Physics 413: Mid-semester test Mar 12, 2013

$dU = TdS + \delta W + \mu dN$ $\qquad \ln(N!) \approx N\ln(N) - N$ $\qquad \coth(x) \approx 1/x + x/3 + \dots$
$\int_{-\infty}^{\infty} e^{-\frac{1}{2}(x-x_0)^2/\sigma^2} = (2\pi\sigma^2)^{1/2}$
$\int_0^\infty dx\, x^2/\cosh^2(x) = \int_0^\infty dx\, x^2(1-\tanh^2(x)) = \pi^2/12$ $\qquad \int_0^\infty dx\, x^2 e^x/(1+e^x)^2 = \pi^2/6$

Problem 1: Random two-level systems (70 points)

An amorphous solid contains $N \gg 1$ of (distinguishable) two-level systems with energies $\epsilon_i/2$ and $-\epsilon_i/2$ ($i = 1 \dots N$). The value of ϵ_i is a random quantity that is uniformly distributed between 0 and ϵ_0.

a) First consider a single two-level system. Use the canonical ensemble to find the partition function $Q_1(\epsilon, T)$, the internal energy $U_1(\epsilon, T)$, and the specific heat $C_1(\epsilon, T)$ as a function of ϵ and the temperature T.

b) Now consider the entire solid. Determine its total specific heat $C_{\text{tot}}(T)$ as a function of temperature for low but nonzero temperatures ($\epsilon_0 \gg k_B T$). The sum over the individual two-level systems can be replaced by an integral over their probability density, $\sum_{i=1}^N \to N \int d\epsilon\, P_\epsilon(\epsilon)$. (Hint: The condition $\epsilon_0 \gg k_B T$ can be used to simplify the bounds of the arising integral.)

c) (5pts BONUS:) Find the average value $\langle\epsilon\rangle$ of the energy ϵ. What would the specific heat be if all two-level systems had the same energy $\langle\epsilon\rangle$? Why does this differ from b)?

Problem 2: Dielectric gas (80 points)

Consider a gas of N noninteracting rod-shaped molecules with moment of inertia I and electrical dipole moment μ in a volume V. In the presence of an external electric field E (in the z-direction), the contribution of the rotational degrees of freedom to the single-particle Hamiltonian reads

$$H_{rot} = \frac{1}{2I}\left(p_\Theta^2 + \frac{p_\phi^2}{\sin^2\Theta}\right) - \mu E\cos(\Theta)$$

where Θ and ϕ are the usual polar and azimuthal angles and p_Θ and p_ϕ are the conjugate momenta.

a) Using the canonical ensemble, calculate the **rotational part** of the partition function of a single molecule. (Reminder: the phase space element in spherical coordinates is $d\Theta\, d\phi\, dp_\Theta\, dp_\phi/h^2$. There is no extra $\sin(\Theta)$ factor. This factor is produced by the integration over p_ϕ.)

b) Obtain the mean polarization $\langle\mu\cos(\Theta)\rangle$ of a single molecule.

c) The dielectric constant ϵ of a dielectric material is defined via $\epsilon E = \epsilon_0 E + P$ where $P = (N/V)\langle\mu\cos(\Theta)\rangle$ is the macroscopic polarization. Find the high-temperature behavior of ϵ (the leading correction to ϵ_0).

Problem 3: Adsorbed atoms in equilibrium with ideal gas (100 points)

a) Consider a classical ideal gas of $N \gg 1$ atoms (mass m) in a volume V. Use the canonical ensemble to calculate its chemical potential μ_{gas} as a function of temperature T and particle number density N/V.

b) Rewrite μ_{gas} as a function of pressure and temperature.

c) Now consider a single adsorption site on a solid surface. It can either be empty (energy 0) or occupied by a gas atom (energy $-\epsilon$ with $\epsilon > 0$). Use the grand-canonical ensemble to calculate the grand partition function of the adsorption site as a function of temperature T and chemical potential μ_{sf}.

d) Calculate the average number of atoms on the absorption site as a function of temperature T, and chemical potential μ_{sf}.

e) The gas and surface are brought into thermal and chemical equilibrium. Find the average number of atoms on the absorption site as a function of the pressure of the ideal gas and the temperature. Discuss the limits of vanishing and infinite pressure. (Hint: In chemical equilibrium the chemical potentials of the adsorbed atoms and the gas atoms are equal.)