Problem Set
Virial expansion in the grand-canonical ensemble

In this Problem, we aim at describing a classical fluid consisting of N particles with mass m occupying a volume V at the temperature T. Let $\mathbf{r}_i$ and $\mathbf{p}_i$ be, respectively, the position and momentum of the i^{th} particle. We assume that the particles are interacting through a pair potential, so that the full Hamiltonian of the system reads

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \mathcal{T}(\mathbf{p}^N) + U(\mathbf{r}^N),$$

with

$$\mathcal{T}(\mathbf{p}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \qquad \text{and} \qquad U(\mathbf{r}^N) = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} u\left(r_{ij}\right),$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here, $\mathbf{r}^N$ and $\mathbf{p}^N$ are, respectively, a compact notation for $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$.

1 Appetizer

(a) Comment on the physical meaning of each term of the Hamiltonian above. Sketch the typical shape of the pair potential $u(r)$ in the case of a van der Waals fluid.

(b) Carefully justify that the canonical partition function reads

$$Z(N) = \frac{1}{N!\Lambda_T^{3N}} \int \mathrm{d}^3\mathbf{r}_1 \ldots \mathrm{d}^3\mathbf{r}_N \; \mathrm{e}^{-\beta U(\mathbf{r}^N)},$$

with $\Lambda_T = \sqrt{2\pi\hbar^2/mk_\mathrm{B}T}$ and where $\beta = 1/k_\mathrm{B}T$.[1] What is the dimension of Λ_T? What is its physical meaning?

2 The ideal gas case

In this part of the Problem, we consider the case of an ideal gas and we denote by $Z^{\mathrm{IG}}(N)$ the corresponding partition function.

(a) Calculate $Z^{\mathrm{IG}}(N)$.

(b) Deduce from the preceding question the equation of state of the ideal gas.

3 Virial expansion in the grand-canonical ensemble

In this third part of the problem we wish to go beyond the ideal gas approximation, and expand the pressure P of the system in powers of the fluid density ρ as

$$\frac{P}{k_\mathrm{B}T} = \sum_{n=1}^{\infty} B_n(T)\rho^n. \tag{1}$$

The quantity $B_n(T)$ is called the n^{th} virial coefficient, and it depends only on temperature and on the particular gas under consideration. The aim of the present part of the Problem is to determine the three first virial coefficients $B_1(T)$, $B_2(T)$, and $B_3(T)$. To this end, it is convenient to work within the grand-canonical ensemble.

[1] Note that $\int_{-\infty}^{+\infty} \mathrm{d}x \; \mathrm{e}^{-x^2} = \sqrt{\pi}$. Proof?

(a) Demonstrate that the grand-canonical partition function $\Xi(\mu)$ can be expressed as

$$\Xi(\mu) = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N}\, Z(N),$$

where $Z(N)$ is the N-body canonical partition function.

(b) Using the results above, and defining $z = \mathrm{e}^{\beta\mu}/\Lambda_T^3$, show that the grand-canonical partition function can be written as an expansion in powers of z,

$$\Xi(\mu) = 1 + \sum_{N=1}^{\infty} \frac{I_N}{N!} z^N,$$

where we have introduced the integral

$$I_N = \int \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 \ldots \mathrm{d}^3\mathbf{r}_N\, \mathrm{e}^{-\beta U(\mathbf{r}^N)}.$$

(c) Note that, obviously, $U(\mathbf{r}^N) = 0$ for $N = 1$. Show then that I_1 has a very simple expression in terms of the volume V.

(d) Notice that, in practice, the N-body potential only depends on the $N-1$ relative coordinates $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ of the particles. Carefully justify that for $N \geqslant 2$,

$$I_N = V \int \mathrm{d}^3\mathbf{r}_{12} \ldots \mathrm{d}^3\mathbf{r}_{1N} \prod_{i<j} \left[1 + f(r_{ij})\right],$$

where we have introduced the Mayer function

$$f(r) = \mathrm{e}^{-\beta u(r)} - 1. \tag{2}$$

(e) Using Euler's relation $\Omega = -PV$, with Ω the grand-potential, show that the pressure can be expressed as a power series in z,

$$P = \frac{k_{\mathrm{B}}T}{V} \sum_{N=1}^{\infty} \frac{J_N}{N!} z^N, \tag{3}$$

where we have introduced the coefficients J_N which have the same dimension as the I_N's.[2] In particular, show that

$$J_1 = I_1, \qquad J_2 = I_2 - I_1^2, \qquad J_3 = I_3 - 3I_1I_2 + 2I_1^3.$$

(f) Show that the average density of particles can be written as $\rho = \partial P/\partial\mu$. Use this result to express ρ as a power series in z:

$$\rho = \frac{1}{V} \sum_{N=1}^{\infty} \frac{J_N}{(N-1)!} z^N. \tag{4}$$

(g) We now have to eliminate z in favor of ρ in Eq. (3) in order to obtain the equation of state. To do so, we notice that Eq. (4) suggests that z is a function of ρ, such that $z = \sum_{m=1}^{\infty} C_m \rho^m$. Deduce from the above considerations that

$$z = \rho - \frac{J_2}{V}\rho^2 + \left(\frac{2J_2^2}{V^2} - \frac{J_3}{2V}\right)\rho^3 + \mathcal{O}(\rho^4).$$

[2] Notice that $\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n-1} x^n/n$.

(h) Use the results above in order to obtain the equation of state as a power series of the density ρ up to order ρ^3 [see Eq. (1)]. In particular, show that the three first virial coefficients read

$$B_1 = 1, \qquad B_2 = \frac{1}{2}\left(V - \frac{I_2}{V}\right), \qquad B_3 = \frac{V^2}{3} - I_2 + \left(\frac{I_2}{V}\right)^2 - \frac{I_3}{3V}.$$

(i) Show that

$$B_2 = -\frac{1}{2}\int \mathrm{d}^3\mathbf{r}\, f(r),$$
$$B_3 = -\frac{1}{3}\int \mathrm{d}^3\mathbf{r}\mathrm{d}^3\mathbf{r}'\, f(r)f(r')f(|\mathbf{r}-\mathbf{r}'|).$$

4 Hard sphere gas

In this last part of the Problem, we consider that the particles correspond to spheres with a diameter a. We assume that such particles interact via a hard-wall potential, which forbids two particles to overlap.

(a) Sketch the hard-wall potential $u(r)$ and the resulting Mayer function $f(r)$ defined in Eq. (2).

(b) Calculate the coefficient B_2 of the hard sphere gas.

(c) Determining the third virial coefficient B_3 is somewhat harder. In order to achieve this, we introduce the Fourier transform $\tilde{g}(\mathbf{q})$ of a function $g(\mathbf{r})$ as

$$\tilde{g}(\mathbf{q}) = \int \mathrm{d}^3\mathbf{r}\ \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}} g(\mathbf{r}),$$

while the inverse transform reads

$$g(\mathbf{r}) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3\mathbf{q}\ \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\tilde{g}(\mathbf{q}).$$

We recall that

$$\int \mathrm{d}^3\mathbf{r}\ \mathrm{e}^{\mathrm{i}(\mathbf{q}-\mathbf{q}')\cdot\mathbf{r}} = (2\pi)^3\,\delta\left(\mathbf{q}-\mathbf{q}'\right),$$
$$\int \mathrm{d}^3\mathbf{q}\ \mathrm{e}^{-\mathrm{i}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{q}} = (2\pi)^3\,\delta\left(\mathbf{r}-\mathbf{r}'\right).$$

(i) Show that the Fourier transform $\tilde{f}(\mathbf{q})$ of the Mayer function (2) only depends on the modulus of $\mathbf{q}$, $|\mathbf{q}| = q$, and reads

$$\tilde{f}(q) = \frac{4\pi}{q}\int_0^\infty \mathrm{d}r\ r\sin(qr)f(r).$$

(ii) Show that

$$B_3 = -\frac{1}{3}\int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}\,\tilde{f}(q)^3.$$

(iii) One defines the Bessel function of the first kind $J_{3/2}(x)$ as

$$J_{3/2}(x) = \sqrt{\frac{2}{\pi x}}\left(\frac{\sin x}{x} - \cos x\right),$$

and we give the integral

$$\int_0^\infty \mathrm{d}x\, x^{-5/2} J_{3/2}(x)^3 = \frac{5}{48\sqrt{2\pi}}.$$

Show that the third virial coefficient of the hard sphere gas is given by

$$B_3 = \frac{5}{18}\pi^2 a^6.$$