Exam 2
Solutions
3.20 MIT
Fall 2001

Problem 1

$$dE = TdS - pdV + Fdl + \mu dN$$
$$E = TS - pV + Fl + \mu N$$

But we are told that we are working under a vacuum so $p = 0$.

(a) What is the characteristic potential (ϕ)?

Our controlling variables are T, F, N so

$$\boxed{\phi = E - TS - Fl}$$

or

$$d\phi = -SdT - ldF + \mu dN$$

Or in terms of a Legendre transform of the entropy:

$$-\beta\phi = \frac{S}{k} - \beta E + \beta Fl$$

(b) What is the partition function (Λ) for this ensemble?

$$\boxed{\Lambda = \sum_j \exp\left[-\beta E_j + \beta F l_j\right]}$$

and

$$-\beta\phi = \ln\Lambda \qquad \text{or} \qquad \boxed{\phi = -kT\ln\Lambda}$$

(c) Write the thermodynamic variables l, S, μ and E as a function of the partition function.

We can start with the equations of state we get from ϕ

$$l = -\left(\frac{\partial\phi}{\partial F}\right)_{T,N} = kT\left(\frac{\partial\ln\Lambda}{\partial F}\right)_{T,N}$$
$$S = -\left(\frac{\partial\phi}{\partial T}\right)_{F,N} = k\ln\Lambda + kT\ln\left(\frac{\partial\ln\Lambda}{\partial T}\right)_{F,N}$$
$$\mu = \left(\frac{\partial\phi}{\partial N}\right)_{T,F} = -kT\left(\frac{\partial\ln\Lambda}{\partial N}\right)_{T,F}$$

and for E we can do the following

$$E = \phi + TS + Fl$$
$$E = -kT\ln\Lambda + kT\ln\Lambda + kT^2\left(\frac{\partial\ln\Lambda}{\partial T}\right)_{F,N} + kTF\left(\frac{\partial\ln\Lambda}{\partial F}\right)_{T,N}$$
$$E = kT^2\left(\frac{\partial\ln\Lambda}{\partial T}\right)_{F,N} + FkT\left(\frac{\partial\ln\Lambda}{\partial F}\right)_{T,N}$$

Problem 2

(a) What is $\frac{\overline{V^2}-\overline{V}^2}{\overline{V}^2}$ at constant T, P, N ?

We are in the isothermal-isobaric ensemble and the partition function is

$$\Delta = \sum_j \exp\left[\frac{-E_j}{kT}\right] \exp\left[\frac{-pV_j}{kT}\right]$$

Follow the three step procedure:

Step 1: Multiply both sides by the partition function

$$\Delta\overline{V} = \sum_j V_j \exp\left[\frac{-E_j}{kT}\right] \exp\left[\frac{-pV_j}{kT}\right]$$

Step 2: Get derivative with respect to mechanical variable's conjugate.

$$\Delta\frac{\partial\overline{V}}{\partial p} + \overline{V}\frac{\partial\Delta}{\partial p} = \frac{\partial}{\partial p}\left(\sum_j V_j \exp\left[\frac{-E_j}{kT}\right] \exp\left[\frac{-pV_j}{kT}\right]\right)$$

$$\Delta\frac{\partial\overline{V}}{\partial p} + \overline{V}\left\{\sum_j \left(-\frac{V_j}{kT}\right) \exp\left[\frac{-E_j}{kT}\right] \exp\left[\frac{-pV_j}{kT}\right]\right\} = \sum_j \left(-\frac{V_j^2}{kT}\right) \exp\left[\frac{-E_j}{kT}\right] \exp\left[\frac{-pV_j}{kT}\right]$$

Step 3: Divide through by the partition function

$$\frac{\partial\overline{V}}{\partial p} + \overline{V}\left(-\frac{\overline{V}}{kT}\right) = \frac{-\overline{V^2}}{kT}$$

$$\overline{V^2} - \overline{V}^2 = -kT\left(\frac{\partial\overline{V}}{\partial p}\right)$$

$$\boxed{\frac{\overline{V^2}-\overline{V}^2}{\overline{V}^2} = -\frac{kT}{\overline{V}^2}\left(\frac{\partial\overline{V}}{\partial p}\right) = \frac{kT}{\overline{V}}\kappa}$$

where $\kappa = -\frac{1}{\overline{V}}\left(\frac{\partial\overline{V}}{\partial p}\right)$ = compressibility.

(b) Evaluate this relationship for an ideal gas.

$$pV = NkT$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right) = \left(\frac{-1}{V}\right)\left(\frac{-NkT}{p^2}\right) = \frac{1}{p}$$

$$\frac{\overline{V^2}-\overline{V}^2}{\overline{V}^2} = \frac{kT}{\overline{V}}\left(\frac{1}{p}\right) = \frac{1}{N}$$

This is a general result for the fluctuation of an extensive variable for an ideal gas. It means the fluctuations are small when N is large.

(c) When can the volume fluctuations become large?

Near a critical point where $\kappa = -\frac{1}{\overline{V}}\left(\frac{\partial\overline{V}}{\partial p}\right) \to \infty$.

Problem 3

(a) The degeneracy

$$\boxed{\Omega = \frac{M!}{N!(M-N)!}}$$

which is the number of ways to distribute N particles and $(M-N)$ vacancies over M surface sites.

(b) N, V, T constant mean the canonical ensemble

$$Q = \sum_j e^{-\beta E_j} = \sum_E \Omega(E) e^{-\beta E}$$

$E = -N\varepsilon$ which depends only on N and not the particular arrangement of the atoms. But since N is fixed, there is only one energy level.

$$\boxed{Q = \frac{M!}{N!(M-N)!} e^{\beta N \varepsilon}}$$

(c) Obtain an expression for the chemical potential of the argon atoms on the surface

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$F = -kT \ln Q = -kT \left\{ \ln\left(\frac{M!}{N!\,(M-N)!}\right) + \beta N \varepsilon \right\}$$

$$F = -kT \left\{ \ln(M!) - N\ln N + N - (M-N)\ln(M-N) + (M-N) \right\} - N\varepsilon$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \left\{ -\ln N - 1 + 1\ln(M-N) + 1 - 1 \right\} - \varepsilon$$

if we let $x = \frac{N}{M}$ we get

$$\boxed{\mu = -\varepsilon + kT \ln\left(\frac{N}{M-N}\right) = -\varepsilon + kT\ln\left(\frac{x}{1-x}\right)}$$

Problem 4

(a) We assumed:

- Boltzmann statistics
- non-interacting particles
- gas particles are indistinguishable
- mono-atomic particles, in which electronic & nuclear excitations are neglected

(b) $\mu = 0$

(c) Yes for both Fermions and Bosons but at high T, low density, high mass

(d) P_{AB} for a totally random solution is equal to $2x_A x_B = 0.5$. Hence, a value of $P_{AB} = 0.25$ represents short-range clustering. This restriction on the number of microstates reduces the entropy. To increase S we need to increase P_{AB} towards 0.5.

Problem 5

	S_{tot}	$\frac{S_{tot}}{2N}$
(a)	$k\ln 1$ or $k\ln 2$	0
(b)	$k\ln N$ (N ways to insert atom)	0
(c)	$-Nk\left[\underbrace{0.01\ln 0.01+0.99\ln 0.99}_{=-.0.056}\right]$	$=-\frac{1}{2}k\left[0.01\ln 0.01+0.99\ln 0.99\right]$
(d)	There are $\frac{4\times 2N}{2}$ number of pairs, each can be exchanged $\rightarrow k\ln 4N$	0