

PHYSICS 140A : STATISTICAL PHYSICS
HW ASSIGNMENT #5 SOLUTIONS

(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_t . The magnetization density is $M = n_t m$. Find the zero field susceptibility $\chi(T) = (\partial M / \partial H)_{H=0}$.

Solution :

(a) First, note that

$$-J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) = 2J - \frac{1}{2}J(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)^2 .$$

Next, construct a table, as in Tab. 1. We see that

$$\zeta = 2e^{\beta(6J+K)} \cosh(4\beta\mu_0 H) + 8e^{-\beta K} \cosh(2\beta\mu_0 H) + 6e^{-\beta(2J-K)} .$$

(b) We have

$$m = \frac{1}{\beta \zeta} \cdot \frac{\partial \zeta}{\partial H} = \frac{4\mu_0 e^{\beta(6J+K)} \sinh(4\beta\mu_0 H) + 8\mu_0 e^{-\beta K} \sinh(2\beta\mu_0 H)}{e^{\beta(6J+K)} \cosh(4\beta\mu_0 H) + 4e^{-\beta K} \cosh(2\beta\mu_0 H) + 3e^{-\beta(2J-K)}}$$

(c) In the limit $H \rightarrow 0$, we have

$$M(T, H) = n_t m(T, H) = \frac{16\beta\mu_0^2 e^{\beta(6J+K)} + 16\beta\mu_0^2 e^{-\beta K}}{e^{\beta(6J+K)} + 4e^{-\beta K} + 3e^{-\beta(2J-K)}} \cdot n_t ,$$

so

$$\chi(T) = \frac{16n_t\mu_0^2}{k_B T} \cdot \frac{e^{(6J+K)/k_B T} + e^{-K/k_B T}}{e^{(6J+K)/k_B T} + 4e^{-K/k_B T} + 3e^{-(2J-K)/k_B T}} .$$

Note that this expression reduces to $4n_t\mu_0^2/k_B T$ when $J = K = 0$, which is the limit of noninteracting spins.

$ \Psi\rangle$	E	$ \Psi\rangle$	E
$ \uparrow\uparrow\uparrow\uparrow\rangle$	$-6J - K - 4\mu_0H$	$ \uparrow\uparrow\uparrow\downarrow\rangle$	$K - 2\mu_0H$
$ \downarrow\downarrow\downarrow\downarrow\rangle$	$-6J - K + 4\mu_0H$	$ \uparrow\uparrow\downarrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\uparrow\downarrow\downarrow\rangle$	$2J - K$	$ \uparrow\downarrow\uparrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\downarrow\uparrow\downarrow\rangle$	$2J - K$	$ \downarrow\downarrow\uparrow\uparrow\rangle$	$K - 2\mu_0H$
$ \uparrow\downarrow\downarrow\uparrow\rangle$	$2J - K$	$ \downarrow\downarrow\uparrow\downarrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\uparrow\downarrow\rangle$	$2J - K$	$ \uparrow\downarrow\uparrow\uparrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\downarrow\uparrow\rangle$	$2J - K$	$ \uparrow\uparrow\downarrow\uparrow\rangle$	$K + 2\mu_0H$
$ \downarrow\downarrow\uparrow\uparrow\rangle$	$2J - K$	$ \uparrow\uparrow\uparrow\downarrow\rangle$	$K + 2\mu_0H$

Table 1: Energy table for problem 1.

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

Solution :

HCl is a diatomic molecule. Let the separation of the nuclei be d . From elementary mechanics, the moment of inertia about the CM is $I = \mu d^2$, where $\mu = m_{\text{H}}m_{\text{Cl}}/(m_{\text{H}} + m_{\text{Cl}})$ is the reduced mass. The molar mass of hydrogen is 1 g/mol, while that of chlorine is 35.5 g/mol. Thus, $\mu = 0.97$ g/mol. I find $d = 0.13$ nm via web sources. Thus, the temperature associated with rotations is

$$\Theta = \frac{\hbar^2}{2\mu d^2 k_{\text{B}}} = \frac{(1.055 \times 10^{-27} \text{ g cm}^2/\text{s})^2}{2 \cdot (0.97 \text{ g}/6.02 \times 10^{23}) \cdot (1.3 \times 10^{-8} \text{ cm})^2 \cdot 1.38 \times 10^{-16} \text{ erg/K}} = 15 \text{ K}.$$

The rotational partition function is

$$\xi_{\text{rot}} = \int_0^{\infty} dL (2L + 1) e^{-L(L+1)\Theta/T} = \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15} \frac{\Theta}{T} + \frac{4}{315} \left(\frac{\Theta}{T}\right)^2 + \dots,$$

where $\Theta = \hbar^2/2Ik_{\text{B}}$. At $T = 300$ K, $\Theta/T = 0.05$, and the above series yields

$$\xi_{\text{rot}} = 20 + 0.33333 + 0.0033333 + 0.0000317 + \dots = 20.336698 \dots$$

(3) In a chemical reaction among σ species,

$$\zeta_1 A_1 + \zeta_2 A_2 + \dots + \zeta_{\sigma} A_{\sigma} = 0,$$

where A_a is a chemical formula and ζ_a is a stoichiometric coefficient. When $\zeta_a > 0$, the corresponding A_a is a *product*; when $\zeta_a < 0$, 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^{th} species. The *equilibrium constant* for the reaction is defined as

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

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

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

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

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 $\text{N}_2 \rightleftharpoons 2\text{N}$ at $T = 5000\text{ K}$, assuming the following: the characteristic temperature of rotation and that of vibration of the N_2 molecule are $\Theta_{\text{rot}} = 2.84\text{ K}$ and $\Theta_{\text{vib}} = 3350\text{ K}$. The dissociation energy, including zero point contributions, is $\Delta = 169.3\text{ kcal mol}^{-1}$. The electronic ground state of N_2 has no degeneracy, but that of the N atom is 4 due to electronic spin.

Solution :

(a) In the GCE, we have

$$\Omega(T, V, \{\mu_a\}) = -k_B T V \sum_{a=1}^{\sigma} \lambda_a^{-3} e^{\mu_a/k_B T} \xi_a,$$

where $\lambda_a = (2\pi\hbar^2/m_a k_B T)^{1/2}$ the thermal wavelength for species a and $\xi_a(T)$ is the internal coordinate partition function for species a . We then have

$$n_a = -\frac{1}{V} \left(\frac{\partial \Omega}{\partial \mu_a} \right)_{T, V, \mu_{b \neq a}} = z_a \lambda_a^{-3} \xi_a,$$

where $z_a = e^{\mu_a/k_B T}$. OK, so we now define

$$x_a = \frac{n_a}{\sum_{b=1}^{\sigma} n_b} = \frac{z_a \lambda_a^{-3} \xi_a}{p/k_B T} = \frac{k_B T \xi_a z_a}{p \lambda_a^3},$$

since $\sum_b n_b = -\Omega/V k_B T = p/k_B T$. (Remember $\Omega = -pV$). Therefore

$$\begin{aligned} \kappa(T, p) &\equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a} \\ &= \prod_{a=1}^{\sigma} \left(\frac{k_B T \xi_a}{p \lambda_a^3} \right)^{\zeta_a} \cdot \prod_{a=1}^{\sigma} z_a^{\zeta_a}. \end{aligned}$$

However,

$$\prod_{a=1}^{\sigma} z_a^{\zeta_a} = \prod_{a=1}^{\sigma} e^{\zeta_a \mu_a / k_B T} = \exp\left(\frac{1}{k_B T} \sum_{a=1}^{\sigma} \zeta_a \mu_a\right) = 1,$$

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

(b) The internal partition function for N is just $\xi_N = (2S + 1)(2I + 1)$, where $S = \frac{3}{2}$ is the total electronic spin from Hund's rules, and $I = 1$ is the nuclear spin. It turns out that we will never need to know the value of I . For for N_2 the internal partition function is

$$\xi_{N_2} = (2I + 1)^2 \cdot \frac{T}{2\Theta_{\text{rot}}} \cdot \frac{e^{\Delta/T}}{1 - e^{-\Theta_{\text{vib}}/T}}.$$

This formula requires some explanation. We appeal to Eqs. 4.288 and 4.289 in the Lecture Notes. Since $T \gg \Theta_{\text{rot}}$, we have

$$\zeta_g \approx \zeta_u \approx \frac{1}{2} \int_0^{\infty} du e^{-u\Theta_{\text{rot}}/T} = \frac{T}{2\Theta_{\text{rot}}},$$

where the factor of $\frac{1}{2}$ comes from summing only over half the allowed L values, *i.e.* either all even or all odd, and where $u = L(L + 1)$ so $du = (2L + 1) dL$. We then have $\xi_{\text{rot}} = (2I + 1)^2 T / 2\Theta_{\text{rot}}$ because $g_g + g_u = (2I + 1)^2$. The vibrational partition function was derived to be $\xi_{\text{vib}} = \frac{1}{2} \text{csch}(\Theta_{\text{vib}}/2T)$, however since we are including the zero point vibrational energy $\frac{1}{2}\hbar\omega_{\text{vib}} = \frac{1}{2}k_B\Theta_{\text{vib}}$ in the dissociation energy, we get the above expression for ξ_{N_2} . According to our result from part (a), we have

$$\begin{aligned} \kappa(T, p) &= 32k_B\Theta_{\text{rot}} \cdot e^{-\Delta/T} \cdot (1 - e^{-\Theta_{\text{vib}}/T}) \cdot \frac{\lambda_{N_2}^3}{p\lambda_N^6} \\ &= 8\sqrt{2} \cdot \frac{k_B\Theta_{\text{rot}}}{p\lambda_N^3} \cdot e^{-\Delta/T} \cdot (1 - e^{-\Theta_{\text{vib}}/T}). \end{aligned}$$

Now we need to evaluate some quantities. The gas constant is

$$R = N_A k_B = 8.314 \text{ J/mol} \cdot \text{K} = 1.986 \times 10^{-3} \text{ kcal/mol} \cdot \text{K},$$

hence at $T = 5000 \text{ K}$, we have $\Delta/k_B T = 17.0$. Furthermore, $\Theta_{\text{vib}}/T = 0.670$. The thermal wavelength of N at this temperature is found to be

$$\lambda_N = \left(\frac{2\pi \cdot (1.055 \times 10^{-27} \text{ g cm}^2/\text{s})^2}{(14 \text{ g}/6.02 \times 10^{23}) \cdot (1.38 \times 10^{-16} \text{ erg/K}) \cdot 5000 \text{ K}} \right)^{1/2} = 6.60 \text{ \AA}.$$

We also have

$$\frac{k_B\Theta_{\text{rot}}}{p\lambda_N^3} = \frac{p_0}{p} \cdot \frac{(1.38 \times 10^{-16} \text{ erg/K}) \cdot (2.84 \text{ K})}{(1.013 \times 10^6 \text{ g/cm} \cdot \text{s}^2)(6.60 \times 10^{-8} \text{ cm})^3} = 1.35 p_0/p,$$

where $p_0 = 1.013 \times 10^5 \text{ Pa}$ is atmospheric pressure. Putting it all together, we obtain

$$\kappa(T = 5000 \text{ K}, p) = 3.09 \times 10^{-7} \cdot \frac{p_0}{p}.$$