PHYSICS 210A : EQUILIBRIUM STATISTICAL PHYSICS
HW ASSIGNMENT #3 SOLUTIONS

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

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

The individual tetramers are otherwise noninteracting.

(a) Find the single tetramer partition function ζ.

(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 $\chi(T) = (\partial M/\partial H)_{H=0}$.

Solution:

(a) Note that we can write

$$\hat{H} = 2J - \tfrac{1}{2}J(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)^2 - \mu_0 H\,(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \quad .$$

Thus, for each of the $2^4 = 16$ configurations of the spins of any given tetramer, only the sum $\sum_{i=1}^4 \sigma_i$ is necessary in computing the energy. We list the degeneracies of these states in the table below. Thus, according to the table, we have

$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$	degeneracy g	energy E
$+4$	1	$-6J - 4\mu_0 H$
$+2$	4	$-2\mu_0 H$
0	6	$-2J$
-2	4	$+2\mu_0 H$
-4	1	$-6J + 4\mu_0 H$

$$\zeta = 6\,e^{-2J/k_{\rm B}T} + 8\,\cosh\!\left(\frac{2\mu_0 H}{k_{\rm B}T}\right) + 2\,e^{6J/k_{\rm B}T}\,\cosh\!\left(\frac{4\mu_0 H}{k_{\rm B}T}\right) \quad .$$

(b) The magnetization per tetramer is

$$m = -\frac{\partial f}{\partial H} = k_{\rm B}T\,\frac{\partial \ln \zeta}{\partial H} = 4\mu_0 \cdot \frac{2\,\sinh(2\beta\mu_0 H) + e^{6\beta J}\sinh(4\beta\mu_0 H)}{3\,e^{-2\beta J} + 4\,\cosh(2\beta\mu_0 H) + e^{6\beta J}\cosh(4\beta\mu_0 H)} \quad .$$

(c) The zero field susceptibility is

$$\chi(T) = \frac{16\, n_\mathrm{t}\, \mu_0^2}{k_\mathrm{B}T} \cdot \frac{1+e^{6\beta J}}{3\,e^{-2\beta J}+4+e^{6\beta J}}$$

Note that for $\beta J \to \infty$ we have $\chi(T) = (4\mu_0)^2 n_\mathrm{t}/k_\mathrm{B}T$, which is the Curie value for a single Ising spin with moment $4\mu_0$. In this limit, all the individual spins are locked together, and there are only two allowed configurations for each tetramer: $|\uparrow\uparrow\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\downarrow\downarrow\rangle$. When $J=0$, we have $\chi = 4\mu_0^2 n_\mathrm{t}/k_\mathrm{B}T$, which is to say four times the single spin susceptibility. *I.e.* all the spins in each tetramer are independent when $J=0$. When $\beta J \to -\infty$, the only allowed configurations are the six ones with $\sum_{i=1}^4 \sigma_i = 0$. In order to exhibit a moment, an energy gap of $2|J|$ must be overcome, hence $\chi \propto \exp(-2\beta|J|)$, which is exponentially suppressed.

(2) A surface consisting of N_s adsorption sites is in thermal and particle equilibrium with an ideal monatomic gas. Each adsorption site can accommodate either zero particles (energy 0), one particle (two states, each with energy ε), or two particles (energy $2\varepsilon + U$).

(a) Find the grant partition function of the surface, $\Xi_\mathrm{surf}(T, N_\mathsf{s}, \mu)$. and the surface grand potential $\Omega_\mathrm{surf}(T, N_\mathsf{s}, \mu)$.

(b) Find the fraction of adsorption sites with are empty, singly occupied, and double occupied. Express your answer in terms of the temperature, the density of the gas, and other constants.

Solution:

(a) The grand partition function is

$$\Xi_\mathrm{surf}(T, N_\mathsf{s}, \mu) = \Big(1 + 2\,e^{\beta(\mu-\varepsilon)} + e^{\beta(2\mu-2\varepsilon-U)}\Big)^{N_\mathsf{s}} \quad ,$$

hence

$$\Omega_\mathrm{surf}(T, N_\mathsf{s}, \mu) = -k_\mathrm{B}T \ln \Xi_\mathrm{surf} = -N_\mathsf{s} k_\mathrm{B}T \ln\Big(1 + 2\,e^{\beta(\mu-\varepsilon)} + e^{\beta(2\mu-2\varepsilon-U)}\Big) \quad .$$

(b) Thermal and particle equilibrium with the gas means that the fugacities of the gas and surface are identical, and for the gas we have $z = n\lambda_T^3$. Thus,

$$\begin{aligned}
\nu_0 &= \frac{1}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_\mathrm{B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_\mathrm{B}T}} \\
\nu_1 &= \frac{2n\lambda_T^3\, e^{-\varepsilon/k_\mathrm{B}T}}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_\mathrm{B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_\mathrm{B}T}} \\
\nu_2 &= \frac{n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_\mathrm{B}T}}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_\mathrm{B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_\mathrm{B}T}} \quad .
\end{aligned}$$

(3) Consider the Hamiltonian below with $\mathcal{N}$ kinetic DOF, $\mathcal{N}_2$ quadratic potential DOF, and $\mathcal{N}_4$ quartic DOF, with $\mathcal{N} \geq \mathcal{N}_2 + \mathcal{N}_4$.

$$\hat{H} = \frac{1}{2}\sum_{i,j}^{\mathcal{N}} m_{ij}^{-1}\, p_i\, p_j + \frac{1}{2}\sum_{i=1}^{\mathcal{N}_2} K_i\, q_i^2 + \frac{1}{4}\sum_{j=\mathcal{N}_2+1}^{\mathcal{N}_2+\mathcal{N}_4} A_j\, q_j^4 \quad .$$

Find the free energy F and the internal energy E in terms of T, V, $\mathcal{N}$, $\mathcal{N}_2$, and $\mathcal{N}_4$. Assume the matrix m_{ij} is nondegenerate.

Solution:

If m_{ij} is nondegenerate, its rank is $\mathcal{N}$. By transforming to an eigenbasis, one finds

$$\int \prod_{l=1}^{\mathcal{N}} \frac{dp_l}{h}\, e^{-m_{ij}^{-1} p_i p_j / 2k_B T} = \left(\frac{k_B T}{2\pi\hbar^2}\right)^{\mathcal{N}/2} \sqrt{\det m} \quad .$$

As for the potential energy, we have

$$\int_{-\infty}^{\infty} dq\, e^{-Kq^2/2k_B T} = \left(\frac{2\pi k_B T}{K}\right)^{1/2}$$

and

$$\int_{-\infty}^{\infty} dq\, e^{-Aq^4/4k_B T} = \left(\frac{4k_B T}{A}\right)^{1/4} \int_{-\infty}^{\infty} du\, e^{-u^4} = \Gamma\big(\tfrac{5}{4}\big)\left(\frac{4k_B T}{A}\right)^{1/4} \quad ,$$

where $\Gamma\big(\frac{5}{4}\big) \approx 0.906402$. Thus, the partition function is

$$Z = C\, V^{\mathcal{N}-\mathcal{N}_2-\mathcal{N}_4}\, (k_B T)^{\frac{1}{2}(\mathcal{N}+\mathcal{N}_2)+\frac{1}{4}\mathcal{N}_4} \quad .$$

where

$$C \equiv \left(\frac{\sqrt{2}\,\Gamma\big(\frac{5}{4}\big)}{\hbar}\right)^{\mathcal{N}} \frac{\sqrt{\det m}}{\prod_i K_i^{1/2} \prod_j A_j^{1/4}} \quad .$$

The free energy is

$$F = -k_B T \ln Z = -k_B T \ln C - (\mathcal{N} - \mathcal{N}_2 - \mathcal{N}_4)\, k_B T \ln V - \big(\tfrac{1}{2}\mathcal{N} + \tfrac{1}{2}\mathcal{N}_2 + \tfrac{1}{4}\mathcal{N}_4\big)\, k_B T \ln(k_B T) \quad .$$

The energy follows from

$$E = \frac{\partial(\beta F)}{\partial \beta} = \big(\tfrac{1}{2}\mathcal{N} + \tfrac{1}{2}\mathcal{N}_2 + \tfrac{1}{4}\mathcal{N}_4\big)\, k_B T \quad .$$

(4) Consider a gas of classical spin-$\frac{3}{2}$ particles, with Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} - \mu_0 H \sum_i S_i^z \quad ,$$

where $S_i^z \in \{-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}\}$ and H is the external magnetic field. Find the Helmholtz free energy $F(T,V,H,N)$, the entropy $S(T,V,H,N)$, and the magnetic susceptibility $\chi(T,H,n)$, where $n = N/V$ is the number density.

Solution:

The partition function is

$$Z = \mathrm{Tr}\, e^{-\hat{H}/k_B T} = \frac{1}{N!} \frac{V^N}{\lambda_T^{dN}} \Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T) \Big)^N \quad ,$$

so

$$F = -N k_B T \ln\!\left(\frac{V}{N\lambda_T^d}\right) - N k_B T - N k_B T \ln\Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T) \Big) \quad ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/m k_B T}$ is the thermal wavelength. The entropy is

$$\begin{aligned} S = -\left(\frac{\partial F}{\partial T}\right)_{V,N,H} &= N k_B \ln\!\left(\frac{V}{N\lambda_T^d}\right) + (\tfrac{1}{2}d + 1) N k_B + N \ln\Big(2\cosh(\mu_0 H/2k_B T) + 2\cosh(3\mu_0 H/2k_B T) \Big) \\ &\quad - \frac{\mu_0 H}{2T} \cdot \frac{\sinh(\mu_0 H/2k_B T) + 3\sinh(3\mu_0 H/2k_B T)}{\cosh(\mu_0 H/2k_B T) + \cosh(3\mu_0 H/2k_B T)} \quad . \end{aligned}$$

The magnetization is

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,V,N} = \tfrac{1}{2} N \mu_0 \cdot \frac{\sinh(\mu_0 H/2k_B T) + 3\sinh(3\mu_0 H/2k_B T)}{\cosh(\mu_0 H/2k_B T) + \cosh(3\mu_0 H/2k_B T)} \quad .$$

The magnetic susceptibility is

$$\chi(T,H,n) = \frac{1}{V}\left(\frac{\partial M}{\partial H}\right)_{T,V,N} = \frac{n\mu_0^2}{4k_B T}\, f(\mu_0 H/2k_B T)$$

where

$$f(x) = \frac{d}{dx}\left(\frac{\sinh x + 3\sinh(3x)}{\cosh x + \cosh(3x)}\right) \quad .$$

In the limit $H \to 0$, we have $f(0) = 5$, so $\chi = 4n\mu_0^2/4k_B T$ at high temperatures. This is a version of Curie's law.