PHYSICS 210A : EQUILIBRIUM STATISTICAL PHYSICS
HW ASSIGNMENT #2 SOLUTIONS

(1) Consider a single classical anharmonic oscillator with the Hamiltonian

$$h = \frac{p^2}{2m} + V(q)$$

with $V(q) = \frac{1}{2}\kappa q^2 - \frac{1}{3}bq^3 + \frac{1}{4}uq^4$.

(a) Write down an expression for the partition function $\zeta(T)$. You may do the p integral exactly, but you will have to leave the rest of the expression in the form of an integral over q.

(b) At low temperatures, the amplitude of the thermal oscillations is small. This means that you may perturb in the coefficients b and u. Find the free energy up to terms of order T^2.

(c) Write down an expression for the heat capacity $c(T)$ valid to first order in T.

Solution:

(a) We have

$$\zeta(T) = \mathrm{Tr}\, e^{-\beta h} = h^{-1}\sqrt{2\pi m k_{\mathrm{B}} T} \int\limits_{-\infty}^{\infty} dq\, e^{-\beta V(q)} \quad .$$

(b) We have

$$\int\limits_{-\infty}^{\infty} dq\, e^{-\kappa q^2/2k_{\mathrm{B}}T}\, q^{2n} = \left(\frac{2\pi k_{\mathrm{B}} T}{\kappa}\right)^{1/2} \frac{(2n)!}{2^n\, n!} \left(\frac{k_{\mathrm{B}} T}{\kappa}\right)^n \quad .$$

Thus,

$$f(T) = -k_{\mathrm{B}} T \ln\left(\sqrt{\frac{m}{2\pi\kappa\hbar^2}}\, k_{\mathrm{B}} T\right) - k_{\mathrm{B}} T \left(\frac{3uk_{\mathrm{B}} T}{4\kappa^2} + \frac{5b^2 k_{\mathrm{B}} T}{4\kappa^3 2}\right) + \mathcal{O}(T^3) \quad .$$

(c) We have

$$c_V(T) = -T\,\frac{\partial^2 f}{\partial T^2} = k_{\mathrm{B}} \left\{1 + \left(\frac{3u}{2\kappa^2} + \frac{5b^2}{2\kappa^3}\right) k_{\mathrm{B}} T + \ldots\right\} \quad .$$

(2) A nonlinear quantum oscillator has the Hamiltonian

$$h = \hbar\omega(n + \tfrac{1}{2}) + \lambda\hbar\omega(n + \tfrac{1}{2})^2 \quad .$$

Here λ is the dimensionless anharmonicity.

(a) Find the partition function $\zeta(u,\lambda)$ to first order in λ, where $u \equiv \hbar\omega/k_{\rm B}T$.

(b) Find the heat capacity to the same order in λ.

Solution:

(a) Let $u = \hbar\omega/k_{\rm B}T$. Then

$$\begin{aligned}\zeta(u,\lambda) &= \sum_{n=0}^{\infty} e^{-u(n+\frac{1}{2})}\, e^{-\lambda u(n+\frac{1}{2})^2} \\ &= \left(1 - \lambda u \frac{\partial^2}{\partial u^2} + \ldots\right) \frac{1}{2\sinh(u/2)} \\ &= \frac{1}{2\sinh(u/2)} \left(1 - \tfrac{1}{2}\lambda u - \frac{\lambda u}{\sinh^2(u/2)} + \ldots\right) \quad .\end{aligned}$$

(b) The heat capacity is given by

$$\begin{aligned}c_V &= -T\,\frac{\partial^2 f}{\partial T^2} = -k_{\rm B}\beta^2\,\frac{\partial^2(\beta f)}{\partial \beta^2} \\ &= k_{\rm B}\left[\frac{\alpha^2}{\sinh^2\alpha} + \frac{8\lambda\alpha^2\cosh\alpha}{\sinh^3\alpha} - \frac{8\lambda\alpha^3}{\sinh^2\alpha} - \frac{12\lambda\alpha^3}{\sinh^4\alpha} + \mathcal{O}(\lambda^2)\right] \quad ,\end{aligned}$$

with $\alpha = \frac{1}{2}u = \frac{\hbar\omega}{2k_{\rm B}T}$.

(3) Consider a one-dimensional system of free identical nonrelativistic particles of mass m, each of which is endowed with an internal degree of freedom S which takes on values $S \in \{-1, 0, 1\}$. The Hamiltonian is

$$H = \sum_{j=1}^{N} \left(\frac{p_j^2}{2m} - hS_j\right) \quad ,$$

where h is a magnetic field (with dimensions of energy). The linear dimension of the system is L.

(a) Find the Helmholtz free energy $F(T, L, N, h)$.

(b) Find the magnetic susceptibility $\chi_{MM} = \frac{1}{L}\frac{\partial M}{\partial h}$, where $\hat{M} = \sum_j S_j$ is the magnetization operator and $M = \langle \hat{M} \rangle$. Do not set $h = 0$ at the end of the calculation.

(c) Define the operator $\hat{Q} = \sum_{j=1}^{N} S_j\, p_j$. Let λ be the conjugate force. Find the susceptibility $\chi_{QQ}(T, h=0, \lambda=0)$.

(d) Working in the grand canonical ensemble, find an expression for $\Omega(T, L, \mu, h, \lambda)$.

(e) What is the lowest order term in h and λ which contributes to the cross-susceptibility $\chi_{QM} = -\frac{1}{L}\frac{\partial^2\Omega}{\partial h\,\partial\lambda}$?

Solution:

(a) The single particle partition function is

$$\zeta(T,L,h) = \sum_{S=-1}^{1} \int_0^L dq \int_0^\infty \frac{dp}{h}\, e^{-\beta p^2/2m}\, e^{\beta h S}$$
$$= \frac{L}{\lambda_T} \sum_{S=-1}^{1} e^{\beta h S} = \frac{L}{\lambda_T}\big(1 + 2\cosh(\beta h)\big) \quad ,$$

with $\lambda_T = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal wavelength. The Helmholtz free energy is then $F = -k_B T \ln Z$ with $Z = \zeta^N/N!$, hence

$$F(T,L,N,h) = -Nk_B T \ln\!\left(\frac{L}{N\lambda_T}\right) - Nk_B T - Nk_B T \ln\!\left(1 + e^{h/k_B T} + e^{-h/k_B T}\right) \quad .$$

(b) Here we may set $\lambda = 0$ but we are asked to keep h finite. We have

$$M = -\frac{\partial F}{\partial h}\bigg|_{\lambda=0} = \frac{2N\sinh(\beta h)}{1 + 2\cosh(\beta h)} \quad .$$

The magnetic susceptibility is then

$$\chi_{MM} = \frac{1}{L}\frac{\partial M}{\partial h} = \frac{2n}{k_B T} \cdot \frac{4 + 2\cosh(h/k_B T)}{\big(1 + 2\cosh(h/k_B T)\big)^2} \quad ,$$

where $n = N/L$ is the number density.

(c) Now we have

$$\zeta(T,L,h,\lambda) = \sum_{S=-1}^{1} \int_0^L dq \int_0^\infty \frac{dp}{h}\, e^{-\beta p^2/2m}\, e^{\beta h S}\, e^{\beta\lambda S p}$$
$$= \frac{L}{\lambda_T} \sum_{S=-1}^{2} e^{\beta h S}\, e^{\beta m \lambda^2 S^2/2} = \frac{L}{\lambda_T}\big(1 + 2\, e^{\beta m\lambda^2/2}\, \cosh(\beta h)\big) \quad ,$$

and

$$F(T,L,N,h,\lambda) = -Nk_B T \ln\!\left(\frac{L}{N\lambda_T}\right) - Nk_B T$$
$$- Nk_B T \ln\!\left(1 + e^{m\lambda^2/2k_B T}\, e^{h/k_B T} + e^{m\lambda^2/2k_B T}\, e^{-h/k_B T}\right) \quad .$$

Note that we have added a term $\Delta H = -\lambda \sum_j S_j\, p_j$ to the Hamiltonian. We now set $h = 0$, and since we also set $\lambda = 0$ at the end of our calculation, we only need to evaluate the free energy to order λ^2, which is $F = F_0 - \frac{1}{3} N m \lambda^2 + \mathcal{O}(\lambda^4)$. Thus $\chi_{QQ}(T, h = 0, \lambda = 0) = \frac{2}{3} n m$.

(d) From $\Xi = e^{-\beta\Omega} = \sum_{N=0}^{\infty} \zeta^N e^{N\beta\mu}/N! = \exp(\zeta e^{\beta\mu})$, we have

$$\Omega(T, L, \mu, h, \lambda) = -L\, k_B T\, \lambda_T^{-1} \left(1 + 2\cosh(h/k_B T)\, e^{m\lambda^2/2k_B T}\right) e^{\mu/k_B T} \quad .$$

(e) We expand Ω in h and λ to obtain

$$\Omega = -L\, k_B T\, \lambda_T^{-1}\, e^{\mu/k_B T} \left(1 + \frac{m\lambda^2}{k_B T} + \frac{h^2}{(k_B T)^2} + \frac{m^2\lambda^4}{8(k_B T)^2} + \frac{m h^2 \lambda^2}{4(k_B T)^3} + \frac{m^3 \lambda^6}{48 (k_B T)^3} + \ldots \right) \quad .$$

The first term which survives the operator $\partial^2/\partial h\, \partial\lambda$ is the term of order $h^2\lambda^2$. Thus, we have $\chi_{QM}(T, \mu, h, \lambda) = h\lambda \cdot m\lambda_T^{-1}\, e^{\mu/k_B T}/(k_B T)^2 + \ldots$, which is of order $h\lambda$. Note that we have computed here the susceptibility *at fixed chemical potential*. Were we to compute it at fixed *density*, we would need to work from the Helmholtz free energy F and not the grand potential Ω. Typically under experimental conditions, it is n which is fixed rather than μ.

(4) Atoms and ions with partially filled shells experience a magnetic field according to the effective Hamiltonian

$$H_{\text{eff}} = g_L \mu_B\, \boldsymbol{J} \cdot \boldsymbol{H}/\hbar \quad ,$$

where $\mu_B = e\hbar/2mc$ is the Bohr magneton (m is the electron mass), J is the total angular momentum, and

$$g_L = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

is the Landé g-factor.

(a) For a gas or solution of N such objects in a volume V, find an expression for the magnetization density, $m = \frac{M}{V} = -\frac{N}{V}\frac{\partial F}{\partial H}$ at finite H and T. Show that $m = n\gamma J B_J(J\gamma H/k_B T)$, where $n = N/V$, $\gamma = g_L \mu_B$, and $B_J(x)$ is a function called the *Brillouin function*. Find and sketch $B_J(x)$ for a few different values of J.

(b) Taking the limit $H \to 0$, you should find $m = \chi H$, where $\chi(T)$ is the magnetic susceptibility. Find $\chi(T)$.

Solution:

(a) The partition function is

$$Z = e^{-F/k_B T} = \sum_{j=-J}^{J} e^{-j\gamma H/k_B T} = \frac{\sinh\left((J + \frac{1}{2})\gamma H/k_B T\right)}{\sinh\left(\gamma H/2k_B T\right)} \,.$$

The magnetization density is

$$M = -\frac{N}{V}\frac{\partial F}{\partial H} = n\gamma J \, B_J(J\gamma H/k_B T) \, ,$$

where $B_J(x)$ is the *Brillouin function*,

$$B_J(x) = \left(1 + \tfrac{1}{2J}\right) \operatorname{ctnh}\left[\left(1 + \tfrac{1}{2J}\right)x\right] - \tfrac{1}{2J} \operatorname{ctnh}(x/2J) \, .$$

The magnetic susceptibility is thus

$$\begin{aligned}\chi(H,T) &= \frac{\partial M}{\partial H} = \frac{nJ^2\gamma^2}{k_B T} \, B_J'(J\gamma H/k_B T) \\ &= (Jg_L)^2 \, (na_B^3) \, (e^2/\hbar c)^2 \left(\frac{e^2/a_B}{k_B T}\right) B_J'(g\mu_B JH/k_B T) \quad .\end{aligned}$$

(b) At $H = 0$,

$$\chi(H=0,T) = \tfrac{1}{3}(g_L \mu_B)^2 \, n \, \frac{J(J+1)}{k_B T} \quad .$$

The inverse temperature dependence is known as *Curie's law*.

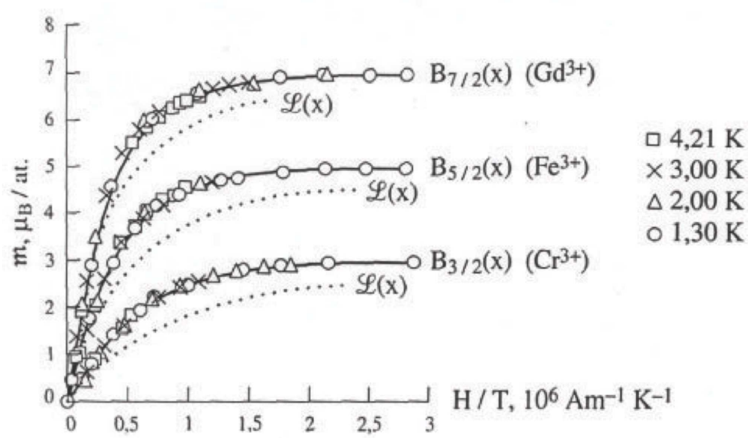

Figure 1: Reduced magnetization curves for three paramagnetic salts and comparison with Brillouin theory predictions. $\mathcal{L}(x) = B_{J\to\infty}(x) = \operatorname{ctnh}(x) - x^{-1}$ is the Langevin function.