NAME:

Physics 112
Spring 2004

Midterm 1 (Solution).

Monday 23 February 2004, 8:10-9:00 a.m.

50 points=50minutes

1) **Thermodynamic identity** (5 points)
Write down the thermodynamic identity (i.e. the full differential with the appropriate macroscopic thermodynamic variables) for the energy U and the free energy F=U-τσ.

$$dU = \tau d\sigma - p dV + \mu dN = T dS - p dV + \mu dN$$

$$dF = -\sigma d\tau - p dV + \mu dN = -S dT - p dV + \mu dN$$

What the natural independent variables to use with U and F?

$$U = U(\sigma, V, N), \qquad F = F(\tau, V, N)$$

2) **Temperature, pressure and chemical potential of an ideal gas** (15 points)

Consider an ideal gas of indistinguishable N spinless particles in a volume V and total energy U. Using our prescription of the number of spatial quantum states per unit phase space volume, integrating in momentum space on the hypersphere where the total energy is U, and keeping carefully track of the numerical coefficients, we can compute the number of states and therefore the entropy at equilibrium. For large N

$$\sigma(U,V,N) = N\log\left[\left(\frac{M}{2\pi\hbar^2}\frac{2U}{3N}\right)^{3/2}\right] + N\left(\log\frac{V}{N} + 5/2\right)$$

Calculate

a) (5 points) the temperature of the ideal gas we consider

$$\frac{1}{\tau} = \left.\frac{\partial\sigma}{\partial U}\right|_{N,V} = \frac{\partial}{\partial U}\left\{ N \log U^{3/2} + \cdots \right\} = \frac{3}{2}\frac{N}{U}$$

$$\therefore \tau = \frac{2U}{3N}$$

What is the average kinetic energy per molecule?

From $U = \frac{3}{2}N\tau$ $\qquad u = \frac{U}{N} = \frac{3}{2}\tau$.

b) (5 points) the pressure

$$\frac{p}{\tau} = \frac{\partial\sigma}{\partial V}\Big|_{U,N} = \frac{N}{V}. \qquad \therefore \underline{p = \frac{N}{V}\tau}.$$

Check that you indeed get the ideal gas law. $\underline{pV = N\tau}.$

c) (5 points) the chemical potential

$$-\frac{\mu}{\tau} = \frac{\partial\sigma}{\partial N}\Big|_{U,V} = \log\left[\left(\frac{M}{2\pi\hbar^2}\frac{2U}{3N}\right)^{3/2}\right] + \log\left(\frac{V}{N}\right).$$

Describe in words how does the chemical potential depends on the concentration N/V at constant temperature?

$\mu \sim \tau\log(N/V)$, so the chemical potential has a log behavior for the concentration because the first term is constant.

3) One dimensional gas (15 points)

We consider an ideal gas of N indistinguishable particles in one dimension. They are contrained in a deep potential well (a "box") of width L. There are in equilibrium with a heat bath at temperature τ.

a. (7 points) Using our general result on the number of spatial quantum states per unit phase space volume, show that the partition function is

$$Z_N \approx \frac{L^N}{N!}\left(\frac{M\tau}{2\pi\hbar^2}\right)^{N/2}$$

The energy of particle in a box $\varepsilon = \frac{\hbar^2\pi^2}{2ML^2}n^2 = \frac{\hbar^2 k_n^2}{2M} = \frac{p^2}{2M}$.

$$\therefore Z_1 = \frac{1}{h}\int dx\,dp\, e^{-\varepsilon/\tau} = \frac{L}{h}\int dp\, e^{-\frac{p^2}{2M\tau}} = \frac{L}{h}(2\pi M\tau)^{1/2}$$

$$\underline{= L\cdot\left(\frac{M\tau}{2\pi\hbar^2}\right)^{1/2}}$$

For the N indistinguishable ideal gas $\quad Z_N = \frac{1}{N!}(Z_1)^N = \underline{\underline{\frac{L^N}{N!}\left(\frac{M\tau}{2\pi\hbar^2}\right)^{N/2}}}$

b. (5 points) Compute the mean energy U and the Helmoltz free energy F of the system

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau}\left\{ \frac{N}{2} \log \tau + \cdots \right\} = \underline{\frac{N}{2}\tau}.$$

$$F = -\tau \log Z_N = \underline{-\tau \log \left\{ \left(\frac{M\tau}{2\pi\hbar^2} \right)^{N/2} \cdot \frac{L^N}{N!} \right\}}.$$

What is the kinetic energy per particle? $u = \frac{U}{N} = \underline{\frac{\tau}{2}}$. in one dimension.

c. (5 points) How would you define the equivalent of the pressure for such a one-dimensional system?

Using the definition of volume as length "L", we can get

$$p = -\left(\frac{\partial F}{\partial L} \right)\Big|_\tau = -\frac{\partial}{\partial L}\left\{ -\tau \log L^N + \cdots \right\} = N\tau \cdot \frac{1}{L}.$$

What is the equivalent of the law of ideal gases?

$$\underline{\underline{pL = N\tau}}$$

4) **Minimization of the free energy for a system at a given temperature** (15 points)

Consider a system at equilibrium at the temperature τ. The probability of state i is of course

$$p_s^o = \frac{\exp\left(-\frac{\varepsilon_s}{\tau}\right)}{Z},$$

with

$$Z = \sum_s \exp\left(-\frac{\varepsilon_s}{\tau}\right).$$

We disturb the system so that it is distributed over its accessible states in accordance to an *arbitrary* probability distribution p_s, which stays *normalized.* We define the (Helmoltz) free energy F as

$$F = U - \tau\sigma \text{ with } U = \sum_s \varepsilon_s p_s$$

where s is the entropy of the p_s probability distribution and want to compare it with the equilibrium free energy

$$F^o = U^o - \tau\sigma^0 \text{ with } U^o = \sum_s \varepsilon_s p_s^o$$

a) (5 points) Show that

$$\sum_s p_s \log\left(p_s^o\right) = -\frac{U}{\tau} - \log Z$$

$$\sum_s p_s \log(p_s^\circ) = \sum_s p_s \left\{ \log\left(\frac{e^{-\varepsilon_s/\tau}}{Z} \right) \right\} = \sum_s p_s \cdot \left(-\frac{\varepsilon_s}{\tau}\right) - \sum_s p_s \log Z$$

$$= -\frac{1}{\tau} \sum_s p_s \varepsilon_s - \left(\sum_s p_s\right) \cdot \log Z = -\frac{U}{\tau} - \log Z$$

b) (5 points) Show that

$$F - F^0 = -\tau \sum_s p_s \log\left(\frac{p_s^o}{p_s}\right)$$

(Hint: replace F^o by its value in terms of log Z).

$$F - F_0 = U - \tau\sigma - (-\tau \log Z) \qquad \text{(from definition)}$$

$$= (U + \tau \log Z) - \tau\sigma$$

$$= -\tau \sum_s p_s \log(p_s^\circ) - \tau\left(-\sum_s p_s \log p_s\right) \qquad \text{from (a)}$$

$$= -\tau \sum_s p_s \left\{ \log(p_s^\circ) - \log(p_s) \right\}$$

$$= -\tau \sum_s p_s \log\left(\frac{p_s^\circ}{p_s}\right)$$

c) (5pts) Using the fact that

$$\log\left(\frac{p_s^o}{p_s}\right) \le \left(\frac{p_s^o}{p_s} - 1\right),$$

show that $F \ge F^0$, with the equality being only obtained if $p_s = p^o{}_s$ for all s. At equilibrium *at constant temperature*, the free energy is minimized!

$$F - F_0 = -\tau \sum_s p_s \log\left(\frac{p_s^\circ}{p_s}\right)$$

$$\therefore -F + F_0 = \tau \sum_s p_s \log\left(\frac{p_s^\circ}{p_s}\right) \le \tau \sum_s p_s \left(\frac{p_s^\circ}{p_s} - 1\right) = 0$$

$$\therefore F \ge F_0$$