PHY304 - Statistical Mechanics

Spring 2021, IISER Mohali

Instructor: Dr. Anosh Joseph

PHY304: Homework 4 Solutions

Due: Monday, February 22, 2021 at 11:00pm.

(Upload your solutions to Moodle as a single `.pdf` file.)

---

1. Consider N massless particles of relativistic ideal gas in a volume V. Calculate the following:

   (a.) Canonical partition function Z.

   (b.) Internal energy $U \equiv U(T, V, N)$.

   (c.) Pressure p.

   (d.) Free energy $F \equiv F(T, V, N)$.

   (e.) Entropy $S \equiv S(T, V, N)$.

Solution:

(a.) We have the kinetic energy

$$K = \sqrt{p^2c^2 + m^2c^4} = cp. \tag{1}$$

the Hamiltonian

$$H(q_\nu, p_\nu) = \sum_{i=1}^{N} cp_i. \tag{2}$$

The partition function is

$$\begin{aligned} Z &= \frac{1}{N!h^{3N}} \int d^{3N}q \int d^{3N}p \; e^{-\beta H(q,p)} \\ &= \frac{V^N}{N!h^{3N}} \left[\int d^3 p e^{-\beta cp} \right]^N . \end{aligned} \tag{3}$$

We have

$$\begin{aligned}\int d^3p\ e^{-\beta cp} &= 4pi \int_0^\infty dp\ p^2\ e^{-\beta cp} \\ &= \frac{4\pi}{(\beta c)^3}\int_0^\infty du\ u^2\ e^{-u} \\ &= \frac{4\pi}{(\beta c)^3}\Gamma(3) = \frac{8\pi}{(\beta c)^3}. \qquad (4)\end{aligned}$$

Thus the partition function becomes

$$Z = \frac{1}{N!}\left[\frac{8\pi V}{(\beta ch)^3}\right]^N. \qquad (5)$$

(b.) Internal energy $U(T,V,N)$ is

$$U = -\frac{\partial}{\partial\beta}\ln Z = 3N\frac{1}{\beta} = 3Nk_BT. \qquad (6)$$

(c.) We have

$$\begin{aligned}p &= \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z \\ &= \frac{1}{\beta}\frac{N}{V} = \frac{1}{3}\frac{U}{V}. \qquad (7)\end{aligned}$$

(d.) The free energy

$$F = -\frac{1}{\beta}\ln Z. \qquad (8)$$

Upon using the Stirling's formula, it becomes

$$F = -Nk_BT\left\{\ln\left(\frac{8\pi V}{(ch)^3}\right) + 3\ln k_BT - \ln N + 1\right\}. \qquad (9)$$

(e.) Entropy S is

$$\begin{aligned}S &= -\left(\frac{\partial F}{\partial T}\right)\Bigg|_{V,N} \\ &= Nk_B\left\{\ln\frac{V}{N} + \ln\frac{8\pi}{(ch)^3} + 3\ln k_BT + 4\right\}. \qquad (10)\end{aligned}$$

■

2. Consider N number of classical non-interacting particles moving inside a volume V. They have the potential energy

$$V(q_\nu) = g \sum_{k=1}^{N} \left(q_{ix}^4 + q_{iy}^4 + q_{iz}^4 \right), \tag{11}$$

with g denoting a positive constant.

Compute the internal energy $U \equiv U(T, V, N)$ of this system.

Hint: You may use

$$\int_0^\infty e^{-x^n} dx = \Gamma(1 + \frac{1}{n}). \tag{12}$$

Solution:

We have the Hamiltonian

$$\begin{aligned} H &= H(q_\nu, p_\nu) \\ &= \sum_{k=1}^{N} \frac{1}{2m} \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \right) + g \sum_{k=1}^{N} \left(q_{ix}^4 + q_{iy}^4 + q_{iz}^4 \right). \end{aligned} \tag{13}$$

The partition function is

$$Z = \frac{1}{h^{3N} N!} \int d^{3N} q \int d^{3N} p e^{-\beta H(q_\nu, p_\nu)}. \tag{14}$$

Since the particles are non-interacting we can separate the position and momentum integrals.

$$Z = Z_q \cdot Z_p. \tag{15}$$

We have

$$\begin{aligned} Z_q &= \int_{-\infty}^{\infty} dq_1 \cdots \int_{-\infty}^{\infty} dq_{3N} \exp\left(-\beta g [q_1^4 + \cdots + q_{3N}^4]\right) \\ &= \left(\int_{-\infty}^{\infty} dq_k \exp\left(-\beta g q_k^4\right) \right)^{3N}. \end{aligned} \tag{16}$$

We have

$$\int_0^\infty e^{-x^n}dx = \Gamma(1+\frac{1}{n}). \tag{17}$$

$$\begin{aligned} Z_q &= \left(\int_{-\infty}^{\infty} dq_k \exp\left(-\beta g q_k^4\right)\right)^{3N} \\ &= 2^{3N}\left(\int_0^\infty du \exp\left(-\beta g u^4\right)\right)^{3N}. \end{aligned} \tag{18}$$

In the above we used $u = q_k$ and the symmetric nature of the integrand under the sign change.

Defining $x = (\beta g)^{1/4}u$, we have $du = \frac{dx}{(\beta g)^{1/4}}$ we have

$$\begin{aligned} Z_q &= 2^{3N}\frac{1}{(\beta g)^{3N/4}}\left(\int_0^\infty dx\ e^{-x^4}\right)^{3N} \\ &= 2^{3N}\frac{1}{(\beta g)^{3N/4}}\left(\Gamma\left(1+\frac{1}{4}\right)\right)^{3N} \\ &= 2^{3N}\frac{1}{(\beta g)^{3N/4}}\left(\Gamma(5/4)\right)^{3N} \\ &= \left[\frac{2\Gamma(5/4)}{(\beta g)^{1/4}}\right]^{3N}. \end{aligned} \tag{19}$$

We have

$$\begin{aligned} Z_p &= \frac{1}{h^{3N}N!}\int_{-\infty}^{\infty}dp_1\int_{-\infty}^{\infty}dp_2\cdots\int_{-\infty}^{\infty}dp_{3N}\exp\left(-\frac{\beta}{2m}[p_1^2+\cdots+p_{3N}^2]\right) \\ &= \frac{1}{h^{3N}N!}\left(\int_{-\infty}^{\infty}dp_k e^{-\frac{\beta}{2m}p_k^2}\right)^{3N} \\ &= \frac{1}{h^{3N}N!}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3N} \\ &= \frac{1}{\lambda^{3N}N!}, \end{aligned} \tag{20}$$

where λ is the thermal wavelength.

Thus the partition function is

$$\begin{aligned} Z &= Z_q \cdot Z_p \\ &= \left[\frac{2\Gamma(5/4)}{(\beta g)^{1/4}}\right]^{3N} \cdot \frac{1}{\lambda^{3N} N!} \\ &= \frac{1}{N!}\left[\frac{2\Gamma(5/4)}{\lambda(\beta g)^{1/4}}\right]^{3N}. \end{aligned} \tag{21}$$

The internal energy is

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\ln Z \\ &= -\frac{\partial}{\partial\beta}\ \ln\frac{1}{N!}\left[\frac{2\Gamma(5/4)}{\lambda(\beta g)^{1/4}}\right]^{3N} \\ &= -\frac{\partial}{\partial\beta}\ \ln\left[\frac{1}{\lambda}\frac{1}{\beta^{1/4}}\right]^{3N} \\ &= -\frac{\partial}{\partial\beta}\ \ln\left[\frac{1}{\beta^{1/2}\beta^{1/4}}\right]^{3N} \\ &= -\frac{\partial}{\partial\beta}\ \ln\beta^{-9N/4} \\ &= \frac{9N}{4}\frac{\partial}{\partial\beta}\ \ln\beta \\ &= \frac{9N}{4}\frac{1}{\beta} = \frac{9N}{4}k_B T. \end{aligned} \tag{22}$$

■