exactly the answer for a homogeneous distribution. The larger  $N$  is (and ours is really really large) the less likely it is to see fluctuations away from this value. So the system will always be homogeneous, because any inhomogeneous state is incredibly unlikely.

Where are we now? We just concluded that the equilibrium state is the state with the largest number of allowed microstates, i.e. the most probable state (in our example, the homogeneous state). On the other hand, we know that the entropy is the extensive quantity that is maximized in the equilibrium state of an isolated system (remember the 2nd law of thermodynamics). It seems reasonable then to expect that the entropy of a state is related to its number of allowed microstates – if one is the largest possible, the other one also reaches its maximum. Can we take  $S \sim \Omega$ ? The answer is no, because in this case  $S$  is not an extensive. If we have a system with entropy  $S_1$  and number of allowed microstates  $\Omega_1$ , and a second one with entropy  $S_2$  and number of allowed microstates  $\Omega_2$ , then the entropy of the combined system is  $S = S_1 + S_2$ , while the total number of allowed microstates for the combined system is  $\Omega = \Omega_1 \times \Omega_2$ . Remember that the log of a product is the sum of the logs,  $\ln \Omega = \ln \Omega_1 + \ln \Omega_2$ , so a choice  $S \sim \ln \Omega$  satisfies both the “extensivity” requirement, and the condition that if  $\Omega \rightarrow \Omega_{max}$ , then  $S \rightarrow S_{max}$ . The proportionality constant must be something with units of entropy, and so we arrive at the famous Boltzmann’s formula:

$$S(E, V, N) = k_B \ln \Omega(E, V, N) \quad (11)$$

where  $k_B$  is Boltzmann’s constant. To summarize, for an isolated system, if we can calculate the multiplicity of a macrostate, we know its entropy and all the rest follows from using  $dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$ . This is the recipe we must follow.

Before looking at an example, we need to complete this discussion by seeing how we can express  $S$  as the microcanonical ensemble average of some microscopic quantity,

$$S = \int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho_{mc}(\mathbf{q}, \mathbf{p}) \dots ? \dots$$

(we claimed that we can do this for any macroscopic quantity). First, what is the microcanonical probability distribution  $\rho_{mc}(\mathbf{q}, \mathbf{p})$ ? This follows from the third postulate: since each allowed microstate has equal probability, and only microstates with  $E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E$  are allowed, then:

$$\rho_{mc}(\mathbf{q}, \mathbf{p}) = \begin{cases} C, & \text{if } E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E \\ 0, & \text{otherwise} \end{cases}$$

The constant  $C$  is obtained from the normalization condition:

$$1 = \int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho_{mc}(\mathbf{q}, \mathbf{p}) = C \int_{E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E} \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} = C \Omega(E, \delta E, N, \dots)$$

from the definition of the multiplicity  $\Omega$  (Eq. (3)). It follows that:

$$\rho_{mc}(\mathbf{q}, \mathbf{p}) = \begin{cases} \frac{1}{\Omega(E, \delta E, N, \dots)}, & \text{if } E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E \\ 0, & \text{otherwise} \end{cases} \quad (12)$$

so in general, the microcanonical ensemble average of any microscopic function  $A(\mathbf{q}, \mathbf{p})$  reduces to:

$$\langle A \rangle_{mc} = \frac{1}{\Omega(E, \delta E, N, \dots)} \int_{E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E} \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} A(\mathbf{q}, \mathbf{p})$$

Let us show that

$$S(E, V, N) = -k_B \langle \ln \rho \rangle = -k_B \int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho(\mathbf{q}, \mathbf{p}) \ln [\rho(\mathbf{q}, \mathbf{p})] \quad (13)$$

holds for a microcanonical ensemble (as we will see later on, this actually holds for any type of ensemble). In this case, we replace  $\rho \rightarrow \rho_{mc}$ , which we know, and find that:

$$-k_B \int \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} \rho_{mc}(\mathbf{q}, \mathbf{p}) \ln [\rho_{mc}(\mathbf{q}, \mathbf{p})] = -\frac{k_B}{\Omega} \ln \left[ \frac{1}{\Omega} \right] \int_{E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \delta E} \frac{d\mathbf{p}d\mathbf{q}}{\mathcal{G}_N h^{Nf}} = -k_B \ln \left[ \frac{1}{\Omega} \right]$$

i.e., indeed we have  $S = k_B \ln \Omega = -k_B \langle \ln \rho \rangle$ . Word of caution: the first part of this equality  $S = k_B \ln \Omega$  is only correct for isolated systems. We will learn later on what to do for closed or open systems. The second part,  $S = -k_B \langle \ln \rho \rangle$  holds for any type of ensemble (i.e., also ensembles of closed, or of open, systems, which are called canonical, respectively grand-canonical ensembles) provided that we use the correct probability density for that type of ensemble.

Now, our example: we have already calculated, for a 3D gas of simple classical atoms of mass  $m$  confined to a volume  $V$ , the value of  $\Omega(E, \delta E, N, V)$ , see Eq. (7). It follows that the entropy  $S(E, V, N)$  of this isolated system is:

$$\begin{aligned} S(E, V, N) &= k_B \ln \Omega = k_B \ln \left[ \frac{1}{N! \Gamma\left(\frac{3N}{2}\right)} V^N E^{\frac{3N}{2}-1} \left(\frac{2m\pi}{h^2}\right)^{\frac{3N}{2}} \delta E \right] \\ &= Nk_B \ln V + \left(\frac{3N}{2} - 1\right) k_B \ln E - k_B \ln N! - k_B \ln \Gamma\left(\frac{3N}{2}\right) + \frac{3N}{2} \ln \left[\frac{2m\pi}{h^2}\right] + k_B \ln \delta E \end{aligned}$$

The last term does not depend on either  $E$ ,  $V$  or  $N$ , so we can ignore it from now on (if you review the argument leading to Eq. (11), the entropy is actually defined only up to an overall constant, and we can include this constant term into that overall constant. It doesn't contribute to partial derivatives, so it won't change the expressions for  $p, T, \mu, \dots$ ). Because  $N$  is a large number, we use Stirling's formula to approximate:

$$\ln N! = N \ln N - N; \quad \ln \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2} - 1\right) \left[\ln\left(\frac{3N}{2} - 1\right) - 1\right]$$

Furthermore, because  $N$  is so large, we can replace  $\frac{3N}{2} - 1 \approx \frac{3N}{2}$  everywhere, to find:

$$S(E, V, N) = Nk_B [\ln V - \ln N] + \frac{3N}{2} k_B \left[ \ln E + \ln \frac{2m\pi}{h^2} - \ln \frac{3N}{2} \right] + \frac{5}{2} Nk_B \rightarrow$$

$$S(E, V, N) = Nk_B \left[ \ln \left\{ \frac{V}{N} \left( \frac{4\pi m E}{3h^2 N} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right]$$

This is indeed an extensive quantity: doubling  $E, V, N$  will precisely double  $S$ .

We now use

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

to find:

$$\begin{aligned}\frac{1}{T} &= \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{3}{2} N k_B \frac{1}{E} \rightarrow E = U = \frac{3}{2} N k_B T \\ \frac{p}{T} &= \left( \frac{\partial S}{\partial V} \right)_{E,N} = N k_B \frac{1}{V} \rightarrow pV = N k_B T \\ \frac{\mu}{T} &= - \left( \frac{\partial S}{\partial N} \right)_{E,V} = -k_B \left[ \ln \left\{ \frac{V}{N} \left( \frac{4\pi m E}{3h^2 N} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right] + \frac{5}{2} k_B = -k_B \ln \left\{ \frac{V}{N} \left( \frac{4\pi m E}{3h^2 N} \right)^{\frac{3}{2}} \right\}\end{aligned}$$

i.e., all the expected relations for a simple ideal gas (of course, we can go on and calculate  $C_V$ ,  $C_P$ ,  $\alpha$ ,  $\kappa$ , but they'll all come out right. Try it!). I hope that right now you are suitably impressed: we have derived these relationships without using any help from experiments, simply by making some assumptions (our postulates) about what the system is likely to be doing, and having some knowledge about its microscopic components (how many degrees of freedom for a simple atom, and what is the microscopic Hamiltonian). We can now repeat the same sort of calculations for any isolated system, and we will look at a few more examples in class (more are discussed in the textbook).

Two more comments before we conclude this part. First, I said awhile back that if one neglects the Gibbs factor  $\mathcal{G}_N = N!$  in this classical calculation, one gets some puzzling results. One problem in that case, as you can convince yourself by redoing the calculation without the  $N!$ , is that the entropy will not be an extensive – which is not right. Also, if we neglect  $N!$  we encounter the so-called Gibbs's paradox – we'll discuss this in the assignment (also, see textbook around page 132).

Second, you might be a bit less than satisfied because of the need for all these ad-hoc adjustments (lose the  $k_B \ln \delta E$  term, replace  $\frac{3N}{2} - 1 \rightarrow \frac{3N}{2}$ ). This looks a bit like fudging, and is not esthetically pleasing. The reason these adjustments are needed is simply because this is a classical calculation, and we know that it cannot be exact: it is an approximation of the exact quantum mechanical calculation we should be doing instead. We will now learn first how to deal with simple quantum statistical microcanonical ensembles. It will turn out that a simple ideal gas is actually not “simple enough” to treat easily as a quantum microcanonical ensemble, and we will need to learn how to treat canonical and grand-canonical ensembles (we'll learn what all these names mean as we go along). We will then do the quantum calculation for the ideal gas in a quantum grand-canonical ensemble, where the calculation will actually be easy. We will learn that at high temperatures (i.e. high energies) the above classically-derived equations are accurate; however, as we lower the temperature and therefore the energy of the system towards its ground-state energy, the classical predictions fail miserably and we really need to know how to do the quantum calculations to understand what happens.

You might wonder why should we really care about low-temperature, quantum behavior, when we live in a fairly high-temperature, classical world? Well, first of all, what “low” or “high” means depends on the system studied. For instance, we will see that the gas of electrons in a metal is, even at room temperature, deep inside the quantum regime! There is no way to understand their behavior, and therefore the properties of any metal (e.g. how the electric current flows through a piece of metal), if we do not know quantum statistical mechanics. Another justification is that a lot of interesting technology nowadays is placed at really low temperatures – think, for example, of all the equipment on a satellite! Finally, you've surely heard of nanotechnology – the drive to make everything smaller and smaller. There are many cases where “small” means that quantum treatment becomes essential for describing the system's behaviour, but it is still “large” enough that statistical mechanics is valid. So knowledge of the quantum behavior is not just to satisfy our curiosity, but it is of actual practical relevance. Besides, it is really cool stuff!