PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #10

Question 1: First-Order Correction to the Ideal Gas Law for Bosons

(a) Use integration by parts to show that $PV = \frac{2}{3}\langle E \rangle$

From the continuous limit of the grand potential, the pressure of the gas is given by:

$$PV = -k_B T \int_0^\infty dE\, g(E) \ln\left(1 - e^{-\beta(E-\mu)}\right) \tag{1}$$

We are given the density of states for non-relativistic bosons:

$$g(E) = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3}\sqrt{E} = CE^{1/2} \tag{2}$$

where C is a constant independent of E.

To apply integration by parts, $\int u\, dv = uv - \int v\, du$, we choose:

$$u = \ln\left(1 - e^{-\beta(E-\mu)}\right)$$
$$dv = g(E)dE = CE^{1/2}dE$$

Taking the derivatives and integrals of these parts:

$$du = \frac{1}{1 - e^{-\beta(E-\mu)}}\left(-e^{-\beta(E-\mu)}\right)(-\beta)\, dE = \frac{\beta}{e^{\beta(E-\mu)} - 1}\, dE$$
$$v = \int CE^{1/2}dE = \frac{2}{3}CE^{3/2} = \frac{2}{3}E\left(CE^{1/2}\right) = \frac{2}{3}Eg(E)$$

Now, evaluate the boundary term $[uv]_0^\infty$:

- As $E \to \infty$, $u \to \ln(1) = 0$ exponentially fast, dominating the polynomial growth of v.
- As $E \to 0$, $v \to 0$ due to the $E^{3/2}$ factor, while $u \to \ln(1 - e^{\beta\mu})$, which is a finite constant for $\mu < 0$.

Thus, the boundary term perfectly vanishes ($[uv]_0^\infty = 0$).

Applying the integration by parts formula to our initial equation:

$$\begin{aligned} PV &= -k_B T\left([uv]_0^\infty - \int_0^\infty v\, du\right) \\ &= -k_B T\left(0 - \int_0^\infty \left[\frac{2}{3}Eg(E)\right]\left[\frac{\beta}{e^{\beta(E-\mu)} - 1}\right] dE\right) \end{aligned} \tag{3}$$

Since $\beta = \frac{1}{k_B T}$, the factors of $k_B T$ and β cancel out:

$$PV = \frac{2}{3} \int_0^\infty dE \frac{g(E)E}{e^{\beta(E-\mu)} - 1} \tag{4}$$

Recognizing the integral as the average energy $\langle E \rangle$, we obtain:

$$\boxed{PV = \frac{2}{3} \langle E \rangle} \tag{5}$$

(b) Express N and solve for the fugacity z

The average number of particles is given by:

$$N = \frac{V}{\lambda_Q^3} g_{3/2}(z) \quad \text{where} \quad g_{3/2}(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^{3/2}} \tag{6}$$

In the limit $z \ll 1$, we expand the sum up to quadratic order ($m = 1$ and $m = 2$):

$$N \approx \frac{V}{\lambda_Q^3} \left(z + \frac{z^2}{2^{3/2}} \right) = \frac{V}{\lambda_Q^3} \left(z + \frac{z^2}{2\sqrt{2}} \right) \tag{7}$$

To solve for z in terms of N, let us define a small parameter $x = \frac{\lambda_Q^3 N}{V} \ll 1$. Our equation is:

$$x = z + \frac{1}{2\sqrt{2}} z^2 \tag{8}$$

We assume a series solution of the form $z = x + ax^2 + \ldots$ and substitute it back into the equation:

$$\begin{aligned} x &= (x + ax^2) + \frac{1}{2\sqrt{2}} (x + ax^2)^2 \\ x &= x + ax^2 + \frac{1}{2\sqrt{2}} x^2 + \mathcal{O}(x^3) \end{aligned} \tag{9}$$

For the equation to hold order-by-order, the x^2 coefficient must be zero:

$$a + \frac{1}{2\sqrt{2}} = 0 \implies a = -\frac{1}{2\sqrt{2}} \tag{10}$$

Substituting a back into our assumed solution for z yields:

$$z \approx x - \frac{1}{2\sqrt{2}} x^2 \tag{11}$$

Replacing x with its original definition gives the fugacity up to quadratic order:

$$\boxed{z = \frac{\lambda_Q^3 N}{V} \left(1 - \frac{1}{2\sqrt{2}} \frac{\lambda_Q^3 N}{V} + \ldots \right)} \tag{12}$$

(c) Derive the first-order correction to the Ideal Gas Law

We begin by evaluating the average energy $\langle E \rangle$:

$$\langle E \rangle = \int_0^\infty dE \frac{g(E)E}{e^{\beta(E-\mu)} - 1} \tag{13}$$

Rewrite the Bose-Einstein factor as a geometric series using the fugacity $z = e^{\beta\mu}$:

$$\frac{1}{e^{\beta(E-\mu)} - 1} = \frac{ze^{-\beta E}}{1 - ze^{-\beta E}} = \sum_{m=1}^{\infty} z^m e^{-m\beta E} \tag{14}$$

Substitute this and the density of states $g(E) = CE^{1/2}$ into the integral:

$$\langle E \rangle = \sum_{m=1}^{\infty} z^m \int_0^\infty dE\,(CE^{1/2})Ee^{-m\beta E} = C \sum_{m=1}^{\infty} z^m \int_0^\infty dE\,E^{3/2}e^{-m\beta E} \tag{15}$$

Using the substitution $u = m\beta E$, $dE = du/(m\beta)$, the integral becomes the Gamma function $\Gamma(5/2) = \frac{3\sqrt{\pi}}{4}$:

$$\int_0^\infty dE\,E^{3/2}e^{-m\beta E} = \frac{1}{(m\beta)^{5/2}} \int_0^\infty u^{3/2}e^{-u}du = \frac{3\sqrt{\pi}}{4}\frac{1}{(m\beta)^{5/2}} \tag{16}$$

To simplify C, we express it in terms of the thermal de Broglie wavelength $\lambda_Q = \frac{h}{\sqrt{2\pi m k_B T}}$:

$$C = \frac{4\pi\sqrt{2}Vm^{3/2}}{h^3} = \frac{2V}{\sqrt{\pi}\lambda_Q^3}\beta^{3/2} \tag{17}$$

Substitute the integral and C back into $\langle E \rangle$:

$$\begin{aligned}\langle E \rangle &= \left(\frac{2V}{\sqrt{\pi}\lambda_Q^3}\beta^{3/2}\right)\left(\frac{3\sqrt{\pi}}{4\beta^{5/2}}\right)\sum_{m=1}^{\infty}\frac{z^m}{m^{5/2}} \\ &= \frac{3}{2}k_B T\frac{V}{\lambda_Q^3}\sum_{m=1}^{\infty}\frac{z^m}{m^{5/2}} \\ &= \frac{3}{2}k_B T\frac{V}{\lambda_Q^3}g_{5/2}(z)\end{aligned} \tag{18}$$

Now, expand $g_{5/2}(z)$ up to quadratic order in z:

$$\langle E \rangle \approx \frac{3}{2}k_B T\frac{V}{\lambda_Q^3}\left(z + \frac{z^2}{2^{5/2}}\right) = \frac{3}{2}k_B T\frac{V}{\lambda_Q^3}\left(z + \frac{z^2}{4\sqrt{2}}\right) \tag{19}$$

Using the result from part (a), $PV = \frac{2}{3}\langle E \rangle$:

$$PV = k_B T\frac{V}{\lambda_Q^3}\left(z + \frac{z^2}{4\sqrt{2}}\right) \tag{20}$$

Finally, substitute the expression for z from part (b), where $x = \frac{\lambda_Q^3 N}{V}$:

$$z + \frac{z^2}{4\sqrt{2}} = \left(x - \frac{1}{2\sqrt{2}}x^2\right) + \frac{1}{4\sqrt{2}}x^2 = x - \frac{1}{4\sqrt{2}}x^2 + \mathcal{O}(x^3) \tag{21}$$

Multiply this result by $k_B T \frac{V}{\lambda_Q^3}$:

$$
\begin{aligned}
PV &= k_B T \frac{V}{\lambda_Q^3} \left(\frac{\lambda_Q^3 N}{V} - \frac{1}{4\sqrt{2}} \left(\frac{\lambda_Q^3 N}{V} \right)^2 \right) \\
&= N k_B T \left(1 - \frac{1}{4\sqrt{2}} \frac{\lambda_Q^3 N}{V} \right) \qquad (22)
\end{aligned}
$$

$$
\boxed{PV = N k_B T \left(1 - \frac{\lambda_Q^3 N}{4\sqrt{2} V} + \dots \right)} \qquad (23)
$$