PHY831 - Midterm I with Solutions, Monday September 26th 2011

Answer all questions. Time for midterm - 50 minutes

Name:

Formulae that might be helpful

$$\int_{-\infty}^{\infty} e^{-ax^2+bx} dx = (\frac{\pi}{a})^{1/2} e^{\frac{b^2}{4a}} \tag{1}$$

Relations between partial derivatives,

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z ; \quad \text{Inversion} \tag{2}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_z \left(\frac{\partial w}{\partial y}\right)_z ; \quad \text{Addition of a variable} \tag{3}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 ; \quad \text{Triple Product} \tag{4}$$

If $A(x, y)$, then,

$$\left(\frac{\partial A}{\partial x}\right)_z = \left(\frac{\partial A}{\partial x}\right)_y + \left(\frac{\partial A}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z ; \quad \text{non} - \text{natural derivative} \tag{5}$$

Response functions are defined as follows;

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial S}\right)_{V,N} \left(\frac{\partial S}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}, \tag{6}$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial S}\right)_{P,N} \left(\frac{\partial S}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N}, \tag{7}$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} = -\left(\frac{\partial lnV}{\partial P}\right)_{S,N}, \tag{8}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\left(\frac{\partial lnV}{\partial P}\right)_{T,N}, \tag{9}$$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial lnV}{\partial T}\right)_{P,N}, \tag{10}$$

1. (10 points) Consider an intensive thermodynamic variable X_i (e.g. E/N) that has a different value in each of N subsystems. Consider each subsystem to have the same volume and that each subsystem is statistically equivalent. Each subsystem is assumed to have a statistical behavior that is Gaussian distributed, so that,

$$P_1(X_i) = \left(2\pi\sigma^2\right)^{-1/2} e^{-\frac{X_i^2}{2\sigma^2}} \tag{11}$$

where we assumed that each subsystem has the same statistical variations, quantified by σ. *Find the probability distribution, $P_N(\overline{X}_N)$ of the quantity,*

$$\overline{X}_N = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{12}$$

This is a special case of the Central limit theorem.

Solution: The probability distribution of $\overline{X}_N$ is given by,

$$P_N(\overline{X}_N) = \left(2\pi\sigma^2\right)^{-N/2} \int_{infty}^{\infty} \prod_i dX_i e^{-\frac{X_i^2}{2\sigma^2}} \delta(\frac{1}{N}\sum_i X_i - \overline{X}_N) \tag{13}$$

Using the delta function representation,

$$\delta(\alpha) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{iy\alpha} dy \tag{14}$$

we find,

$$P_N(\overline{X}_N) = \left(2\pi\sigma^2\right)^{-N/2} \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \prod_i dX_i e^{-\frac{X_i^2}{2\sigma^2}} e^{iy(\frac{1}{N}\sum_i X_i - \overline{X}_N)} \tag{15}$$

which is equivalent to

$$P_N(\overline{X}_N) = \left(2\pi\sigma^2\right)^{-N/2} \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iy\overline{X}_N} [I]^N \tag{16}$$

where

$$I = \int_{-\infty}^{\infty} dX e^{-\frac{X^2}{2\sigma^2}} e^{iy\frac{X}{N}} = \left(2\pi\sigma^2\right)^{1/2} e^{-\frac{\sigma^2 y^2}{2N^2}} \tag{17}$$

Finally,

$$P_N(\overline{X}_N) = \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iy\overline{X}_N} e^{-\frac{\sigma^2 y^2}{2N}} = \frac{1}{(2\pi\sigma_N^2)^{1/2}} e^{-\frac{\overline{X}_N^2}{2\sigma_N^2}} \tag{18}$$

where $\sigma_N = \sigma/N^{1/2}$

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2. (10 points) *From the fundamental thermodynamic relation show that,*

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}. \tag{19}$$

Solution: Since the independent variables in the expression are T, P, we consider the Gibb's free energy $G(T, P, N)$, so that,

$$dG = -SdT + VdP + \mu dN = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN \tag{20}$$

hence,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S; \qquad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V. \tag{21}$$

This leads to the Maxwell relation,

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{22}$$

Now take a temperature derivative at constant pressure of this equation, to find,

$$-\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_{T,N}\right)_{P,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \tag{23}$$

We can change the order of the derivatives of the expression on the left hand side, and use the fact that $C_P = T(\partial S/\partial T)_P$ to write,

$$-\left(\frac{\partial (C_P/T)}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}; \quad \text{or} \quad \left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \tag{24}$$

which solves the problem.

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3. (10 points) The canonical partition function, Z, of a classical particle system with N particles at temperature T in a cubic box of size V, is given by,

$$Z = \frac{1}{N!h^{3N}}\int d^3r_1...d^3r_N \int d^3p_1....d^3p_N e^{-\beta H}. \tag{25}$$

where H is the Hamiltonian, while $\vec{r}_i, \vec{p}_i$ are the positions and momenta of the i^{th} particle and h is Planck's constant. *(i) From Eq. (14) find the Helmholtz free energy, $F(T,V,N)$, for a non-relativistic ideal monatomic gas. (ii) From your expression for F and using the thermodynamic relations for dF, find expressions for (a) the entropy, (b) the pressure and (c) the chemical potential of the gas. (iii) Confirm that your expressions satisfy $U = F + TS = 3Nk_BT/2$.*

Solution. For an ideal gas, the integrals over position give V^N, while the integrals over momenta separate into $3N$ Gaussian integrals, so that,

$$Z = \frac{V^N}{N!h^{3N}} I^{3N} \quad \text{where} \quad I = \int_{-\infty}^{\infty} e^{-\beta p^2/2m} = \left(\frac{2m\pi}{\beta}\right)^{1/2}. \tag{26}$$

This may be written as,

$$Z = \frac{V^N}{\lambda^{3N} N!} \quad \text{where} \quad \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

is the thermal de Broglie wavelength. Note that the partition function is dimensionless. The thermal de Broglie wavelength is an important length scale in gases. If the average interparticle spacing, $L_c = (V/N)^{1/3}$ is less than λ quantum effects are important, while if $L_c > \lambda$, the gas can be treated as a classical gas. We shall use this parameter later to decide if particles in atom traps are expected to behave as classical or quantum systems. From the canonical partition function we find the Helmholtz free energy,

$$F = -k_B T ln(Z) = -k_B T ln(\frac{V^N}{\lambda^{3N} N!}) \tag{29}$$

This expression is in terms of its natural variables $F(T,V,N)$, so we can find all of the thermodynamics from it as follows:

$$dF = -SdT - PdV + \mu dN = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \tag{30}$$

and hence

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_B ln(\frac{V^N}{\lambda^{3N} N!}) + \frac{3}{2} N k_B \tag{31}$$

The internal energy is found by combining (29) and (31), so that,

$$U = F + TS = \frac{3}{2} N k_B T \tag{32}$$

The pressure is given by,

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T \frac{N}{V} = \frac{k_B N T}{V}, \tag{33}$$

which is the ideal gas law, while the chemical potential is,

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_B T ln(\frac{\lambda^3 N}{V}) \tag{34}$$