PHYSICS 140A : STATISTICAL PHYSICS
HW ASSIGNMENT #5

(1) Consider a system composed of N spin tetramers, each of which is described by a Hamiltonian

$$\hat{H} = -J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) - K\sigma_1\sigma_2\sigma_3\sigma_4 - \mu_0 H(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \ .$$

The individual tetramers are otherwise noninteracting.

(a) Find the single tetramer partition function ζ. *Suggestion: construct a table of all the possible tetramer states and their energies.*

(b) Find the magnetization per tetramer $m = \mu_0\langle\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4\rangle$.

(c) Suppose the tetramer number density is $n_{\rm t}$. The magnetization density is $M = n_{\rm t} m$. Find the zero field susceptibility $\chi(T) = (\partial M/\partial H)_{H=0}$.

(2) Look up the relevant parameters for the HCl molecule and find the corresponding value of $\Theta_{\rm rot}$. Then compute the value of the rotational partition function $\xi_{\rm rot}(T)$ at $T = 300\,{\rm K}$, showing the contribution from each of the terms in eqn. 4.266 of the Lecture Notes.

(3) In a chemical reaction among σ species,

$$\zeta_1\,{\rm A}_1 + \zeta_2\,{\rm A}_2 + \cdots + \zeta_\sigma\,{\rm A}_\sigma = 0 \ ,$$

where ${\rm A}_a$ is a chemical formula and ζ_a is a stoichiometric coefficient. When $\zeta_a > 0$, the corresponding ${\rm A}_a$ is a *product*; when $\zeta_a < 0$, ${\rm A}_a$ is a *reactant*. (See §2.13.1 of the Lecture Notes.) The condition for equilibrium is

$$\sum_{a=1}^{\sigma} \zeta_a\,\mu_a = 0 \ ,$$

where μ_a is the chemical potential of the $a^{\rm th}$ species. The *equilibrium constant* for the reaction is defined as

$$\kappa(T,p) = \prod_{a=1}^{\sigma} x_a^{\zeta_a} \ ,$$

where $x_a = n_a \big/ \sum_{b=1}^{\sigma} n_b$ is the fraction of species a.

(a) Working in the grand canonical ensemble, show that

$$\kappa(T,p) = \prod_{a=1}^{\sigma} \left(\frac{k_{\rm B} T\,\xi_a(T)}{p\lambda_a^3}\right)^{\zeta_a} \ .$$

Note that the above expression does not involve any of the chemical potentials μ_a.

(b) Compute the equilibrium constant $\kappa(T, p)$ for the dissociative reaction $N_2 \rightleftharpoons 2\,N$ at $T = 5000\,K$, assuming the following: the characteristic temperature of rotation and that of vibration of the N_2 molecule are $\Theta_{rot} = 2.84\,K$ and $\Theta_{vib} = 3350\,K$. The dissociation energy, including zero point contributions, is $\Delta = 169.3\,\mathrm{kcal\,mol}^{-1}$. The electronic ground state of N_2 has no degeneracy, but that of the N atom is 4 due to electronic spin.