

Gibbs classical statistical mechanics II

Applications of canonical ensemble

Up to now the Gibbs statistical mechanics has been applied only to the ideal gas. Let us now discuss two simple though nontrivial applications.

Real gases

- Since the Hamilton function reads

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{\substack{i,j=1 \\ i < j}}^N v_{ij}(\mathbf{r}_i - \mathbf{r}_j), \quad (1)$$

where v_{ij} is the potential energy due to interaction i -th and j -th particles. The partition function equals

$$Q_N(T, V) \equiv \frac{1}{N!} \int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \exp\left[-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T}\right] = \frac{1}{N!} \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{\frac{3N}{2}} Z_N. \quad (2)$$

The momentum integrals are performed as in case of the ideal gas and the configuration integral Z_N is

$$Z_N \equiv \int d^3r_1 d^3r_2 \dots d^3r_N \exp\left[-\beta \sum_{\substack{i,j=1 \\ i < j}}^N v_{ij}(\mathbf{r}_i - \mathbf{r}_j)\right], \quad (3)$$

where $\beta \equiv \frac{1}{k_B T}$.

- Using the notation

$$e^{-\beta v_{ij}(\mathbf{r}_i - \mathbf{r}_j)} \equiv 1 + f_{ij}(\mathbf{r}_i - \mathbf{r}_j), \quad (4)$$

we write down

$$\exp\left[-\beta \sum_{\substack{i,j=1 \\ i < j}}^N v_{ij}(\mathbf{r}_i - \mathbf{r}_j)\right] = \prod_{\substack{i,j=1 \\ i < j}}^N (1 + f_{ij}(\mathbf{r}_i - \mathbf{r}_j)). \quad (5)$$

- The gas under consideration is assumed to be weakly non-ideal that is it is sufficiently hot and dilute. Consequently, the average potential energy of a molecule is much smaller than the kinetic energy

$$k_B T \gg \langle v_{ij} \rangle. \quad (6)$$

Therefore

$$\exp\left[-\beta \sum_{\substack{i,j=1 \\ i < j}}^N v_{ij}(\mathbf{r}_i - \mathbf{r}_j)\right] \approx 1 + \sum_{\substack{i,j=1 \\ i < j}}^N f_{ij}(\mathbf{r}_i - \mathbf{r}_j). \quad (7)$$

- The expression (7) substituted into (3) gives

$$\begin{aligned}
 Z_N &= \int d^3r_1 d^3r_2 \dots d^3r_N \left(1 + \sum_{\substack{i,j=1 \\ i < j}}^N f_{ij}(\mathbf{r}_i - \mathbf{r}_j) \right) \\
 &= V^N + V^{N-2} \sum_{\substack{i,j=1 \\ i < j}}^N \int d^3r_i d^3r_j f_{ij}(\mathbf{r}_i - \mathbf{r}_j) \\
 &= V^N + \frac{N(N-1)}{2} V^{N-2} \int d^3r_1 d^3r_2 f_{12}(\mathbf{r}_1 - \mathbf{r}_2). \tag{8}
 \end{aligned}$$

- One introduces the center-of-mass and relative coordinates of the molecules 1 and 2

$$\mathbf{R} \equiv \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 \tag{9}$$

and obtains

$$Z_N = V^N + \frac{N^2}{2} V^{N-1} \int d^3r f(\mathbf{r}), \tag{10}$$

where $N(N-1) \approx N^2$ and the indices 1 and 2 are dropped.

- The partition function (2) thus equals

$$Q_N(T, V) = Q_N^0(T, V) \left(1 + \frac{N^2}{2V} \int d^3r f(\mathbf{r}) \right), \tag{11}$$

where

$$Q_N^0(T, V) = \frac{V^N}{N!} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3N}{2}} \tag{12}$$

is the ideal-gas partition function.

- The potential is assumed to be spherically symmetric and then

$$\int d^3r f(\mathbf{r}) = 4\pi \int_0^\infty dr r^2 (e^{-\beta v(r)} - 1). \tag{13}$$

- Fig 1 shows a typical inter-molecular potential which is strongly repulsive at small distances and attractive at bigger ones. We assume that $\beta v(r) \gg 1$ for $r < r_c$ and $|\beta v(r)| \ll 1$ for $r > r_c$. Then,

$$e^{-\beta v(r)} - 1 \approx \begin{cases} -1 & \text{for } r < r_c, \\ -\beta v(r) & \text{for } r > r_c, \end{cases} \tag{14}$$

and

$$\int d^3r f(\mathbf{r}) = -\frac{4\pi}{3} r_c^3 + 4\pi\beta\alpha, \tag{15}$$

where the (positive) parameter α equals

$$\alpha \equiv \int_{r_c}^\infty dr r^2 |v(r)|. \tag{16}$$

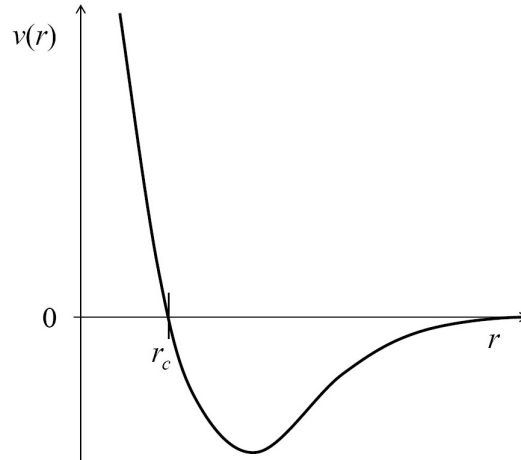


Figure 1: Typical shape of inter-molecular potential

- With the result (15) the partition function (11) becomes

$$Q_N(T, V) = Q_N^0(T, V) \left[1 + \frac{N^2}{V} \left(-\frac{2\pi r_c^3}{3} + \frac{2\pi\alpha}{k_B T} \right) \right]. \quad (17)$$

The second term in the square bracket is only a small correction – it is much smaller than unity.

- The free energy is

$$F(T, V) \equiv -k_B T \ln Q_N(T, V) = F^0(T, V) + \frac{2\pi r_c^3}{3} \frac{k_B T N^2}{V} - 2\pi\alpha \frac{N^2}{V}, \quad (18)$$

where $F^0(T, V)$ is the free energy of the ideal gas. We have used here the approximation $\ln(1+x) \approx x$ which holds for $|x| \ll 1$.

- The gas internal energy is found in the following way. The definition of $F \equiv U - TS$ gives $U = F + TS$. Since $dF = dU - TdS - SdT = dQ - pdV - TdS - SdT = -pdV - SdT$ and

$$S = -T \left(\frac{\partial F}{\partial T} \right)_V, \quad (19)$$

and

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V. \quad (20)$$

- Using the result (18) we get

$$U = \frac{3}{2} N k_B T - 2\pi\alpha \frac{N^2}{V}. \quad (21)$$

The repulsive interaction plays no role here.

- The pressure is

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} + \frac{2\pi r_c^3}{3} \frac{k_B T N^2}{V^2} - 2\pi\alpha \frac{N^2}{V^2}. \quad (22)$$

As seen, the repulsive (attractive) interaction increases (decreases) the pressure.

- Let us confront the result (22) with the well-known van der Waals equation of state

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = N k_B T, \quad (23)$$

where the parameters a & b characterize the gas. The van der Waals pressure is

$$p = \frac{Nk_B T}{V - Nb} - a \frac{N^2}{V^2} \approx \frac{Nk_B T}{V} - a \frac{N^2}{V^2} + b \frac{k_B T N^2}{V^2}, \quad (24)$$

where the approximate equality holds under the assumption that the ‘excluded volume effect’ is only a small correction.

- Comparing the pressures (22) and (24) we get

$$a = 2\pi\alpha, \quad b = \frac{2\pi}{3} r_c^3. \quad (25)$$

We have achieved the goal of statistical mechanics – the phenomenological parameters a and b are expressed through the microscopic quantities α and r_c .

- The method to obtain the partition function of a real gas can be systematically improved by going beyond the linear terms in f in Eq. (7). Then we get the *cluster expansion* with the gas density $\rho \equiv N/V$ as a small parameter.

Classical model of a crystal

- A crystal is treated as a system of N independent harmonic oscillators of the Hamiltonian function

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} + \frac{\chi}{2} (\mathbf{a}_i - \mathbf{r}_i)^2 \right), \quad (26)$$

where χ is the Young or elasticity modulus and \mathbf{a}_i the equilibrium position of the i -th atom.

- The partition function is

$$Q_N(T, V) = \int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \exp \left[-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p})}{k_B T} \right] = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3N}{2}} Z_N, \quad (27)$$

where the factor $1/N!$ is not included as the atoms are distinguishable due to their positions in a crystal lattice. The momentum integrals are computed as in the case of ideal gas and the configuration integral equals

$$Z_N = \prod_{i=1}^N \int d^3r_i \exp \left(-\frac{\beta\chi}{2} (\mathbf{a}_i - \mathbf{r}_i)^2 \right). \quad (28)$$

- Using the coordinates $\mathbf{q}_i \equiv \mathbf{r}_i - \mathbf{a}_i$, one finds

$$Z_N = \left[\int_{-\infty}^{\infty} dq \exp \left(-\frac{\beta\chi}{2} q^2 \right) \right]^{3N} = \left(\frac{2\pi k_B T}{\chi} \right)^{\frac{3N}{2}}, \quad (29)$$

and

$$Q_N(T, V) = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3N}{2}} \left(\frac{2\pi k_B T}{\chi} \right)^{\frac{3N}{2}} = \left(\frac{k_B T}{\hbar} \sqrt{\frac{m}{\chi}} \right)^{3N}. \quad (30)$$

- The crystal's energy equals

$$U = -\frac{\partial}{\partial \beta} \ln Q_N(T, V) = 3Nk_B T, \quad (31)$$

which gives the heat capacity as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk_B. \quad (32)$$

One sees that the heat capacity of a given amount of substance is two times bigger when it is in the crystalline than in the gas form. This is the well-known Dulong-Petit law