

MICROCANONICAL, CANONICAL, AND GRAND CANONICAL DISTRIBUTIONS

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1 Microcanonical distribution

We recall from the previous lectures

- **Phase space volume** for a system of N identical particles:

$$d\Gamma = \frac{d^3\mathbf{q}_1 \dots d^3\mathbf{q}_N d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N}{N!h^{3N}} \quad (1)$$

(Lebesgue measure suitably normalized)

- **Energy surface** Γ_E , specified by $H(x) = E$.
- **Energy shell** of thickness $\delta E \ll E$, i.e.,

$$\Gamma_{E,\delta E} = \{x \in \Gamma : E \leq H(x) \leq E + \delta E\}. \quad (2)$$

- (System confined in $\Lambda \subset \mathbb{R}^3$ of finite volume.) **Microcanonical distribution**

$$\mathbb{P}_{E,\Delta E}\{A\} = \frac{|A \cap \Gamma_{E,\delta E}|}{|\Gamma_{E,\delta E}|}, \quad A \text{ subset of } \Gamma, \quad (3)$$

(Lebesgue measure restricted to the shell of constant energy and normalized to the volume of the shell).

- **Microcanonical partition function or density of states**

$$\Omega(E) = \int \delta(E - H(x)) d\Gamma \quad (4)$$

(volume of Γ_E).

- **Volume of the energy shell**

$$|\Gamma_{E,\delta E}| = \Omega(E)\delta E \quad (5)$$

- **Volume of** $\Gamma_{\leq E} = \{x \in \Gamma | H \leq E\}$

$$\Gamma(E) = \int_{H \leq E} d\Gamma = \int^E \Omega(E) dE \quad (6)$$

whence

$$\Omega(E) = \frac{d\Gamma(E)}{dE}. \quad (7)$$

- **average of quantity** $Y = Y(x)$:

$$\mathbb{E}\{Y\} = \frac{1}{\Omega(E)} \int_{\Gamma} Y(x) \delta(E - H(x)) d\Gamma = \frac{1}{\Omega(E)} \frac{d}{dE} \int_{H(x) \leq E} Y(x) d\Gamma \quad (8)$$

2 $\Omega(E)$ of the ideal gas

$N \gg 1$ particles in a vessel Λ of volume $|\Lambda| = V$,

$$H(q, p) = \frac{p^2}{2m} = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m}, \quad \Gamma_E : \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} = E, \quad \mathbf{p}_i \in \Lambda.$$

$$\Gamma_{\leq E} = \left[\text{sphere in dim} = 3N \text{ of radius } R = \sqrt{2mE} \right] \times V^N$$

Thus (recalling (1))

$$\Gamma(E) = |\Gamma_{\leq E}| = c_{3N} (2mE)^{3N/2} \frac{V^N}{h^{3N} N!}, \quad (9)$$

where

$$C_n = \frac{\pi^{n/2}}{(n/2)!}, \quad (n/2)! = \Gamma\left(\frac{n}{2} + 1\right), \quad \Gamma(x+1) = \int_0^\infty t^x e^{-t} dt$$

is the volume of the unit sphere in n dimensions. Whence,

$$\Omega(E) = \frac{d\Gamma_{\Lambda}(E)}{dE} = C_{3N} \frac{3N}{2} (2m) (2mE)^{(3N/2)-1} \frac{V^N}{h^{3N} N!} \quad (10)$$

and

$$|\Gamma_{E, \delta E}| = \Omega(E) \delta E \quad (11)$$

Since $N \sim 10^{23}$ we are interested in the asymptotic of $|\Gamma_{E, \delta E}|$ for N and V large such that

$$N/V = n = \text{const.}, \quad E/N = \varepsilon = \text{const.}$$

To this end, we introduce the function

$$S(E, N, V) = \log |\Gamma_{E, \delta E}| \quad (12)$$

N.B. At this stage this “ S -function” is only introduced for mathematical convenience, and no thermodynamic meaning is attributed to it; later on we shall see that it provides the microscopic interpretation of the thermodynamic entropy at equilibrium.

Asymptotic estimate We have

$$\begin{aligned} S(E, N, V) &= \log \left(\frac{\pi^{3N/2}}{(3N/2)!} \frac{V^N}{h^{3N} N!} \right) + \left(\frac{3N}{2} - 1 \right) \log(2mE) + \log \left(\frac{3N}{2} 2m\delta E \right) \\ &= \underbrace{\log \left(\frac{\pi^{3N/2}}{(3N/2)!} \frac{V^N}{h^{3N} N!} \right)}_I + \frac{3N}{2} \log(2mE) + O(\log N) \end{aligned}$$

We now use Stirling formula $\log N! = N \log N - N + O(\log N)$ to evaluate the first term

$$\begin{aligned} I &= \frac{3N}{2} \log \frac{\pi}{h^2} + \log \left(\frac{V^N}{(3N/2)^{3N/2} e^{-3N/2} N^N e^{-N}} \right) + O(\log N) \\ &= \frac{3N}{2} \log \frac{\pi}{h^2} + N \log \frac{V}{N} - \frac{3N}{2} \log \frac{3N}{2} + \frac{5}{2}N + O(\log N) \end{aligned}$$

whence

$$\begin{aligned} S(E, N, V) &= N \log \left[\frac{V}{N} \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2}N + O(\log N) \\ &= N \left\{ \log \left[v \left(\frac{4\pi m}{3h^2} \varepsilon \right)^{3/2} \right] + \frac{5}{2} \right\} + O(\log N), \quad v = V/N, \quad \varepsilon = E/N \\ &= N \underbrace{\left(\log v + \frac{3}{2} \log \varepsilon + \frac{3}{2} \log \frac{4\pi m}{3h^2} + \frac{5}{2} \right)}_{s(v, \varepsilon)} + O(\log N) \end{aligned} \tag{13}$$

Note that (neglecting logarithmic corrections) $S(E, N, V)$ is extensive, i.e.,

$$S(E, N, V) = N s(v, \varepsilon). \tag{14}$$

We have thus established the following proposition:

Proposition 1

The volume of the energy shell of the ideal gas of N particles is asymptotically

$$|\Gamma_{E, \delta E}| \asymp e^{S(N, V, E)} = e^{N s(v, \varepsilon)}$$

where

$$v = V/N, \quad \varepsilon = E/N$$

and

$$s(v, \varepsilon) = N \left(\log v + \frac{3}{2} \log \varepsilon + \frac{3}{2} \log \frac{4\pi m}{3h^2} + \frac{5}{2} \right)$$

Note that the dependence on δE drops out and that we would have obtained the same result for the volume of $\Gamma_{\leq E}$ (exercise). So we have

$$\Omega(E) \asymp \Gamma(E) \asymp e^{N s(v, \varepsilon)} \tag{15}$$

N.B “ \asymp ” expresses an equality relationship on a logarithmic scale: $a_n \asymp b_n$ means that

$$\lim_{n \rightarrow \infty} \frac{1}{n} \log a_n = \lim_{n \rightarrow \infty} \frac{1}{n} \log b_n.$$

3 Some morals from the ideal gas

- For the ideal gas $\Omega(E)$ is positive and monotonically increasing for $E > 0$. This is expected to be true also for general systems and has been proven for many realistic models.

- Also the specific estimate

$$|\Gamma_{E,\delta E}| \asymp e^{Ns(v,\varepsilon)} \quad (16)$$

is expected to be true also for general systems and has been proven for many realistic models.

- More precisely, one considers the description of a large system in the limit $E, N, V, \Lambda \rightarrow \infty$ such that $E/N \rightarrow e$, $N/V \rightarrow n$ with e, n finite. This is called the **thermodynamic limit**. In particular, one wishes to show that existence of the limit

$$\frac{\log |\Gamma_{E,\delta E}|}{N} \rightarrow s(e, n),$$

where $s(e, n)$ is of course different from that of the ideal gas, but like the that of the ideal gas is **convex**. This is in general difficult to prove [explain] (after 1960-70 for “almost” realistic systems).

- (16) is basically a **large deviations** estimate with s the rate function. Roughly, the reason is the following:

The energy is fluctuating in the interval $[E, E + \delta E]$ (random variable) and is of the form

$$H(x) = \sum_k E_k(x)$$

where

$$E_k(x) = H_k(x_k) + \sum_{i \neq k} V(q_i - q_k)$$

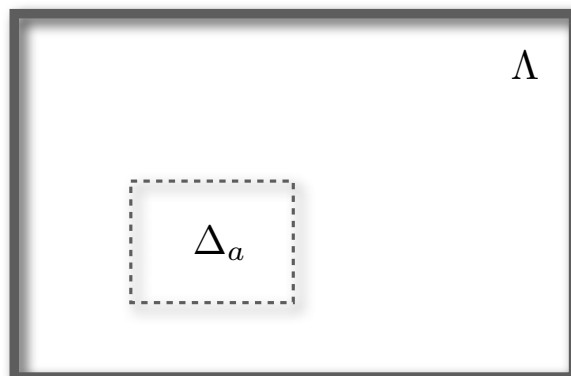
The probability distribution of $\frac{1}{N} H(x)$,

$$\frac{1}{|\Gamma_{E,\delta E}|} \left| \Gamma_{\frac{1}{N} H(x)=y} \right|$$

is expected to concentrate exponentially with N on the mean value e

4 Canonical distribution of a subsystem

We wish to compute the limit distribution of the state of the particles in any finite subvolume Δ_a .



Splitting

$$\Lambda = \Delta_a + \Delta_b \quad (\Delta_b = \Lambda \setminus \Delta_a), \quad x = (x_a, x_b)$$

where x_a is the state of the particle in Δ_a and x_b the state of the particles in Δ_b . In the microcanonical ensemble are constants the total number of particle

$$N(x) = N_a(x_a) + N_b(x_b) = N$$

and the total energy

$$H(x) = H_a(x_a) + H_b(x_b) + V(x_a, x_b) = E.$$

We shall assume that the interaction energy is negligible so that

$$H(x) = H_a(x_a) + H_b(x_b) = E$$

Understanding the splitting For any $x = (x_a, \dots, x_N)$, let $S(x)$ be the subset of $\{1, 2, \dots, N\}$ for which $x_i \in \Delta_a$. Then x can then be split into

$$X_a(x) = (X_{a_1}(x), \dots, X_{a_{N_a}}(x)) \quad \text{and} \quad X_b(x) = (X_{b_1}(x), \dots, X_{b_{N_b}}(x)),$$

where the X_{1i} and the X_{2i} are placed in the same order as in x . (For example, if $x = (x_1, x_2, x_3, x_4, x_5)$ and $S(x) = \{2, 3, 5\}$ then $X_a(x) = (x_2, x_3, x_5)$ and $X_b(x) = (x_1, x_4)$).

Calculation of the average of any quantity in Δ_a If $Y_a = f(X_a, N_a)$ is any symmetric function of the state of the particles in Δ_a , then its average can be computed as follows:

$$\begin{aligned} \int_{H \leq E} f(X_a(x), N_a(x)) d\Gamma &= \sum_S \int_{H \leq E, S(x)=S} f(X_a(x), |S|) d\Gamma \\ &= \sum_S \int_{H \leq E} f(X_a(x), |S|) \frac{dx}{N!} \\ &= \sum_S \int_{H_a(x_a) + H_b(x_b) \leq E} f(x_a, |S|) \frac{dx_a dx_b}{N!} \\ &= \sum_{N_a} \binom{N}{N_a} \int \frac{1}{N!} f(x_a, N_a) dx_a \int_{H_b \leq E - H_a} dx_b \\ &= \sum_{N_a} \int f(x_a, N_a) \frac{dx_a}{N_a!} \int_{H_b \leq E - H_a} \frac{dx_b}{(N - N_a)!} \\ &= \sum_{N_a} \int f(x_a, N_a) \Gamma_b(E - H_a(x_a), N - N_a) \frac{dx_a}{N_a!} \end{aligned}$$

Thus

$$\mathbb{E}\{Y_a\} = \frac{1}{\Omega(E, N)} \sum_{N_a} \int f(x_a, N_a) \Omega_b(E - H_a(x_a), N - N_a) \frac{dx_a}{N_a!}$$

We hence see that the probability of having N_a particles in Δ_a with state x_a has probability density

$$\frac{\Omega_b(E - H_a(x_a), N - N_a)}{\Omega(E, N)} \frac{dx_a}{N_a!}$$

Consider now the function $f(x_a, N_a) = 1$ iff $H_a(x_a) \leq E_a$ and $N_a = N_a$. Then

$$\begin{aligned} \mathbb{P} \{H_a \leq E_a, N_a = N_a\} &= \frac{1}{\Omega(E, N)} \int_{H_a(x_a) \leq E_a} \Omega_b(E - H_a(x_a), N - N_a) \frac{dx_a}{N_a!} \\ &= \frac{1}{\Omega(E, N)} \int_{E' \leq E_a} \Omega_b(E - H_a, N - N_a) \Omega_a(H_a, N) dH_a \end{aligned}$$

so the joint density of E_a and N_a is

$$\frac{\Omega_b(E - E_a, N - N_a) \Omega_a(E_a, N_a) dE_a}{\Omega(E, N)}$$

From this result we see that $\Omega(E, N)$ is composed by convolution, because the total integral is one:

$$\Omega(E, N) = \sum_N \int \Omega_a(E_a, N_a) \Omega_b(E - E_a, N - N_a) dE_a \quad (17)$$

Summary:

Proposition 2

Consider a system in Λ with a m.can. distribution defined by E, N . Then if $\Lambda = \Delta_a + \Delta_b$ with $\Delta_a \cap \Delta_b = \emptyset$ and if the interaction between particles in Δ_a and Δ_b is negligible, the state (X_a, N_a) has probability distribution

$$\mathbb{P} \{X_a \in dx_a, N_a = N_a\} = \frac{\Omega_b(E - H_a(x_a), N - N_a) dx_a}{\Omega(E, N) N_a!},$$

the variables H_a and N_a have distribution

$$\mathbb{P} \{H_a \in dE_a, N_a = N_a\} = \frac{\Omega_b(E - E_a, N - N_a) \Omega_a(E_a, N_a) dE_a}{\Omega(E, N)},$$

and

$$\Omega(E, N) = \sum_{N_a} \int \Omega_a(E_a, N_a) \Omega_b(E - E_a, N - N_a) dE_a$$

5 Canonical and grand canonical distribution for the ideal gas

$$\Omega(E, N) = \frac{(2m\pi)^{3N/2}}{(3N/2)!} (3N/2) E^{(3N/2)-1} \frac{V^N}{N!}$$

so in the limit

$$N \rightarrow \infty, \quad \frac{E}{N} \rightarrow \epsilon, \quad \frac{N}{V} \rightarrow n, \quad E_a, V_a, N_a = \text{const.}$$

we obtain¹

$$\begin{aligned} \frac{\Omega_b(E_b, N_b) dx_a}{\Omega(E, N) N_a!} &= \frac{dx_a}{N_a!} (2\pi m)^{-3N_a/2} \frac{(3N/2)!}{(3N_b/2)!} \frac{3N_b/2}{3N/2} \frac{E_b^{(3N_b/2)-1}}{E^{(3N/2)-1}} \frac{V_b^{N_b}}{V^N} \frac{N!}{N_b!} \\ &\approx \frac{dx_a}{V_a^N} \left(\frac{V_a}{V}\right)^{N_a} \left(\frac{V_b}{V}\right)^{N_b} \binom{N}{N_a} (2\pi m)^{-3N_a/2} \frac{(3N/2\epsilon)^{3N/2}}{(3N_b/2\epsilon)^{3N_b/2}} \frac{E_b^{(3N_b/2)}}{E^{(3N/2)}} \end{aligned}$$

¹Stirling's formula : $n! = \sqrt{2\pi n}(n/e)^n$.

$$\approx \frac{dx_a}{V_a^{N_a}} \frac{(nV_a)^{N_a}}{N_a!} e^{-nV_a} (2\pi m)^{-3N_a/2} (3/2e)^{3N_a/2} (N/N_b)^{3N_a/2} (E_b/E)^{3N_a/2} (N_b/E_b)^{3N_a/2}$$

the last 3 factors tend to

$$\begin{aligned} (N/N_b)^{3N/2} &= \left(1 - \frac{N_a}{N}\right)^{-3N/2} \rightarrow e^{3N_a/2} \\ (E_b/E)^{3N/2} &= \left(1 - \frac{E_a}{E}\right)^{3N/2} \rightarrow e^{-3E_a/(2\epsilon)} \\ (N_b/E_b)^{3N_a/2} &\rightarrow \epsilon^{-3N_a/2} \end{aligned}$$

so the probability distribution for N_a and x_a converges to

$$\begin{aligned} \mathbb{P}_\infty\{X_a \in dx_a, N_a = N_a\} &= \frac{(nV_a)^{N_a}}{N_a!} e^{-nV_a} \left(\frac{4m\pi\epsilon}{3}\right)^{-3N_a/2} e^{-3H_a(x_a)/(2\epsilon)} \frac{dx_a}{V_a^{N_a}} \\ &= \frac{(nV_a)^{N_a}}{N_a!} e^{-nV_a} \left(\frac{4m\pi\epsilon}{3}\right)^{-3N_a/2} e^{-\frac{3}{4m\epsilon} \sum_{i=1}^N |\mathbf{p}_{a_i}|^2} \frac{dq_a dp_a}{V_a^{N_a}} \end{aligned}$$

Let us now highlight the main features of the probability distribution so obtained. To this end, let us drop the indices “1” and ∞ , call Δ the finite region of volume $V = |\Delta|$, let x, N denote the state of the gas in Δ , an rewrite the above formula as

$$\mathbb{P}\{X_\Delta \in d\Gamma, N_\Delta = N\} = \frac{(nV)^N}{N!} e^{-nV} \left(\frac{4m\pi\epsilon}{3}\right)^{-3N/2} e^{-\frac{3}{4m\epsilon} \sum_{i=1}^N |\mathbf{p}_i|^2} \frac{dq dp}{V^N} \quad (18)$$

It gives the joint probability of having N particles in Δ in the state $x = (q, p)$

(a) The momenta $p = (\mathbf{p}_1, \dots, \mathbf{p}_N)$ have a normal distribution

$$\left(\frac{4m\pi\epsilon}{3}\right)^{-3N/2} e^{-\frac{3}{4m\epsilon} \sum_{i=1}^N |\mathbf{p}_i|^2}$$

with variance $2m\epsilon/3$, so the average kinetic energy of a particle is

$$\left\langle \frac{|\mathbf{p}_i|^2}{2m} \right\rangle = \epsilon$$

(b) By integrating out q and p one obtains the marginal distribution of N_Δ

$$\mathbb{P}\{N_\Delta = N\} = \int \mathbb{P}\{X_\Delta \in d\Gamma, N_\Delta = N\} = \frac{(nV)^N}{N!} e^{-nV}$$

Thus, the positions in space form a Poisson process with density n . Hence

$$\mathbb{E}\{N_\Delta\} = nV \equiv \bar{N}, \quad \text{Var}(N_\Delta) = nV$$

so that

$$\mathbb{P}\{N_\Delta = N\} = e^{-\bar{N}} \frac{\bar{N}^N}{N!}$$

(c) If the number of particles in Δ is fixed to have the value N , the conditional distribution is

$$\begin{aligned}\mathbb{P}\{X \in d\Gamma | N_{\Delta} = N\} &= \frac{\mathbb{P}\{X_{\Delta} \in d\Gamma, N_{\Delta} = N\}}{\mathbb{P}\{N_{\Delta} = N\}} \\ &= \left(\frac{4m\pi\epsilon}{3}\right)^{-3N/2} e^{-\frac{3}{4m\epsilon} \sum_{i=1}^N |\mathbf{p}_i|^2} \frac{dqdp}{V^N}\end{aligned}\quad (19)$$

(d) The probability formula (18) has the following form

$$\mathcal{Z}^{-1} e^{-\beta H_N(x) + \beta \mu N} \frac{dx}{N!} \quad (20)$$

where

$$\begin{aligned}\mathcal{Z} &= e^{-\bar{N}} \\ \beta &= \frac{3}{2\epsilon} \\ H_N(x) &= \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} \\ \mu &= \frac{1}{\beta} \ln \left[\frac{\bar{N}}{V} \left(\frac{2\pi m}{\beta} \right)^{-3/2} \right]\end{aligned}$$

(e) The probability formula (19) has the following form

$$Z^{-1} e^{-\beta H_N(x)} \frac{dx}{N!} \quad (21)$$

where

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2}$$

6 Canonical distribution for the general case

Proposition 3 (Gibbs-Boltzmann's law)

The distribution of the state of a small subsystem in a large system with finite densities of particles and energy has a probability density proportional to

$$e^{-\beta H_N(x) + \beta \mu N} \frac{dx}{N!} \quad (22)$$

This is a very general law which was discovered by Boltzmann. (The exponential factor is often called the B-factor.)

It is easy to verify it in the situation where we have an arbitrary system in Δ_a with a fixed no. of particles in contact with an ideal gas in Δ_b , a heat bath (that is, formula (22)). The two parts can exchange energy, but the interaction energy can be neglected.

The particles in Δ_a and Δ_b need not to be of the same type. Then

$$\begin{aligned}\Gamma(E, N_a, N_b) &= \int_{H_a(x_a) + H_b(x_b) \leq E} \frac{dx_a}{N_a!} \frac{dx_b}{N_b!} = \int \frac{dx_a}{N_a!} \Gamma_b(E - H_a(x_a), N_b) \\ &= \int \Gamma_b(E - H_a(x_a), N_b) \Omega_a(E_a, N_a) dE_a\end{aligned}$$

whence

$$\Omega(E, N_a, N_b) = \int \Omega_a(E_a, N_a) \Omega_b(E - E_a, N - N_a) dE_a \quad (23)$$

so the probability density for X_a is proportional to

$$\Omega_b(E - H_a(x_a), N - N_a) \frac{dx_a}{N_a!}.$$

Since

$$\Omega_b(E_b, N_b) = K(N_b) E_b^{(3N_b/2)-1},$$

we see that the density is proportional to

$$\begin{aligned}(E - H_a(x_a))^{3N_b/2-1} &= (\text{const.}) \left(1 - \frac{H_a(x_a)}{E}\right)^{3N_b/2-1} \rightarrow \\ &\rightarrow (\text{const.}) e^{-3/(2\epsilon) H_a(x_a)},\end{aligned}$$

and hence it converges to

$$\frac{e^{-\beta H_a(x_a)} dx_a}{Z} \frac{1}{N_a!}, \quad \beta = \frac{3}{2\epsilon}, \quad Z = \int e^{-\beta E_a} \Omega_a(E_a, N_a) dE_a. \quad (24)$$

The distribution so obtained is called **canonical** and is more important in practice than the m. can. one since very often one is interested in precisely this situation where the system is in contact with a **heath bath**.

The normalization constant

$$Z = Z_\Lambda(N, \beta) = \int e^{-\beta H_N(x)} \frac{dx}{N!} = \int e^{-\beta E} \Omega(E, N) dE$$

is called the **canonical partition function**.

The exponential form means that if two systems do not interact: $H(x_a, x_b) = H_a(x_a) + H_b(x_b)$, then they are also independent:

$$e^{-\beta H(x_a, x_b)} = e^{-\beta H_a(x_a)} e^{-\beta H_b(x_b)}$$

and this is a considerable simplification.

7 Equivalence of ensembles

In general $H(x)$ has a distribution very sharply concentrated around its average when N is large, so **one gets the same results concerning most averages as in the m.can. ensemble where $H(x)$ is fixed to this value, because the conditional distribution of x given that $H(x) = E$ is the m.can. distribution.** (The B-factor is constant on each energy shell.)