Physics 721: Tutorial
2022.02.25

Please hand in this tutorial on Friday, 4 March 2022.

We know from the analysis of the grand canonical potential that

$$\mathfrak{Z}(z,T,V) = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \sum_r \mathrm{e}^{-\beta E_r} = \exp\left[\frac{PV}{k_\mathrm{B}T}\right]. \tag{1}$$

1. Show that
$$\langle N\rangle = z\frac{\partial \ln \mathfrak{Z}}{\partial z}. \tag{2}$$

2. Derive the ideal gas equation of state using properties of $\mathfrak{Z}$, using eqs. (1) and (2).

3. The *virial expansion* is obtained by investigating the thermodynamic limits of the pressure and density:
$$\frac{P}{k_\mathrm{B}T} = \lim_{V\to\infty}\frac{\ln\mathfrak{Z}}{V} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell \tag{3}$$
$$\frac{\langle N\rangle}{V} = \lim_{V\to\infty}\frac{z}{V}\frac{\partial\ln\mathfrak{Z}}{\partial z} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} \ell b_\ell z^\ell. \tag{4}$$
We determine an equation that has the form of the *virial expansion* as below. The virial expansion is given in terms of the virial coefficients a_ℓ:
$$\frac{P}{k_\mathrm{B}T} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} a_\ell \times \left(\lambda^3\frac{\langle N\rangle}{V}\right)^\ell. \tag{5}$$
It is our task to derive the coefficients a_1, a_2, etc. We do this by combining equations (3) and (4). Solve for z power by power to derive expressions for a_1 in terms of b_1, a_2 in terms of b_1 and b_2, and a_3 in terms of b_1, b_2, and b_3.

4. Calculate a_2 for the potential energy
$$V(\vec{r}) = \begin{cases} \infty, & r\le\alpha \\ 0, & r>\alpha \end{cases}$$
where $\alpha > 0$.

5. Calculate a_2 for the potential energy
$$V(\vec{r}) = \begin{cases} \infty, & r\le\alpha \\ -v_0, & a\le r<2\alpha \\ 0, & r>2\alpha \end{cases}$$
where $\alpha > 0$, and $v_0 > 0$. Does a_2 ever change sign as a function of temperature?