Post-Lecture Question 7

(a) For an ideal gas, $U(\{\mathbf{r}_i\}) \equiv 0$.

$$\begin{aligned} Q^{\text{id}}(N,V,T) &= \frac{1}{\Lambda^{3N}N!}\int \prod_{i=1}^{N} \mathrm{d}^3\mathbf{r}_i \\ &= \frac{V^N}{\Lambda^{3N}N!} \end{aligned}$$

$$\begin{aligned} \mu^{\text{id}} &= -k_BT\ln\left[\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\cdot\frac{\Lambda^{3N}N!}{V^N}\right] \\ &= -k_BT\ln\left[\frac{V}{\Lambda^3(N+1)}\right] \\ &= k_BT\ln\left[\frac{N+1}{V}\Lambda^3\right] \\ &\approx k_BT\ln\rho\Lambda^3 \end{aligned}$$

(b)

$$\begin{aligned} \mu_{\text{ex}} &= \mu - \mu^{\text{id}} \\ &= -k_BT\ln\left[\frac{\frac{1}{\Lambda^{3(N+1)}(N+1)!}\int\prod_{i=1}^{N+1}\mathrm{d}^3\mathbf{r}_i\, e^{-\beta U(\{\mathbf{r}_i\}_{i=1}^{N+1})}}{\frac{1}{\Lambda^{3N}N!}\int\prod_{i=1}^{N}\mathrm{d}^3\mathbf{r}_i\, e^{-\beta U(\{\mathbf{r}_i\}_{i=1}^{N})}}\right] \\ &= -k_BT\ln\left[\frac{\int\mathrm{d}^3\mathbf{r}_{N+1}\int\prod_{i=1}^{N}\mathrm{d}^3\mathbf{r}_i\, e^{-\beta\Delta U}e^{-\beta U(\{\mathbf{r}_i\}_{i=1}^{N})}}{V\int\prod_{i=1}^{N}\mathrm{d}^3\mathbf{r}_i\, e^{-\beta U(\{\mathbf{r}_i\}_{i=1}^{N})}}\right] \\ &= -k_BT\ln\left[\frac{\mathrm{d}^3\mathbf{r}_{N+1}\left\langle e^{-\beta\Delta U}\right\rangle_N}{V}\right] \\ &= -k_BT\ln\left\langle e^{-\beta\Delta U}\right\rangle_N \end{aligned}$$

assuming the system is homogeneous, where $\langle\ldots\rangle$ means the average over the configuration space of the N particles in a canonical ensemble.

(c)
- Insertion.

$$\Delta U = \begin{cases} \infty & \text{overlap}: \quad P = \dfrac{4\pi\sigma^3N}{3V} \\ 0 & \text{no overlap}: \quad P = 1-\dfrac{4\pi\sigma^3N}{3V} \end{cases}$$

$$\left\langle e^{-\beta\Delta U}\right\rangle_N = P_{\text{no overlap}} = 1-\frac{4N\pi\sigma^3}{3V}$$

$$\mu^{\text{ex}} = -k_BT\ln\left[1-\frac{4N\pi\sigma^3}{3V}\right]$$

- Removal.
  $\Delta U \equiv 0$ as the removed particle is guarenteed to have no overlap with the other $N-1$ particles.

$$\left\langle e^{-\beta\Delta U}\right\rangle_N = 1$$

$$\mu^{\text{ex}} = -k_BT\ln 1 = 0$$