

## 7. Statistical mechanics

### 7.1. The Problem

Consider the concept of pressure. One can start from the dimensional analysis:

$$[P] = Pa = \frac{kg \cdot m}{s^2 \cdot m^2} \Rightarrow P = 2mv_x I$$

This follows also from the molecular considerations. Each molecule has a momentum (on average)  $mv_x$ . The flux of the molecules colliding with the surface of our reservoir is  $I$ . The factor of 2 originates from the fact that the molecules reflect from the surface. The flux can also be described as  $I = v_x n$ , where  $n$  is the concentration of the particles.

At each collision, the particle may have different amount of kinetic energy (momentum), but there are many particles. Very many. So we feel only a time-averaged value.

$$\text{Averaging over time: } \bar{L} = \frac{1}{T} \int_0^T L(t) dt$$

In equilibrium, nothing depends on time, so **we can substitute the averaging over time with the averaging over realizations (events)**.

$$\bar{L} = \sum_i L_i \cdot \omega(L_i) = \int dL = \int L(q, p) \cdot \rho(q, p) dq dp$$

Here:

$L_i$  - possible values of the function  $L$  (in discrete case) = realizations

$\omega(L_i)$  - probability to get the particular realization  $L_i$

$\rho(q, p) = \frac{dL}{L dq dp}$  - probability density of the system's states

$dL$  - is a number of systems (points in Gamma-space) that have  $q \in [q, q + dq]$  and  $p \in [p, p + dp]$

$L$  - is the number of configurational points on the phase trajectory.

We want to find  $\rho(q, p)$

## 7.2. Basic concepts and definitions

Definition: **Ergodic system** = a system for which a time-average is equal to an average over realizations.

Example: A jar with 50 black and 50 white balls. In it is a window. We shake the jar and look into this window every second for 100 years, noticing the color of a ball in that window. Eventually and realize that we see black in 50% of cases and white in 50%. **This system is ergodic.**

Now, 2 black balls have stick to the bottom of the jar. As a result, our time-averaged results will be different from what we know based on the proportions of the differently colored balls in the jar. **This system is not ergodic.**

Another example: A 1-D Harmonic oscillator.

Note: All the derivations in a standard statistical mechanics are correct only for ergodic systems.

Definition:  **$\mu$ -space.** A space of a single molecule: 6-dimensional. An image of 1 molecule is 6-dimensional point. An image of 1 mole of molecules is  $6 \times 10^{23}$  – 6 dimensional points.

Definition:  **$\Gamma$ -space.** A space of a mole of molecules:  $6 \times 6 \times 10^{23}$  – dimensional. An image of 1 mole of molecules is a single  $6 \times 6 \times 10^{23}$  dimensional point.

Definition: points in the  $\Gamma$ -space are called **configurational points**.

Definition: **Phase trajectory** – is a sequence of the configurational points.

Definition: **Microstate** (configuration, 1 configurational point) – is defined by positions and momenta of all particles in a system.

Definition: **Macrostate** – is defined by all macroscopic parameters (P, T, V, etc.) of a system.

Definition: **Gibbs' ensemble** – is a collection of microstates corresponding to a given macrostate.

Classification:

- **Microcanonical** (NVE, meaning  $N = \text{const}$ ,  $V = \text{const}$ ,  $E = \text{const}$ )
- **Canonical** (NVT, possible energy exchange with the environment such that  $E_{\text{exch}} \ll E$ )
- **Grand canonical** ( $\mu$ TV, possible energy exchange, and mass exchange, such that  $E_{\text{exch}} \ll E$  and  $N_{\text{exch}} \ll N$ )

Theorem: Phase trajectory does not intersect itself.

**Proof:** ad absurdum: Assume there is a point of self-intersection → if we choose it as a starting point, there will be several pathways of system evolution → contradiction with the determinism of classical mechanics.

Theorem (Liouville): The density of configurational points is constant along the phase trajectory.

**Proof:** We start with a continuity equation, which states:

$$\frac{\partial \rho}{\partial t} + \text{div} \vec{J} = 0$$

$\vec{J} = \rho \cdot \dot{\vec{z}}$  is a flux in the phase space, where  $\dot{\vec{z}} = \begin{pmatrix} \dot{q} \\ \dot{p} \end{pmatrix}$

So:

$$\begin{aligned} \text{div}(\rho \cdot \dot{\vec{z}}) &= (\vec{\nabla}_z, \rho \cdot \dot{\vec{z}}) = \sum_i \left[ \frac{\partial(\rho \dot{q}_i)}{\partial q_i} + \frac{\partial(\rho \dot{p}_i)}{\partial p_i} \right] = \rho \sum_i \left[ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] + \sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] = \\ &= \rho \sum_i \left[ \frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} \right] + \sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] = \sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] \end{aligned}$$

Here we used Hamiltonian equations of motion

Substituting everything back to the continuity equation, we obtain:

$$\frac{\partial \rho}{\partial t} + \text{div} \vec{J} = 0 = \frac{\partial \rho}{\partial t} + \sum_i \left[ \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] = \frac{d\rho}{dt}.$$

Which proves the theorem.

Ergodic hypothesis: During its evolution, a system will visit all points of a phase space belonging to a given energy level. That is:  $\rho(q, p) = \text{const}$ .

In other words: All microstates with the same energy are equally probable

Consequences: **Boltzmann** ( N! ) = = = **Gibbs** (Th Liouville + Ergodic hypothesis)

### 7.3. Maxwell-Boltzmann distribution

Assume the macroscopic parameters ( $N$ ,  $V$ ,  $E$ ,  $T$ , etc.) are defined. They define certain constraints on the set of points in the phase space (microstates) that are consistent with this macrostate. For instance, for a harmonic oscillator, different total energy values will define different circles. Each circle, in this case is a “volume” of the phase space that corresponds to given total energy.

One can subdivide a phase space volume into many small cells of width  $\Delta q$  and  $\Delta p$ . Although Boltzmann merely hypothesized this, one can recall the uncertainty principle, which suggests these width could be related to each other. The number of such cells is large, but finite, if  $V$  and  $E$  are fixed.

Further, the following constraints are present:

$$\sum_i N_i = N = \text{const}$$

$$\sum_i E_i N_i = E = \text{const}$$

Here,  $N_i$  is the number of particles in the cell with index  $i$ ,  $N$  is the total number of particles,  $E_i$  is the energy of the cell with index  $i$ ,  $E$  is the total energy of the system.

The main assumptions of the Boltzmann's theory:

- 1) All microstates are equally probable
- 2) Macrostate is defined by defining the number of particles in each cell of the phase space:  
 $\{N_i, i = 1, \dots, K\}$
- 3) Each macrostate is realized by a certain number of microstates
- 4) Equilibrium state is the one that is realized by the largest number of microstates

Using the constraints and the assumptions, we can derive the distribution. First, the number of microstates is given by:

$$\Omega = \frac{N!}{\prod_{k=1}^K N_k!}$$

The numerator describes the total number of permutations of  $N$  particles. Each  $N_k!$  term in the denominator accounts for all permutations of  $N_k$  particles in the cell  $k$ . This is needed, because the particles are indistinguishable.

Example: consider 6 particles in 3 cells.

- a) If the distributions is:  $N_1 = 6, N_2 = N_3 = 0$ , then  $\Omega = \frac{6!}{6!0!0!} = 1$ . There is only 1 way to distribute 6 particles into a given cell. We don't care into which cell the particles are put.

- b) If the distributions is:  $N_1 = N_2 = N_3 = 2$ , then  $\Omega = \frac{6!}{2!2!2!} = 90$ . As you can see this is a uniform distribution, and is realized by the largest number of microstates.

The maximum of  $\Omega$  coincides with the maximum of  $\ln \Omega$ , but the latter is easier to work with. Using the Sterling approximation,  $\ln N! \approx N \ln N - N$ , which is satisfied for large  $N$ , we obtain:

$$\ln \Omega = \ln N! - \ln \left( \prod_{k=1}^K N_k! \right) \approx N \ln N - N - \sum_{k=1}^K (N_k \ln N_k - N_k) = N \ln N - \sum_{k=1}^K N_k \ln N_k$$

In the last equation, we utilized the condition on the total number of particles.

To find general distribution, we find maximum of  $\ln \Omega$ , but under given constraints. This can be achieved via the unconstrained maximization of the functional  $\tilde{\Omega} = \ln \Omega + \alpha \left( \sum_i N_i - N \right) + \beta \left( \sum_i E_i N_i - E \right)$ . The extremum condition is:

$$\begin{aligned} \frac{d\tilde{\Omega}}{dN_j} &= \frac{d}{dN_j} \left[ \left( N \ln N - \sum_{k=1}^K N_k \ln N_k \right) + \alpha \left( N - \sum_i N_i \right) + \beta \left( E - \sum_i E_i N_i \right) \right] = \\ &= -(1 + \ln N_j) - \alpha - \beta E_j = 0, \forall j = 1, \dots, K \end{aligned}$$

So, we obtain:

$$\ln N_i = 1 - \alpha - \beta E_i \Rightarrow N_i = A \exp(-\beta E_i)$$

This is, essentially, our main result. The coefficient  $A$  can be found from the normalization condition:

$$\sum_{i=1}^K N_i = N = A \sum_{i=1}^K \exp(-\beta E_i) \Rightarrow A = \frac{N}{\sum_{i=1}^K \exp(-\beta E_i)}$$

Finally,

$$\omega(E_i) = \frac{N_i}{N} = \frac{\exp(-\beta E_i)}{\sum_{j=1}^K \exp(-\beta E_j)}$$

is the probability to find system in the state with energy  $E_i$

This is called a **Maxwell-Boltzmann distribution**.

## 7.4. Gibbs ensembles and distributions

### A. Microcanonical distribution.

This case follows directly from the Liouville theorem:

$$\rho(q, p) = \text{const for } [E, E + dE].$$

Here, the constant value,  $const$ , is of course different for different total energy layers  $[E_i, E_i + dE]$  and  $[E_j, E_j + dE]$ .

Consider the differential of the probability to find a system in a given energy state:

$$d\omega(E) = \rho(q, p) d\Gamma(E) = \rho(q, p) N! h^{3N} \Omega(E) dE,$$

Here  $d\Gamma(E)$  is the phase space volume that corresponds to energy interval  $[E, E + dE]$ ,

$$\Omega(E) = \frac{1}{N! h^{3N}} \frac{d\Gamma(E)}{dE} \text{ is the energy density of states}$$

In other words, for the microcanonical distribution we obtain:

$$d\omega(E) = const \cdot \Omega(E) dE$$

A discrete analog will be:

$$\omega(E_i) = const \cdot \Omega(E_i)$$

With the constant, given from the normalization condition:  $\sum_i \omega(E_i) = 1$ , so:

$$\omega(E_i) = \frac{\Omega(E_i)}{\sum_i \Omega(E_i)} - \text{microcanonical Gibbs distribution.}$$

Example:

Consider computing  $d\Gamma(E)$  for 1 particle:

$$d\Gamma(E) = dq dp = dx \cdot dy \cdot dz \cdot dp_x \cdot dp_y \cdot dp_z = dV \cdot p^2 dp \sin \theta d\theta d\varphi$$

in the last equation, we have switched to polar coordinates.

When integrating over all 6 degrees of freedom, one obtains:

$$\int d\Gamma = \int dV \cdot p^2 dp \sin \theta d\theta d\varphi = 4\pi V \int p^2 dp = \frac{4}{3} \pi p^3 V$$

So, you can see that the phase space volume is equal to the product of the volumes in coordinate (cube or any arbitrary shape of volume  $V$ ) and momentum (sphere) spaces.

Assuming we deal with a free particle, the momentum and total energy are related as:  $E = E_{kin} = \frac{p^2}{2m}$ .

$$\text{So: } \Gamma(E) = \frac{4}{3} \pi (2mE)^{3/2} V$$

Then, we can compute the density of states:

$$\Omega(E) = \frac{1}{h^3} \frac{d\Gamma(E)}{dE} = \frac{1}{h^3} \frac{4}{3} \pi \frac{3}{2} 2m(2mE)^{\frac{1}{2}} EV = \frac{4\pi V m \sqrt{2mE}^{3/2}}{h^3}$$

For a system of N non-interacting particles, we obtain, by analogy:

$$\Omega(E) = \frac{1}{N! h^{3N}} \frac{d\Gamma(E)}{dE} \sim \text{const} \cdot E^{3N/2-1}$$

### ***B. Canonical distribution.***

Consider a system with energy  $E_i$  and the number of particles  $N_i$ . The system of interest is immersed into a bigger system (thermostat) with energy  $E_t$  and the number of particles  $N_t$ , such that:

$$E_i + E_t = E = \text{const}$$

$$N_i + N_t = N = \text{const}$$

We allow energy exchange, between the system and thermostat, but such that  $E_{exch} < E_i \ll E_t$ .

A microcanonical distribution is applicable to the overall system ("system" + thermostat), so we have:

$$\omega(E_i, E_t) = P\{E_{syst} = E_i, E_{thermostat} = E_t\}$$

This expression means – the probability to find the system in a state with energy  $E_i$  and the thermostat in a state with energy  $E_t$ .

Because of the  $E_{exch} < E_i \ll E_t$  condition, the system and thermostat can be considered independent, so:

$$\begin{aligned} \omega(E_i, E_t) &= P\{E_{syst} = E_i, E_{thermostat} = E_t\} = P\{E_{syst} = E_i\} P\{E_{thermostat} = E_t\} = \text{const} \cdot \Omega(E_i) \cdot \Omega(E_t) = \\ &= \text{const} \cdot \Omega(E_i) \cdot \Omega(E - E_i) \end{aligned}$$

Introduce a new function:

$$\sigma(E - E_i) = \ln \Omega(E - E_i)$$

Because of  $E_i \ll E_t$ , we can apply a Taylor expansion in terms of  $E_i$ :

$$\sigma(E - E_i) \approx \sigma(E) - \left( \frac{\partial \sigma}{\partial E} \right)_{E_i=0} E_i + \dots$$

$$\text{So, } \omega(E_i, E_t) = \omega(E_i) = \text{const} \cdot \Omega(E_i) \cdot \exp \left\{ \sigma(E) - \left( \frac{\partial \sigma}{\partial E} \right)_{E_i=0} E_i \right\} = \text{const}' \cdot \Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\}.$$

Here, we dropped the dependence on the energy of thermostat,  $E_t$ , because it is much larger than the energy of the target system.

Here  $\left(\frac{\partial \sigma}{\partial E}\right)_{E_i=0} \equiv \frac{1}{\theta}$ , and  $\theta$  is called **statistical temperature**.

$const'$  can be determined from the normalization conditions, leading to:

$$\omega(E_i) = \frac{\Omega(E_i) \cdot \exp\left\{-\frac{E_i}{\theta}\right\}}{\sum_j \Omega(E_j) \cdot \exp\left\{-\frac{E_j}{\theta}\right\}}$$

This is **canonical Gibbs distribution** – same as Maxwell-Boltzmann distribution

### C. Thermal equilibrium.

Consider two systems, 1 and 2, which are in equilibrium with each other and are statistically independent.

The probability to have energy  $E_{i,1}$  in system 1 is  $\omega(E_{i,1}) = A_1 \Omega(E_{i,1}) \cdot \exp\left(-\frac{E_{i,1}}{\theta_1}\right)$ . Analogously, for the system 2, we have:  $\omega(E_{i,2}) = A_2 \Omega(E_{i,2}) \cdot \exp\left(-\frac{E_{i,2}}{\theta_2}\right)$ .

For the combined system 1+2, we get:

$$\omega(E_i) = A_1 A_2 \Omega(E_{i,1}) \cdot \Omega(E_{i,2}) \cdot \exp\left(-\frac{E_{i,1}}{\theta_1} - \frac{E_{i,2}}{\theta_2}\right) = A \Omega(E_i) \cdot \exp\left(-\frac{E_i}{\theta}\right)$$

Because the number of states in the combined system is just the product of the numbers of states in each sub-system (since 1 and 2 are statistically-independent):

$$\Omega(E_{i,1}) \cdot \Omega(E_{i,2}) = \Omega(E_i)$$

Then, we look at the condition:

$$A_1 A_2 \exp\left(-\frac{E_{i,1}}{\theta_1} - \frac{E_{i,2}}{\theta_2}\right) = A \exp\left(-\frac{E_i}{\theta}\right)$$

If we assume energy additivity,  $E_i = E_{i,1} + E_{i,2}$ , then the above equality can be satisfied only if:

$$\theta = \theta_1 = \theta_2.$$

This is nothing but the 0-th law (postulate) of thermodynamics – thesis about existence of the temperature function that takes the same values for all parts of a system that are in equilibrium with each other. That is why the constant  $\theta$  is called statistical temperature.

Recall the fundamental Gibbs' equation:



$$TdS = dU + pdV - \mu dn$$

From which we obtain:  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,n}$  at the same time, we have:  $\left( \frac{\partial \sigma}{\partial E} \right)_E = \frac{1}{\theta}$ .

One can see the following connections:

$$S = k_B \sigma = k_B \ln \Omega$$

and

$$\theta = k_B T$$

#### **D. Grand canonical distribution.**

The construction is similar as for the canonical one, only we also allow exchange of the particles. Analogously to the canonical situation, the exchange is assumed to be sufficiently small:

$$N_{exch} < N_i \ll N_t.$$

A microcanonical distribution is applicable to the overall system ("system" + thermostat), so we have:

$$\omega(E_i, N_i, E_t, N_t) = P\{E_{syst} = E_i, N_{syst} = N_i, E_{thermostat} = E_t, N_{thermostat} = N_t\}$$

This expression means – the probability to find the system in a state with energy  $E_i$  and number of particles  $N_i$  and the thermostat in a state with energy  $E_t$  and number of particles  $N_t$ .

Because of the  $E_{exch} < E_i \ll E_t$  and  $N_{exch} < N_i \ll N_t$  conditions, the system and thermostat can be considered independent, so:

$$\begin{aligned} \omega(E_i, N_i, E_t, N_t) &= P\{E_{syst} = E_i; N_{syst} = N_i\} P\{E_{thermostat} = E_t; N_{thermostat} = N_t\} = \\ &= const \cdot \Omega(E_i, N_i) \cdot \Omega(E_t, N_t) = const \cdot \Omega(E_i, N_i) \cdot \Omega(E - E_i, N - N_i) \end{aligned}$$

Introduce a new function:

$$\sigma(E - E_i, N - N_i) = \ln \Omega(E - E_i, N - N_i)$$

Because of  $E_i \ll E_t$  and  $N_i \ll N_t$ , we can apply a Taylor expansion in terms of  $E_i$  and  $N_i$ :

$$\sigma(E - E_i) \approx \sigma(E) - \left( \frac{\partial \sigma}{\partial E} \right)_{\substack{E_i=0 \\ N_i=0}} E_i - \left( \frac{\partial \sigma}{\partial N} \right)_{\substack{E_i=0 \\ N_i=0}} N_i \dots$$

So,

$$\omega(E_i, N_i, E_t, N_t) = \omega(E_i, N_i) = \text{const} \cdot \Omega(E_i, N_i) \cdot \exp \left\{ \sigma(E) - \left( \frac{\partial \sigma}{\partial E} \right)_{E_i=0, N_i=0} E_i - \left( \frac{\partial \sigma}{\partial N} \right)_{E_i=0, N_i=0} N_i \right\}$$

$$= \text{const}' \cdot \Omega(E_i, N_i) \cdot \exp \left\{ -\frac{E_i - \mu N_i}{\theta} \right\}$$

Here, we have defined  $\left( \frac{\partial \sigma}{\partial N} \right)_{E_i=0, N_i=0} \equiv -\frac{\mu}{\theta}$  - **chemical potential**

From the normalization, we obtain the distribution:

$$\omega(E_i, N_i) = \frac{\Omega(E_i, N_i) \cdot \exp \left\{ -\frac{E_i - \mu N_i}{\theta} \right\}}{\sum_{E_i, N_i} \Omega(E_i, N_i) \cdot \exp \left\{ -\frac{E_i - \mu N_i}{\theta} \right\}} \quad \text{- grand canonical distribution}$$

### 7.5. Partition function and its relationship with thermodynamic functions.

In the above derivations, we utilized:

$$Z = \sum_{E_i} \Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\} \quad \text{canonical partition function}$$

$$\tilde{Z} = \sum_{E_i, N_i} \Omega(E_i, N_i) \cdot \exp \left\{ -\frac{E_i - \mu N_i}{\theta} \right\} \quad \text{grand canonical partition function}$$

Important: The partition function is defined up to a multiplicative factor. The factor is related to the choice of the zero energy level. Indeed, if all energy levels are shifted by a constant value:  $E_i \rightarrow E_i + \varepsilon$ , the partition function changes as:  $Z \rightarrow Z \cdot \exp \left( -\frac{\varepsilon}{\theta} \right)$ . It is common to choose energy levels such that zero on the energy scale corresponds to energy of the system at absolute zero,  $U_0$

$$1. \text{ Internal energy: } U - U_0 = \langle E \rangle \equiv \sum_i E_i \omega(E_i) = \theta^2 \frac{\partial \ln Z}{\partial \theta} = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

Proof:

$$\begin{aligned} \theta^2 \frac{\partial \ln Z}{\partial \theta} &= \theta^2 \frac{1}{Z} \frac{\partial Z}{\partial \theta} = \theta^2 \frac{1}{Z} \frac{\partial}{\partial \theta} \left[ \sum_i \Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\} \right] = \theta^2 \frac{1}{Z} \left[ \sum_i \frac{E_i}{\theta^2} \Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\} \right] = \\ &= \frac{1}{Z} \sum_i E_i \Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\} = \sum_i E_i \frac{\Omega(E_i) \cdot \exp \left\{ -\frac{E_i}{\theta} \right\}}{Z} = \sum_i E_i \omega(E_i) = \langle E \rangle \end{aligned}$$

2. **Average number of particles:**  $\langle N \rangle \equiv \sum_{i,N} N \omega(E_i, N) = \theta \frac{\partial \ln \tilde{Z}}{\partial \mu}$

Proof:

$$\begin{aligned} \theta \frac{\partial \ln \tilde{Z}}{\partial \mu} &= \theta \frac{1}{\tilde{Z}} \frac{\partial \tilde{Z}}{\partial \mu} = \theta \frac{1}{\tilde{Z}} \frac{\partial}{\partial \mu} \left[ \sum_{i,N} \Omega(E_i, N) \cdot \exp \left\{ -\frac{E_i - \mu N}{\theta} \right\} \right] = \theta \frac{1}{\tilde{Z}} \left[ \sum_{i,N} \frac{N}{\theta} \Omega(E_i, N) \cdot \exp \left\{ -\frac{E_i - \mu N}{\theta} \right\} \right] = \\ &= \frac{1}{\tilde{Z}} \sum_{i,N} N \Omega(E_i, N) \cdot \exp \left\{ -\frac{E_i - \mu N}{\theta} \right\} = \sum_{i,N} N \frac{\Omega(E_i, N) \cdot \exp \left\{ -\frac{E_i - \mu N}{\theta} \right\}}{\tilde{Z}} = \sum_{i,N} N \omega(E_i, N) = \langle N \rangle \end{aligned}$$

3. **Helmholtz free energy:**  $F - U_0 = -k_B T \ln Z$

Proof: In phenomenological thermodynamics, we have derived equation  $\frac{\partial}{\partial T} \left( \frac{F}{T} \right) = -\frac{U}{T^2}$

Using the first expression, we get:

$$\frac{\partial}{\partial T} \left( \frac{F}{T} \right) = -\frac{U}{T^2} = -k_B \frac{\partial \ln Z}{\partial T} = \frac{\partial}{\partial T} (-k_B \ln Z) \Rightarrow \frac{F}{T} = \frac{U_0}{T} - k_B \ln Z$$

from which we immediately obtain the main result

4. **Entropy:**  $S = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T}$

Proof: This results follows from simple algebra and relationships between thermodynamics functions

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T}$$

5. **Pressure:**  $P = - \left( \frac{\partial F}{\partial V} \right)_T = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_T$

One can use relationships between thermodynamic variables to derive all other relationships.

## 7.6. Calculation of molecular partition function.

### A. General formulation

The total partition function of N particles can be represented as:

$$Z = \frac{Z_{mol}^N}{N!} Z_{conf}$$

Here, N! accounts for the quantum-mechanical indistinguishability of particles,

$Z_{mol}$  - is the **molecular partition function** (for a single particle, in the ideal gas approximation): accounts for internal degrees of freedom of each independent particle

$$Z_{conf} = \int \dots \int \exp\left(-\frac{U(q_1, q_2, \dots, q_N)}{k_B T}\right) dq_1 dq_2 \dots dq_N - \text{configurational integral} - \text{accounts for interactions}$$

between particles of the gas (real gases)

The total energy of each particle can be represented as a sum of various contributions:

$$E = E_{tr} + E_{vib} + E_{rot} + E_{el} + E_{spin} + E_{nucl}$$

Correspondingly, the molecular partition function factorizes:

$$Z_{mol} = Z_{tr} \cdot Z_{vib} \cdot Z_{rot} \cdot Z_{el} \cdot Z_{spin} \cdot Z_{nucl}$$

### B. Computing the configurational integral

$$Z_{conf} = \int \dots \int \exp\left(-\frac{U(q_1, q_2, \dots, q_N)}{k_B T}\right) dq_1 dq_2 \dots dq_N$$

Each spatial coordinate is 3-dimensional, so the overall integral is 6N-dimensional.

Assume pair-wise interactions:

$$\begin{aligned} \exp\left(-\frac{U(q_1, q_2, \dots, q_N)}{k_B T}\right) &= \exp\left(-\frac{1}{k_B T} \sum_{\substack{i,j \\ i < j}} U(r_{ij})\right) = \prod_{\substack{i,j \\ i < j}} \exp\left(-\frac{U(r_{ij})}{k_B T}\right) = \prod_{\substack{i,j \\ i < j}} (1 + f_{ij}) = \\ &= 1 + \sum_{\substack{i,j \\ i < j}} f_{ij} + \sum_{\substack{i,j,i < j \\ k,l,k < l}} f_{ij} f_{kl} + \dots \end{aligned}$$

Definition: Mayer's function  $f_{ij} = f(r_{ij}) = \exp\left(-\frac{U(r_{ij})}{k_B T}\right) - 1$

Then

$$\begin{aligned}
Z_{conf} &\approx \int \dots \int \left[ 1 + \sum_{i,j,i < j} f_{ij} \right] dq_1 dq_2 \dots dq_N = V^N + V^{N-2} \sum_{i,j,i < j} \int f_{ij} dq_i dq_j = \\
&= V^N + V^{N-2} \frac{N^2}{2} \int f_{12} dq_1 dq_2 = V^N + V^{N-2} \frac{N^2}{2} 4\pi V \int_0^\infty f(r) r^2 dr = V^N \left( 1 + \frac{N^2}{2V} \beta \right)
\end{aligned}$$

Where  $\beta \equiv 4\pi \int_0^\infty f(r) r^2 dr$

Consider computing  $\beta$  using the hard spheres potential:

$$U(r) = \begin{cases} \infty, & r \in [0, 2R] \\ < 0, & r > 2R \end{cases}$$

$$\begin{aligned}
\beta &\equiv 4\pi \int_0^\infty f(r) r^2 dr = 4\pi \int_0^{2R} f(r) r^2 dr + 4\pi \int_{2R}^\infty f(r) r^2 dr = 4\pi \int_0^{2R} -r^2 dr + 4\pi \int_{2R}^\infty \left[ \exp\left(-\frac{U(r)}{k_B T}\right) - 1 \right] r^2 dr = \\
&\approx -4\pi \frac{r^3}{3} \Big|_0^{2R} + 4\pi \int_{2R}^\infty \left[ -\frac{U(r)}{k_B T} \right] r^2 dr = -\frac{32\pi R^3}{3} - \frac{4\pi}{k_B T} \int_{2R}^\infty U(r) r^2 dr
\end{aligned}$$

### C. Computing the electronic partition function

$$Z_{el} = \sum_i g_i \exp\left(-\frac{\epsilon_i^{el}}{k_B T}\right) = \exp\left(-\frac{\epsilon_0^{el}}{k_B T}\right) \sum_i g_i \exp\left(-\frac{\epsilon_i^{el} - \epsilon_0^{el}}{k_B T}\right) = q_0 Q$$

Here,  $Q = \sum_i g_i \exp\left(-\frac{\epsilon_i^{el} - \epsilon_0^{el}}{k_B T}\right)$  is **practical partition function**.

We can compute it, because we know all the energy gaps,  $\epsilon_i^{el} - \epsilon_0^{el}$ , but the electronic energy of the ground state can vary depending on chosen conventions.

$g_i$  are the degeneracies of electronic states.

Since the electronic energy levels are usually well separated from the ground state level, the electronic partition function (practical) is just the degeneracy of the ground electronic state.

Exceptions:

- Metals (gaps are small)
- High temperature

### D. Computing translational partition function

$$\begin{aligned}
Z &= \int \exp\left(-\frac{E}{k_B T}\right) \Omega(E) dE = \int \exp\left(-\frac{p^2}{2mk_B T}\right) \frac{d\Gamma(p)}{h^3} = \\
&= \int \exp\left(-\frac{p^2}{2mk_B T}\right) \frac{dV \cdot p^2 dp \sin \theta d\theta d\varphi}{h^3} = \frac{4\pi V}{h^3} \int_0^\infty p^2 \exp\left(-\frac{p^2}{2mk_B T}\right) dp = \\
&= V \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2}
\end{aligned}$$

Here, we utilized the integral

$$I_{2n} = \int_{-\infty}^{+\infty} \exp(-\alpha x^2) x^{2n} dx = \frac{(2n-1)(2n-3)\dots 3 \cdot 1}{2^n} \sqrt{\frac{\pi}{\alpha^{2n+1}}}$$

### E. Computing vibrational partition function

Harmonic oscillator model:  $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2$ , where  $\omega = \sqrt{\frac{k}{m}}$  vibrational frequency,

yields the energy levels:  $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ .

The energy of the ground state is chosen to be zero (consider it absorbed into the  $q_0$  term when splitting the partition function into the practical one and the gauge term). Then,

$$Z_{vib} = \sum_{n=0}^{\infty} \exp(\hbar\omega n) = x = \exp(\hbar\omega) = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} = \left(1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right)^{-1}$$

Real N-atomic molecule contains 3N-6 vibrations (3N-5 in linear molecule). Frequencies of all modes may be different, so the resulting molecular vibrational partition energy will be a product of the contributions from all modes:

$$Z_{vib} = \prod_{i=1}^{3N-6(5)} \left(1 - \exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right)^{-1}$$

### F. Computing rotational partition function

Rigid rotor model yields rotational energy levels:  $E_J = \frac{h^2}{8\pi^2 I} J(J+1) = BhJ(J+1)$ , where  $B = \frac{h^2}{8\pi^2 I}$  is a rotational constant,  $I$  is the component of the inertia tensor.

The degeneracies of the levels are:  $g_J = 2J + 1$

Thus,

$$Z = \frac{1}{\sigma} \sum_J (2J+1) \exp\left(-\frac{Bh}{k_B T} J(J+1)\right) = \frac{1}{\sigma} \sum_J (2J+1) \exp\left(-\frac{T_R}{T} J(J+1)\right)$$

$$T_R = \frac{Bh}{k_B} \text{ effective rotational temperature.}$$

$\sigma$  symmetry number (e.g. H-Cl = 1, Cl-Cl = 2, NH<sub>3</sub> = 3, etc.)

There are two main cases:

**Classical:**  $T \gg T_R$ , then the summation can be replaced by the integration:

$$\begin{aligned} Z &= \frac{1}{\sigma} \sum_J (2J+1) \exp\left(-\frac{T_R}{T} J(J+1)\right) \rightarrow Z = \frac{1}{\sigma} \int_0^\infty (2J+1) \exp\left(-\frac{T_R}{T} J(J+1)\right) dJ = \\ &= \frac{1}{\sigma} \int_0^\infty d(J(J+1)) \exp\left(-\frac{T_R}{T} J(J+1)\right) = -\frac{1}{\sigma} \frac{T}{T_R} \int_0^\infty d\left(-\frac{T_R}{T} J(J+1)\right) \exp\left(-\frac{T_R}{T} J(J+1)\right) = \\ &= -\exp\left(-\frac{T_R}{T} J(J+1)\right) \Big|_0^\infty \frac{1}{\sigma} \frac{T}{T_R} = \frac{1}{\sigma} \frac{T}{T_R} = \frac{1}{\sigma} \frac{k_B T}{Bh} \end{aligned}$$

**Quantum:**  $T \sim T_R$  - explicit summation