

Physics 210A — Spring 2024
Problem Set #3 Solutions

1. **Weakly-interacting gas**

(a) The canonical partition function is

$$\begin{aligned} Z(\beta, V, N) &= \frac{1}{N!} \frac{1}{h^{3N}} \prod_{i=1}^N \int d^3 r_i \int d^3 p_i \exp \left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} - \beta \sum_{i<j} u(|\vec{r}_i - \vec{r}_j|) \right] \\ &= \frac{1}{N!} \left(\frac{1}{h^3} \int d^3 p e^{-\beta p^2/2m} \right)^N I_N, \end{aligned} \quad (1)$$

where

$$I_N = \prod_{i=1}^N \int d^3 r_i \exp \left[-\beta \sum_{i<j} u(|\vec{r}_i - \vec{r}_j|) \right]. \quad (2)$$

Therefore, the grand partition function is

$$\mathcal{Z}(\beta, V, \mu) = \sum_{N=1}^{\infty} Z(\beta, V, N) e^{\beta \mu N} = \sum_{N=0}^{\infty} \frac{1}{N!} I_N \zeta^N. \quad (3)$$

The first few coefficients are $I_0 = 1$, $I_1 = \int d^3 r = V$, and

$$I_2 = \int d^3 r_1 \int d^3 r_2 e^{-\beta u(|\vec{r}_1 - \vec{r}_2|)}. \quad (4)$$

To order ζ^2 , we have

$$\beta PV = \log \mathcal{Z}(\beta, V, \mu) = \log \left[1 + \sum_{N=1}^{\infty} \frac{1}{N!} I_N \zeta^N \right] = V\zeta + \frac{1}{2}(I_2 - V^2)\zeta^2 + \mathcal{O}(\zeta^3). \quad (5)$$

(b) The density is

$$\rho = \frac{\bar{N}}{V} = \frac{1}{\beta V} \frac{\partial \log \mathcal{Z}}{\partial \mu} = \frac{\zeta}{V} \frac{\partial \log \mathcal{Z}}{\partial \zeta} = \zeta + V^{-1}(I_2 - V^2)\zeta^2 + \mathcal{O}(\zeta^3). \quad (6)$$

To invert this, we expand $\zeta = a_1 \rho + a_2 \rho^2 + \mathcal{O}(\rho^3)$ and substitute into the above.

Equating coefficients of equal powers of ρ , we find $a_1 = 1$ and $a_2 = V^{-1}(V^2 - I_2)$, hence

$$\zeta = \rho + V^{-1}(V^2 - I_2)\rho^2 + \mathcal{O}(\rho^3). \quad (7)$$

(c) Substituting Eq. (7) into Eq. (5), we obtain

$$\beta P = \rho + B_2 \rho^2 + \mathcal{O}(\rho^3), \quad (8)$$

with

$$\begin{aligned} B_2 &= \frac{1}{2} V^{-1} (V^2 - I_2) \\ &= \frac{1}{2} V^{-1} \int d^3 r_1 \int d^3 r_2 [1 - e^{-\beta u(|\vec{r}_1 - \vec{r}_2|)}] \\ &= \frac{1}{2} V^{-1} \int d^3 R \int d^3 r [1 - e^{-\beta u(r)}] \\ &= \int d^3 r \frac{1}{2} [1 - e^{-\beta u(r)}]. \end{aligned} \quad (9)$$

In the third line we changed integration variables to the center of mass coordinates $\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$. Hence, $B_2 = \int d^3r f(r)$ with $f(r) = \frac{1}{2} [1 - e^{-\beta u(r)}]$. The virial expansion is valid when the kinetic energy of the particles dominates over their potential energy, i.e., in the limit of low density or high temperature. More quantitatively, it should hold when the second-order term is much smaller than the first-order term: $B_2\rho \ll 1$.

- (d) For a repulsive potential such as $u(r) = A/r$, $f(r)$ starts from one and decays to zero. So B_2 is always positive, corresponding to an increase in pressure due to the repulsive interaction.
- (e) For the given potential,

$$\begin{aligned} B_2 &= \int_0^{r_0} 4\pi r^2 dr \frac{1}{2} + \int_{r_0}^{\infty} 4\pi r^2 dr \frac{1}{2} \{1 - \exp[\beta u_0 e^{-(r-r_0)/\ell}]\} \\ &= \frac{2}{3}\pi r_0^3 - 2\pi\beta u_0 \int_{r_0}^{\infty} dr r^2 e^{-(r-r_0)/\ell} + \dots \\ &= \frac{2}{3}\pi r_0^3 - 2\pi\beta u_0 \ell (r_0^2 + 2r_0\ell + 2\ell^2) + \dots \end{aligned} \quad (10)$$

So B_2 changes its sign from positive to negative with decreasing temperature. This implies a gas to liquid phase transition.

2. Fluctuation in occupation number

We have

$$\begin{aligned} \mathcal{P}_{\text{BE}}(n, T, \mu) &= \mathcal{Z}_{\text{BE}}^{-1} e^{-\beta n(\varepsilon - \mu)}, \\ \mathcal{P}_{\text{FD}}(n, T, \mu) &= \mathcal{Z}_{\text{FD}}^{-1} e^{-\beta n(\varepsilon - \mu)}, \\ \mathcal{P}_{\text{MB}}(n, T, \mu) &= \mathcal{Z}_{\text{MB}}^{-1} (n!)^{-1} e^{-\beta n(\varepsilon - \mu)}. \end{aligned} \quad (11)$$

The partition functions are

$$\begin{aligned} \mathcal{Z}_{\text{BE}}(T, \mu) &= \sum_{n=0}^{\infty} e^{-\beta n(\varepsilon - \mu)} = [1 - e^{-\beta(\varepsilon - \mu)}]^{-1}, \\ \mathcal{Z}_{\text{FD}}(T, \mu) &= \sum_{n=0}^1 e^{-\beta n(\varepsilon - \mu)} = 1 + e^{-\beta(\varepsilon - \mu)}, \\ \mathcal{Z}_{\text{MB}}(T, \mu) &= \sum_{n=0}^{\infty} (n!)^{-1} e^{-\beta n(\varepsilon - \mu)} = \exp[e^{-\beta(\varepsilon - \mu)}]. \end{aligned} \quad (12)$$

From this, we compute $\langle n \rangle$:

$$\begin{aligned} \langle n \rangle_{\text{BE}} &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_{\text{BE}}}{\partial \mu} = [e^{\beta(\varepsilon - \mu)} - 1]^{-1}, \\ \langle n \rangle_{\text{FD}} &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_{\text{FD}}}{\partial \mu} = [e^{\beta(\varepsilon - \mu)} + 1]^{-1}, \\ \langle n \rangle_{\text{MB}} &= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_{\text{MB}}}{\partial \mu} = e^{-\beta(\varepsilon - \mu)}. \end{aligned} \quad (13)$$

In terms of $\langle n \rangle$, the probabilities are

$$\begin{aligned}\mathcal{P}_{\text{BE}}(n, T, \mu) &= \langle n \rangle^{-1} e^{-\beta n(\varepsilon - \mu)}, \\ \mathcal{P}_{\text{FD}}(n, T, \mu) &= \langle n \rangle e^{-\beta n(\varepsilon - \mu)}, \\ \mathcal{P}_{\text{MB}}(n, T, \mu) &= (n!)^{-1} e^{-\langle n \rangle} e^{-\beta n(\varepsilon - \mu)}.\end{aligned}\tag{14}$$

For the fluctuations, we have

$$\begin{aligned}\langle (n - \langle n \rangle)^2 \rangle_{\text{BE}} &= \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}_{\text{BE}}}{\partial \mu^2} = [e^{\beta(\varepsilon - \mu)} - 1]^{-2} e^{\beta(\varepsilon - \mu)} = \langle n \rangle + \langle n \rangle^2, \\ \langle (n - \langle n \rangle)^2 \rangle_{\text{FD}} &= \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}_{\text{FD}}}{\partial \mu^2} = [e^{\beta(\varepsilon - \mu)} + 1]^{-2} e^{\beta(\varepsilon - \mu)} = \langle n \rangle - \langle n \rangle^2, \\ \langle (n - \langle n \rangle)^2 \rangle_{\text{MB}} &= \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}_{\text{MB}}}{\partial \mu^2} = e^{-\beta(\varepsilon - \mu)} = \langle n \rangle,\end{aligned}\tag{15}$$

and therefore,

$$\begin{aligned}\Delta n_{\text{BE}} / \langle n \rangle &= (\langle n \rangle^{-1} + 1)^{1/2}, \\ \Delta n_{\text{FD}} / \langle n \rangle &= (\langle n \rangle^{-1} - 1)^{1/2}, \\ \Delta n_{\text{MB}} / \langle n \rangle &= \langle n \rangle^{-1/2}.\end{aligned}\tag{16}$$

The Bose and Fermi distributions reduce to the classical result in the limit of low occupation number, when $\langle n \rangle \ll 1$. Quantum statistics becomes important when $\langle n \rangle$ is of order one.

3. Compressibility of a free electron gas

(a) From the lecture, the grand potential is

$$\log \mathcal{Z}(\beta, V, \mu) = \sum_{\alpha} \log [1 + e^{-\beta(\varepsilon_{\alpha} - \mu)}] = \int d\varepsilon \mathcal{D}(\varepsilon) \log [1 + e^{-\beta(\varepsilon - \mu)}].\tag{17}$$

For free electrons, the density of states in d dimensions is

$$\begin{aligned}\mathcal{D}(\varepsilon) &= 2V \int \frac{d^d k}{(2\pi)^d} \delta(\varepsilon - \hbar^2 k^2 / 2m) \\ &= \frac{2V A_d}{(2\pi)^d} \int_0^{\infty} dk k^{d-1} \delta(\varepsilon - \hbar^2 k^2 / 2m) \\ &= \frac{V A_d (2m / \hbar^2)^{d/2}}{(2\pi)^d} \int_0^{\infty} dE E^{d/2-1} \delta(\varepsilon - E) \\ &= \frac{V A_d (2m / \hbar^2)^{d/2}}{(2\pi)^d} \Theta(\varepsilon) \varepsilon^{d/2-1},\end{aligned}\tag{18}$$

where $A_d = 2\pi^{d/2} / \Gamma(d/2)$ is the surface area of a d -dimensional unit sphere and the extra

factor of 2 accounts for spin degeneracy. The pressure is

$$\begin{aligned}
P &= \frac{\log \mathcal{Z}}{\beta V} = \frac{1}{\beta V} \int d\varepsilon \mathcal{D}(\varepsilon) \log [1 + e^{-\beta(\varepsilon-\mu)}] \\
&= \frac{A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d \beta} \int_0^\infty d\varepsilon \varepsilon^{d/2-1} \log [1 + e^{-\beta(\varepsilon-\mu)}] \\
&= \frac{2A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d d} \int_0^\infty d\varepsilon \frac{\varepsilon^{d/2}}{e^{\beta(\varepsilon-\mu)} + 1} \\
&= \frac{2A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d d} \int_0^\infty d\varepsilon \varepsilon^{d/2} n_F(\varepsilon).
\end{aligned} \tag{19}$$

We integrated by parts to get the third line, and in the last line, $n_F(\varepsilon) = [e^{\beta(\varepsilon-\mu)} + 1]^{-1}$ is the Fermi-Dirac distribution. The density is

$$\begin{aligned}
\rho &= \frac{1}{\beta V} \frac{\partial \log \mathcal{Z}}{\partial \mu} = \frac{1}{V} \int d\varepsilon \frac{\mathcal{D}(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1} \\
&= \frac{A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d} \int_0^\infty d\varepsilon \varepsilon^{d/2-1} n_F(\varepsilon).
\end{aligned} \tag{20}$$

(b) In the limit $T \rightarrow 0$, $n_F(\varepsilon) = \Theta(\varepsilon_F - \varepsilon)$ is a step function. Therefore,

$$\rho = \frac{A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{d/2-1} = \frac{2A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d d} \varepsilon_F^{d/2}, \tag{21}$$

and

$$P = \frac{2A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d d} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{d/2} = \frac{2A_d(2m/\hbar^2)^{d/2}}{(2\pi)^d (d/2 + 1)d} \varepsilon_F^{d/2+1}. \tag{22}$$

Eliminating ε_F , we find the equation of state:

$$P = \frac{(2\pi)^2}{d+2} \left(\frac{d}{2A_d} \right)^{2/d} \frac{\hbar^2}{m} \rho^{2/d+1}. \tag{23}$$

(c) The compressibility is

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{\rho} \left(\frac{\partial P}{\partial \rho} \right)^{-1} = \frac{d}{(2\pi)^2} \left(\frac{2A_d}{d} \right)^{2/d} \frac{m}{\hbar^2} \rho^{-2/d-1}. \tag{24}$$

4. Vibrational specific heat of solids

(a) The energy levels for each oscillator are $E_n = (n + \frac{1}{2})\hbar\omega$, with $n = 0, 1, 2, \dots$. The partition function of a single oscillator is

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}, \tag{25}$$

and the total partition function is $Z = Z_1^{3N}$. The mean energy per atom is

$$\bar{\varepsilon} = -\frac{1}{N} \frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}\hbar\omega + \frac{3\hbar\omega}{e^{\beta\hbar\omega} - 1}. \tag{26}$$

(b) The specific heat is

$$C_V = \frac{\partial \bar{\varepsilon}}{\partial T} = \frac{3k_B(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = 3k_B(\beta\hbar\omega)^2 \operatorname{csch}^2(\beta\hbar\omega/2). \quad (27)$$

In the limit $T \rightarrow \infty$,

$$C_V = \frac{3k_B(\beta\hbar\omega)^2}{(\beta\hbar\omega)^2} = 3k_B, \quad (28)$$

which is the Dulong-Petit law. As $T \rightarrow 0$,

$$C_V = 3k_B(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}, \quad (29)$$

which approaches zero exponentially.

(c) Generalizing Eq. (26) to the case where the oscillators have different frequencies labeled by mode index s and momentum \mathbf{k} , the mean energy per atom is

$$\bar{\varepsilon} = \Omega \sum_s \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1}. \quad (30)$$

Here the $\hat{\Omega}$ indicates that we are integrating over the first Brillouin zone of the crystal and Ω is the unit cell volume. We have neglected the temperature-independent zero-point energy of the phonons. Note also that the chemical potential of the phonons is zero because they can be freely created and destroyed. Eq. (30) may be rewritten as

$$\bar{\varepsilon} = \int d\omega \mathcal{D}(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \quad (31)$$

where

$$\mathcal{D}(\omega) = \Omega \sum_s \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \delta[\omega - \omega_s(\mathbf{k})] \quad (32)$$

is the phonon density of states. At high temperature, $\beta\hbar\omega \ll 1$ and

$$\bar{\varepsilon} \approx \int d\omega \mathcal{D}(\omega) \frac{\hbar\omega}{\beta\hbar\omega} = k_B T \int d\omega \mathcal{D}(\omega) = 3rk_B T, \quad (33)$$

where r is the number of atoms in the unit cell of the crystal (so $3r$ is the number of phonon modes).

(d) For a linearly dispersing mode,

$$\mathcal{D}(\omega) = \Omega \int \frac{d^3k}{(2\pi)^3} \delta(\omega - v|\mathbf{k}|) = \Omega \int_0^\infty \frac{k^2 dk}{2\pi^2} \delta(\omega - vk) = \frac{\Omega}{2\pi^2 v^3} \omega^2. \quad (34)$$

(e) The Debye frequency ω_D is determined by the normalization condition $\int_0^{\omega_D} d\omega \mathcal{D}(\omega) = 3$:

$$3 = \frac{\Omega}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \omega^2 = \frac{\Omega}{6\pi^2 v^3} \omega_D^3, \quad (35)$$

hence $\omega_D = (2\pi^2 v^3 / \Omega)^{1/3}$ and $\mathcal{D}(\omega) = 9\omega^2 / \omega_D^3$. The energy per atom is

$$\bar{\varepsilon} = \frac{9}{\omega_D^3} \int_0^{\omega_D} d\omega \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} = \frac{9k_B T^4}{T_D^3} \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}, \quad (36)$$

and the specific heat is

$$\bar{\varepsilon} = \frac{\partial \bar{\varepsilon}}{\partial T} = \frac{9}{4} k_B \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} x^4 \operatorname{csch}^2(x/2). \quad (37)$$

- (f) For $T \ll T_D$, we may extend the upper limit of the integral in Eq. (38) to infinity. We obtain

$$C_V = \frac{12}{5}\pi^2 k_B (T/T_D)^3. \quad (38)$$

The temperature dependence of the heat capacity as $T \rightarrow 0$ is determined by $\mathcal{D}(\omega)$ at low frequency. This is in turn determined from the linear dispersion of $\omega(\mathbf{k})$ at small k and does not depend on Debye's approximation. Only the dimensionless proportionality constant ($\frac{12}{5}\pi^2$ for the Debye model) will depend on the high-frequency behavior of $\mathcal{D}(\omega)$. For a d -dimensional solid, $\mathcal{D}(\omega) \propto \omega^{d-1}$, so $C_V \propto T^d$ in d dimensions. This is in contrast to the electronic contribution to the heat capacity which is always linear in T .

5. Ideal Bose gas in two dimensions

- (a) The density of states is

$$\begin{aligned} \mathcal{D}(\varepsilon) &= A \int \frac{d^2k}{(2\pi)^2} \delta(\varepsilon - \hbar^2 k^2/2m) \\ &= \frac{A}{2\pi} \int_0^\infty dk k \delta(\varepsilon - \hbar^2 k^2/2m) \\ &= \frac{Am}{\pi \hbar^2} \int_0^\infty dE \delta(\varepsilon - E) \\ &= \frac{Am}{\pi \hbar^2} \Theta(\varepsilon). \end{aligned} \quad (39)$$

Here $A = L^2$ is the area of the system.

- (b) From the lecture, the grand potential is

$$\log \mathcal{Z}(\beta, A, \mu) = - \int d\varepsilon \mathcal{D}(\varepsilon) \log [1 - e^{-\beta(\varepsilon - \mu)}] = - \frac{Am}{\pi \hbar^2} \int_0^\infty d\varepsilon \log (1 - f e^{-\beta\varepsilon}), \quad (40)$$

where $f = e^{\beta\mu}$ is the fugacity. The pressure is

$$P = \frac{\log \mathcal{Z}}{\beta A} = - \frac{g}{\beta} \int_0^\infty d\varepsilon \log (1 - f e^{-\beta\varepsilon}) = \frac{g}{\beta^2} \text{Li}_2(f), \quad (41)$$

where $g = m/\pi \hbar^2$ is the density of states per unit area and $\text{Li}_2(z) = \sum_{n=1}^\infty \frac{z^n}{n^2}$ is the dilogarithm. The density is

$$\rho = \frac{1}{\beta A} \frac{\partial \log \mathcal{Z}}{\partial \mu} = g \int_0^\infty d\varepsilon \frac{f e^{-\beta\varepsilon}}{1 - f e^{-\beta\varepsilon}} = - \frac{g}{\beta} \log(1 - f). \quad (42)$$

We may invert this to obtain

$$f = 1 - e^{-\beta\rho/g}. \quad (43)$$

The equation of state is therefore

$$P = \frac{g}{\beta^2} \text{Li}_2(1 - e^{-\beta\rho/g}). \quad (44)$$

- (c) Expanding Eq. (44) to second-order in ρ , we have

$$P = \frac{\rho}{\beta} - \frac{\rho^2}{4g} + \dots \quad (45)$$

(d) Bose-Einstein condensation occurs when $\mu = 0$, or $f = 1$. However, from Eq. (43), we see that $f < 1$ at any finite temperature, so no Bose-Einstein condensation occurs in the thermodynamic limit. For a finite size system, the particles have a minimum wavevector $k_0 = \pi/L$ and corresponding minimum energy $\varepsilon_0 = \hbar^2 k_0^2 / 2m$. This cuts off the logarithmic divergence of the integral in Eq. (42) at $f = 1$. Instead, we find

$$\rho = g \int_{\varepsilon_0}^{\infty} d\varepsilon \frac{e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}} = -\frac{g}{\beta} \log(e^{\beta\varepsilon_0} - 1) \approx \frac{g}{\beta} \log(1/\beta\varepsilon_0). \quad (46)$$

Solving for β , we obtain the Bose-Einstein condensation temperature

$$T_{\text{BE}} = \frac{\rho/gk_B}{\log(k_B T_{\text{BE}}/\varepsilon_0)} \sim \frac{1}{\log L}. \quad (47)$$