Exercise/ We derive the high temperature equation of state for a Bose gas.

We recall that the average number of particles in the state with energy E is given by the Bose-Einstein distribution

$$\frac{1}{z^{-1}e^{\beta E}-1}.$$

We also know that the number of energy eigenstates with energy in the range $[E, E+dE]$ is given by the density of states

$$g(E) = \frac{V m^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \sqrt{E}$$

Thus, the total number of particles in the gas is given by

$$N = \int_0^\infty \frac{g(E)}{z^{-1}e^{\beta E}-1}\, dE .$$

Let us compute this integral using the expansion $z \ll 1$.

$$N = \frac{V m^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \int_0^\infty \frac{\sqrt{E}}{z^{-1}e^{\beta E}-1}\, dE = \frac{V m^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \cdot \frac{1}{\beta^{3/2}} \int_0^\infty \sqrt{\beta E}\, \frac{z e^{-\beta E}}{1 - z e^{-\beta E}}\, d(\beta E)$$

$$\approx \frac{V m^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \cdot \frac{z}{\beta^{3/2}} \int_0^\infty \sqrt{x}\, e^{-x}(1 + z e^{-x})\, dx \quad =$$

$$\frac{Vm^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \cdot \frac{1}{\beta^{3/2}} \cdot \frac{\sqrt{\pi}}{2} z\left(1 + z/2\sqrt{2}\right) = \frac{Vz}{\lambda^3}\left(1 + z/2\sqrt{2}\right),$$

where λ is the de Broglie thermal wavelength.

We can now use this expression to solve for z (which will be useful below).

$$z \approx \frac{N}{V} \cdot \lambda^3 \left(1 + z/2\sqrt{2}\right)^{-1} \approx \frac{\lambda^3 N}{V}\left(1 - z/2\sqrt{2}\right)$$

$$\Rightarrow z\left(1 + \lambda^3 N/V \cdot \frac{1}{2\sqrt{2}}\right) = \lambda^3 N/V \Rightarrow$$

$$z \approx \frac{\lambda^3 N}{V}\left(1 - \frac{1}{2\sqrt{2}} \frac{\lambda^3 N}{V}\right).$$

We can now observe that $z \ll 1 \iff \lambda^3 N/V \ll 1$. That is, the thermal wavelength is much smaller than the interparticle separation, so the $z \ll 1$ limit is the high temperature limit.

We wish to compute the equation of state, so given that we are working in the grand canonical ensemble, we can use the fact that the grand canonical potential Φ obeys

$$\Phi = -\frac{1}{\beta} \log \mathcal{Z} = -pV.$$

Using the grand partition function for the Bose gas (derived elsewhere),

$$\mathcal{Z} = \prod_r \frac{1}{1-e^{-\beta(E_r-\mu)}}$$

we get

$$pV = -\frac{1}{\beta}\sum_r \log\left(1-e^{-\beta(E_r-\mu)}\right) \approx$$

$$-\frac{1}{\beta}\int_0^\infty g(E)\log(1-ze^{-\beta E})\,dE \quad =$$

$$-\frac{1}{\beta}\frac{Vm^{3/2}}{\pi^2\hbar^3\sqrt{2}}\int_0^\infty \sqrt{E}\,\log(1-ze^{-\beta E})\,dE \quad =$$

$$\frac{1}{\beta}\frac{Vm^{3/2}}{\pi^2\hbar^3\sqrt{2}}\frac{2}{3}\int_0^\infty E^{3/2}\cdot\frac{\beta ze^{-\beta E}}{1-ze^{-\beta E}}\,dE \quad =$$

$$\frac{1}{\beta}\frac{Vm^{3/2}}{\pi^2\hbar^3\sqrt{2}}\frac{2}{3}\int_0^\infty (\beta E)^{3/2}\frac{1}{\beta^{3/2}}\beta ze^{-\beta E}\cdot\frac{1}{1-ze^{-\beta E}}\,d(\beta E)\frac{1}{\beta}$$

$$\approx \frac{Vm^{3/2}}{\pi^2\hbar^3\sqrt{2}}\frac{2}{3}\frac{z}{\beta^{5/2}}\int_0^\infty x^{3/2}e^{-x}(1+ze^{-\beta E})\,dx =$$

$$\frac{V m^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \frac{2}{3} \frac{z}{\beta^{5/2}} \cdot \frac{3\sqrt{\pi}}{4}\left(1+\frac{1}{4\sqrt{2}} z\right) =$$

$$\frac{V}{\lambda^3}\frac{z}{\beta}\left(1+\frac{1}{4\sqrt{2}} z\right) \approx$$

$$\frac{V}{\lambda^3}\cdot\frac{1}{\beta}\frac{\lambda^3 N}{V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}\right)\left(1+\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}\right)\right)$$

$$\approx N k_B T\left(1-\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}\right) \iff$$

$$\boxed{pV = N k_B T\left(1-\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}\right)}$$

Thus, the high temperature equation of state of a Bose gas looks like that of the ideal gas, but its first virial coefficient is negative, meaning that the pressure of a Bose gas is <u>lower</u> than that of the ideal gas. We can intuitively see why this might be the case, given the heuristic that bosons "like" to be in the same state as one another.