10.40 Thermodynamics **Fall 2003**
Problem Set 7

Problems 10.8 Text

Solution:

With $\underline{A} = -kT \ln Q_N$:

$$\mu_i = (\partial \underline{A}/\partial N_i)_{T,\underline{V},N_j[i]} = \underset{\text{if pure } i}{(\partial \underline{A}/\partial N_i)_{T,\underline{V}}} = -kT\left(\frac{\partial \ln Q_N}{\partial N_i}\right)_{T,\underline{V}} \tag{1}$$

From Calculus:

$$\mu_i = \lim_{\substack{\frac{\Delta N}{N} \to 0 \\ N \to \infty}} \left[-kT\left[\frac{\ln Q_{N+1} - \ln Q_N}{(N+1) - N}\right]\right] = -kT \ln\left[\frac{Q_{N+1}}{Q_N}\right] \tag{2}$$

where $\Delta N = N + 1 - N$ is consistent with concept of particle insertion. Now for Q_N

$$Q_N = Q_{int} Q_{CM} = \frac{q_{int}^N q_{trans}^N Z_N^*}{N!\, h^{3N}} = \frac{q_{int}^N}{N\ \Lambda^{3N}} Z_N^* = \left(\frac{Q_{t,i}^*}{\underline{V}}\right)^N \frac{Z_N^*}{N!} \tag{3}$$

where

$$\frac{Q_{t,i}^*}{\underline{V}} = \frac{q_{int} q_{trans}}{\underline{V} h^3}$$

similarly for Q_{N+1}:

$$Q_{N+1} = \left(\frac{Q_{t,i}^*}{\underline{V}}\right)^{N+1} \frac{Z_{N+1}^*}{N!}$$

$$\mu_i = -kT \ln\left[\frac{\left(\frac{Q_{t,i}^*}{\underline{V}}\right)^{N+1} \left(\frac{Z_{N+1}^*}{(N+1)!}\right)}{\left(\frac{Q_{t,i}^*}{\underline{V}}\right)^{N} \left(\frac{Z_N^*}{N!}\right)}\right] = -kT \ln\left[\frac{Q_{t,i}^*}{\underline{V}(N+1)} \frac{Z_{N+1}^*}{Z_N^*}\right] \tag{4}$$

For large N, we can replace $N + 1$ with N. Thus as $N \to \infty$

$$\mu_i = -kT \ln\left[\frac{Q_{t,i}^*}{N\underline{V}} \frac{Z_{N+1}^*}{Z_N^*}\right] \qquad \text{QED!} \tag{5}$$

(b) **Using the definition of the configuration integral given in Eq. (10-76):**

$$\frac{Z_{N+1}^*}{Z_N^*} = \frac{\int \dots \int \exp\left[-\Phi_{N+1}/kT\right] dr_1 \dots dr_{N+1}}{\int \dots \int \exp\left[-\Phi_N/kT\right] dr_1 \dots dr_N} \tag{6}$$

Via pairwise additivity:

$$\Phi_{N+1}(r_1,\ldots, r_{N+1}) - \Phi_N(r_1,\ldots, r_N) = \sum_{i=1}^{N+1} \Phi_{i,N+1} = 2\Phi_{N+1} \quad (7)$$

where the sum runs over all binaries and the factor of 2 avoids double counting. Thus,

$$\Phi_{N+1} = \frac{1}{2}\sum_{i=1}^{N+1} \Phi_{i,j=N+1} \quad (8)$$

where Eq. (8) defines the total PE of the N+1 particle due to its insertion into a system of N particles. Eq. (6) can be factored into parts:

$$\frac{Z^*_{N+1}}{Z^*_N} = \frac{\int\ldots\int \exp\,[-\Phi_N/kT]dr_1\ldots dr_N \int \exp\,[-2\Phi_{N+1}/kT]\, dr_{N+1}}{\int\ldots\int \exp[-\Phi_N/kT]dr_1\ldots dr_N} \quad (9)$$

$$\frac{Z^*_{N+1}}{Z^*_N} = \int \exp\left[\frac{-2\Phi_{N+1}}{kT}\right] dr_{N+1}$$

A physical interpretation suggests that we insert particle N+1 into system of N particles with all particles fixed in place. Alternatively we could have written Eq. (6) as

$$\frac{Z^*_{N+1}}{Z^*_N} = \frac{\int dr_{N+1} \int\ldots\int \exp\,[-2\Phi_{N+1}/kT]\, \exp\,[-\Phi_N/kT]\, dr_1\ldots dr_N}{\int\ldots\int \exp\,[-\Phi_N/kT]\, dr_1\ldots dr_N}$$

$$= \underline{V}\langle\exp[-2\Phi_{N+1}/kT]\rangle \quad (10)$$

where the < > term is the Boltzmann-weighted ensemble average.