Problem 12.1 Widom insertion method

(a) According to the laws of thermodyn.:

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} \cong \frac{F(N+1) - F(N)}{N+1-N} = \frac{F(N+1) - F(N)}{1}$$

$$= -k_BT\left(\ln Z_{N+1} - \ln Z_N\right) = -k_BT \ln \frac{Z_{N+1}}{Z_N}$$

$$= -k_BT \ln \left\{ \frac{\frac{V^{N+1}}{\lambda^{3(N+1)}(N+1)!} \int d\vec{s}^{(N+1)}\, e^{-\beta \mathcal{H}_{N+1}}}{\frac{V^N}{\lambda^{3N}N!} \int d\vec{s}^{(N)}\, e^{-\beta \mathcal{H}_N}} \right.$$

where the prefactors come from rescaling the spatial integrals and the momentum integrals and $\mathcal{H}_{N+1}$, $\mathcal{H}_N$ correspond to the Hamilton function ($= \mathcal{U}$)

$$= -k_BT \ln \left\{ \frac{V}{\lambda^3 (N+1)} \right\}$$

$$- k_BT \ln \left\{ \int d\vec{s}_{N+1} \frac{\int d\vec{s}^{(N)}\, e^{-\beta \mathcal{H}_N}\, e^{-\beta \Delta \mathcal{U}}}{\int d\vec{s}^{(N)}\, e^{-\beta \mathcal{H}_N}} \right\}$$

with $\Delta \mathcal{U} = \mathcal{H}_{N+1} - \mathcal{H}_N$

the difference in internal energy from adding a particle

$$= -k_BT \ln\left\{\frac{V}{\lambda^3 (N+1)}\right\} - k_BT \ln \left\{ \int d\vec{s}_{N+1} \left\langle e^{-\beta \Delta \mathcal{U}} \right\rangle \right\} = \mu_{id} + \mu_{exc}$$