

# Solutions to Pathria's Statistical Mechanics

## Chapter 3

SM-at-THU

March 20, 2016

**Problem 3.1**

**Problem 3.2**

**Problem 3.3**

**Problem 3.4**

**Problem 3.5**

Since the Helmholtz free energy  $A(N, V, T)$  has the property:

$$A(\lambda N, \lambda V, T) = \lambda A(N, V, T)$$

Differentiate with respect to  $\lambda$  and substitute  $\lambda = 1$  immediately yields

$$N \left( \frac{\partial A}{\partial N} \right)_{V,T} + V \left( \frac{\partial A}{\partial V} \right)_{N,T} = A$$

### Problem 3.6

### Problem 3.7

$$\begin{aligned}
 C_p - C_V &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_V \\
 &= \left(\frac{\partial(E + pV)}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_V \\
 &= p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial E}{\partial V}\right)_\beta \left(\frac{\partial V}{\partial T}\right)_p \\
 &= \left(\frac{\partial V}{\partial T}\right)_p \left(p + \left(\frac{\partial E}{\partial V}\right)_\beta\right) \\
 &= -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} \left(p - \frac{\partial^2 \ln Q}{\partial \beta \partial V}\right) \\
 &= -\frac{k\left(\beta \frac{\partial^2 \ln Q}{\partial \beta \partial V} - \frac{\partial \ln Q}{\partial V}\right)^2}{\left(\frac{\partial^2 \ln Q}{\partial V^2}\right)_\beta} \\
 &= \text{desired formula.}
 \end{aligned}$$

As for classical ideal gas,  $\left(\frac{\partial E}{\partial V}\right)_\beta = 0$ ,  $pV = NkT$ , we soon get that the above result is  $Nk$ .

### Problem 3.8

For classical ideal gas

$$\begin{aligned}
 \ln\left(\frac{Q_1}{N}\right) + T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P &= \ln\left\{\frac{V}{h^3 N}(2\pi mkT)^{3/2}\right\} + T\frac{\partial}{\partial T} \ln\left\{\frac{N}{h^3 P}(2\pi m)^{3/2}(kT)^{3/5}\right\} \\
 &= \ln\left\{\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2} \\
 &= \frac{S}{Nk}
 \end{aligned}$$

### Problem 3.9

For an ideal monatomic gas, its heat capacity  $C$  would be  $3R/2$ . While assume the whole process is quasistatic, it would obey

$$pV = RT$$

$$dU = -pdV + dQ = CdT$$

So we can get

$$\frac{5}{2}pdV + \frac{3}{2}Vdp = dQ$$

For adiabatical process,  $dQ=0$ , so the ratio of the final pressure to initial pressure would be

$$\frac{p_f}{p_i} = (1/2)^{5/3}$$

For the process with heat, the equation is difficult to solve, but naively thinking, for a process that the pressure doesn't change, it need heat to be added, so the final pressure would be higher than adiabatical process.

### Problem 3.11

Suppose  $pV^n = C$ , so the work done is

$$\Delta W = \int_{V_1}^{V_2} \frac{C}{V^n} dV = \frac{C}{n-1} (V_2^{1-n} - V_1^{1-n}) \quad (1)$$

The energy difference is given by

$$\Delta U = p_2 V_2 - p_1 V_1 = C(V_2^{1-n} - V_1^{1-n}) \quad (2)$$

Therefore, the heat absorbed is

$$\Delta Q = C \frac{n-2}{n-1} (V_2^{1-n} - V_1^{1-n}) \quad (3)$$

### Problem 3.12

The Hamiltonian of the classical system can be written as:

$$H = \sum_i^N \frac{\mathbf{p}_i^2}{2m} + \sum_i^N U(\mathbf{x}_i) \quad (4)$$

So the partition function of the system is:

$$\begin{aligned} Q(\beta, N, V) &= \frac{1}{N! h^{3N}} \int \prod_{i=1}^N d^3 x_i d^3 p_i e^{-\beta H(x, p)} \\ &= \frac{1}{N!} \left[ \left( \frac{2\pi m \beta^{-1}}{h^2} \right)^{3N/2} \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right] \end{aligned} \quad (5)$$

So the Helmholtz potential is  $A = -kT \ln Q$  and the entropy  $S$  is the derivative of free energy:

$$\begin{aligned} S &= -\frac{\partial A}{\partial T} \\ &= -\frac{\partial}{\partial T} \left\{ -kT \ln \left[ \frac{1}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{3N/2} \left( \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right) \right] \right\} \\ &= -\frac{\partial}{\partial T} \left\{ -NkT \ln \left[ \frac{1}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \left( \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] - NkT \right\} \\ &= Nk \ln \left[ \frac{1}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \left( \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] + \frac{3}{2} Nk + \frac{1}{T} \frac{\int \prod_i d^3 x_i \sum_i U(\mathbf{x}_i) e^{-\beta U(\mathbf{x}_i)}}{\int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)}} + Nk \\ &= \frac{5Nk}{2} + Nk \ln \left[ \frac{1}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \left( \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] + \frac{\bar{U}}{T} \\ &= \frac{5Nk}{2} + Nk \ln \left[ \frac{1}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} e^{\frac{\bar{U}}{NkT}} \left( \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] \\ &= Nk \left\{ \frac{5}{2} + \ln \left[ \frac{\bar{V}}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right] \right\} \end{aligned} \quad (6)$$

Up till now we have shown the entropy of such a system. So if the potential energy is just a constant, the “free volume” is the common volume of classical ideal gas.

Then consider about the hard sphere gas. The potential energy is:

$$U(\mathbf{x}_i) = \begin{cases} 0 & |\mathbf{x}_i - \mathbf{x}_j| > D \\ \infty & |\mathbf{x}_i - \mathbf{x}_j| < D \end{cases}$$

It is obvious that the average of potential energy is  $\bar{U} = 0$ , so the free volume is

$$\begin{aligned} \bar{V}^N &= \int \prod_i d^3 x_i e^{-\beta U(\mathbf{x}_i)} \\ &= \int d^3 x_N \int d^3 x_{N-1} \cdots \int d^3 x_1 e^{-\beta U(\mathbf{x}_i)} \\ &= V \left( V - \frac{4\pi}{3} D^3 \right) \left( V - 2 \cdot \frac{4\pi}{3} D^3 \right) \cdots \left( V - \frac{N-1}{3} 4\pi D^3 \right) \end{aligned} \quad (7)$$

Define  $v_0 = \pi D^3/6$  is the volume a sphere, so the gas-law will be:

$$\begin{aligned} P &= \frac{NkT}{\bar{V}} \frac{\partial \bar{V}}{\partial V} \\ &= kT \left( \frac{1}{V} + \frac{1}{V-8v_0} \cdots \frac{1}{V+8(N-1)v_0} \right) \\ &\simeq kT \left( \frac{N + N^2 \frac{4v_0}{V}}{V} \right) \\ &= kT \frac{N}{V \frac{1}{1+4Nv_0/V}} \\ &\simeq \frac{NkT}{V - 4Nv_0} \end{aligned} \quad (8)$$

This result is the same as we have seen in Problem 1.4.

### Problem 3.13

(a) Use classical method, it is easy to get partition function.

$$Q_N = \frac{1}{N_1! N_2!} \left[ \frac{V}{h^3} (2\pi m_1 kT)^{\frac{3}{2}} \right]^{N_1} \left[ \frac{V}{h^3} (2\pi m_2 kT)^{\frac{3}{2}} \right]^{N_2}$$

For the same reason. We get the partition function of another system:

$$Q_N = \frac{1}{(N_1 + N_2)!} \left[ \frac{V}{h^3} (2\pi m kT)^{\frac{3}{2}} \right]^{N_1 + N_2}$$

$m$  is mixed mass.

$$m = \frac{N_1 m_1 + N_2 m_2}{N_1 + N_2}$$

### Problem 3.15

We have  $Q_1(V, T) = \int g(\epsilon) e^{-\beta\epsilon} d\epsilon$ . For 3-D extreme relativistic gas,  $\epsilon = pc$ , hence we have

$$\begin{aligned} g(p)dp &= \frac{V}{h^3} 4\pi p^2 dp = \frac{4\pi V}{h^3} \frac{\epsilon^2}{c^2} \frac{d\epsilon}{c} = g(\epsilon) d\epsilon \\ \therefore g(\epsilon) &= \frac{4\pi V}{(hc)^3} \epsilon^2 \\ \therefore Q_1(V, T) &= \int_0^\infty g(\epsilon) d\epsilon = \frac{4\pi V}{(hc)^3} \int_0^\infty \epsilon^2 e^{-\beta\epsilon} d\epsilon = 8\pi V \left( \frac{kT}{hc} \right)^3 \end{aligned}$$

$\therefore$  for  $N$  molecules,

$$Q_N(V, T) = \frac{1}{N!} \left\{ 8\pi V \left( \frac{kT}{hc} \right)^3 \right\}^N$$

From  $Q_N(V, T)$ , it's easy to calculate:

$$\begin{aligned} P &= \frac{1}{\beta} \frac{\partial Q}{\partial V} = \frac{N}{V} kT \\ U &= -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = 3NkT \\ \gamma &= \frac{4}{3} \end{aligned}$$

As stated in section 3.4,  $g(E)$  can be obtained from the inverse Laplace transform, i.e.,

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta) d\beta$$

in our case,  $Q(\beta) = Q_N(V, T)$ , hence

$$\begin{aligned} g(E) &= \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta) d\beta \\ &= \frac{(8\pi V)^N}{N!(hc)^{3N}} \text{Res} \left[ \frac{e^{\beta E}}{\beta^{3N}} \right]_{\beta=0} \\ &= \frac{(8\pi V)^N E^{3N-1}}{N!(3N-1)!(hc)^{3N}} \end{aligned}$$

### Problem 3.16

We can get the partition function of the system by utilizing equation (3.5.5):

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q, p)} d\omega \quad (9)$$

Since the particles in this system obey the energy-momentum relationship  $\epsilon = pc$ , and the particles can only move in one dimension, equation.(9) becomes:

$$Q_N(L, T) = \frac{1}{(3N)! h^{3N}} \int e^{-\beta |p|c} d^{3N} p d^{3N} x \quad (10)$$

Then we can get the partition function:

$$Q_N(V, T) = \frac{1}{(3N)!} \left[ 2L \frac{kT}{hc} \right]^{3N} \quad (11)$$

And we can study the thermodynamics of this system:

$$P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial L} = \frac{3N}{V} kT$$

$$U = -\frac{\partial \ln Q}{\partial \beta} = 3NkT$$

$$\gamma = \frac{4}{3}$$

Using the inversion formula (3.4.7), we can derive an expression of the density of states  $g(E)$ . From equation (3.4.7):

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta) d\beta$$

$$= \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} \frac{1}{(3N)!} \left[ \frac{2L}{hc} \right]^{3N} \frac{e^{\beta E}}{\beta^{3N}} d\beta \quad (12)$$

Since the integrand have only one singularity,  $\beta = 0$ , we can calculate this integration by using Residue Theorem:

$$g(E) = \frac{1}{2\pi i} \frac{E^{3N-1}}{(3N)!} \left[ \frac{2L}{hc} \right]^{3N} \int_{\beta' - i\infty}^{\beta' + i\infty} \frac{e^{\beta E}}{(\beta E)^{3N}} d(\beta E)$$

$$= \frac{1}{2\pi i} \frac{E^{3N-1}}{(3N)!} \left[ \frac{2L}{hc} \right]^{3N} \int_{\beta' - i\infty}^{\beta' + i\infty} \frac{1}{(\beta E)^{3N}} \sum_{j=0}^{\infty} \frac{E^j}{j!} d(\beta E) \quad (13)$$

$$= \frac{1}{2\pi i} \frac{E^{3N-1}}{(3N)!(3N-1)!} \left[ \frac{2L}{hc} \right]^{3N}$$

### Problem 3.17

$$\int [U - H(p, q)] e^{-\beta H(p, q)} d\omega = 0$$

$$\Rightarrow \int \left[ \frac{\partial U}{\partial \beta} - H(p, q)U + H^2(p, q) \right] e^{-\beta H(p, q)} d\omega = 0$$

$$\Rightarrow \int \left[ \frac{\partial U}{\partial \beta} - U^2 + H^2(p, q) \right] e^{-\beta H(p, q)} d\omega = 0$$

$$\Rightarrow \langle H^2 \rangle - U^2 = -\frac{\partial U}{\partial \beta}$$

That is the desired equation.

### Problem 3.18

$$\begin{aligned} \langle (\Delta E)^3 \rangle &= \langle E^3 - 2E^2 \langle E \rangle + 2E \langle E \rangle^2 - \langle E \rangle^3 \rangle \\ &= \langle E^3 \rangle - 2\langle E^2 \rangle \langle E \rangle + \langle E \rangle^3 \end{aligned}$$

Considering the relations below

$$\begin{aligned}\langle E \rangle &= \frac{E_r \exp(-\beta E_r)}{\exp(-\beta E_r)} \\ \langle E^2 \rangle &= \frac{E_r^2 \exp(-\beta E_r)}{\exp(-\beta E_r)} \\ C_V &= \frac{\langle E^2 \rangle - \langle E \rangle^2}{kT^2} \\ k^2 \left\{ T^4 \left( \frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right\} &= -\frac{1}{\beta^2} \frac{\partial}{\partial \beta} \{ \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \} + \frac{2}{\beta} (\langle E^2 \rangle - \langle E \rangle^2)\end{aligned}$$

We have

$$\langle E^3 \rangle = k^2 \left\{ T^4 \left( \frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right\}$$

### Problem 3.19

$$< \frac{dG}{dt} > = < \sum p_i \frac{dq_i}{dt} > + < \sum q_i \frac{dp_i}{dt} > = 0$$

Above equation has used equation (3.7.5) and equation (3.7.6). The equation (3.7.5) and equation (3.7.6) both come from (3.7.2), so validity of one equation implies another's.

### Problem 3.21

(a) Classically, the harmonic equation of motion leads to  $x = A \sin \omega t$ . As a result, the kinetic energy and potential energy will be  $m\omega^2 A^2 \cos^2 \omega t / 2$  and  $m\omega^2 A^2 \sin^2 \omega t / 2$  respectively. Average them it's easy to see that  $\bar{K} = \bar{U} = m\omega^2 A^2 / 4$ .

Quantum-mechanically,  $\psi = \sum_n c_n \psi_n$  where  $\psi_n$  is the  $n$ -th Hermitian polynomial. Using the recursive relations, we have

$$\bar{K} = -\frac{\hbar^2}{2m} \sum_n |c_n|^2 \int \psi^* \frac{d^2}{dx^2} \psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2} \sum_n |c_n|^2 E_n \quad (14)$$

$$\bar{U} = \frac{m\omega^2}{2} \sum_n |c_n|^2 \int \psi^* x^2 \psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2} \sum_n |c_n|^2 E_n \quad (15)$$

(b) In Bohr-sommerfeld model, a quantized orbits are hypothesized, namely  $m_e v r = n\hbar$ . In the  $n$ -th orbit, the total energy is  $E_n = -Z^2 k^2 e^4 m_e / 2\hbar^2 n^2$ . The radius of which is  $r_n = n^2 \hbar^2 / Z k e^2 m_e$ . By a naive calculation  $\bar{U} = -Z^2 k^2 e^4 m_e / \hbar^2 n^2$  and  $\bar{T} = Z^2 k^2 e^4 m_e / 2\hbar^2 n^2$ .

In the Schroedinger hydrogen atom,  $\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi)$ . The kinetic energy is given by

$$\begin{aligned}\bar{T} &= \frac{\hbar^2}{2m} \int \psi_{nlm}^* \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) \psi_{nlm} r^2 \sin \theta dr d\theta d\phi \\ &= \frac{\hbar^2}{2m} \int R_{nl}(r) \left( \frac{1}{n^2 a^2} \right) R_{nl}(r) r^2 dr \\ &= \frac{e^2}{2an^2}\end{aligned} \quad (16)$$

so  $\bar{U} = -e^2 / an^2$ .  $a$  is the Bohr radius.

(c) This is also a central force case. The results are quite identical to (b).

## Problem 3.22

Anharmonic Oscillator.

This anharmonic oscillator has the Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{1}{4}kx^4$$

So the canonical partition function of the system is:

$$Q = \frac{1}{h} \int dp dx e^{-\beta \left( \frac{p^2}{2m} + \frac{1}{4}kx^4 \right)} \quad (17)$$

Use the “equipartition theorem”, we can get the following result:

$$\left\langle x \frac{\partial H}{\partial x} \right\rangle = kT \quad (18)$$

Thus because  $\partial H / \partial x = kx^3$ , we can get

$$x \frac{\partial H}{\partial x} = kx^4 = 4V$$

So the expectation value of the potential is  $\langle V \rangle = kT/4$ . For the same reason, we can get the mean value of the kinetic energy:

$$\langle K \rangle = \frac{1}{2} \left\langle p \frac{\partial H}{\partial p} \right\rangle = \frac{kT}{2} \quad (19)$$

So clearly we can get  $\langle K \rangle = 2\langle V \rangle$ .

## Problem 3.23

According to the equation 3.7.15

$$\frac{PV}{NkT} = 1 - \frac{1}{NdkT} * \sum_{i < j} \overline{\frac{\partial u(r_{ij})}{\partial r_{ij}}} r_{ij}$$

For the ideal gas. There is not interaction term.

$$PV = NkT$$

The Hamiltonian of the system happens to be a quadratic function of its coordinates. The virial theorem states that

$$\nu_0 = -3NkT$$

So we can infer that

$$\nu_0 = -3PV$$

Let's consider the interaction between the particles and walls of container.

$$\nu_0 = -P \int (\nabla \cdot \mathbf{r}) dV = -3PV$$

They show walls of container are the main factor interaction with particles.



### Problem 3.25

Consider a particle inside a box with  $\dot{q}_i$  and  $p_i$ , the volume of the box is  $V$ . If the particle hits an area  $\Delta S$  on a wall during time  $\Delta t$ , it has to be in volume  $\dot{q}_i \Delta S \Delta t$ . Also, the momentum  $p_i$  it has must be oriented to the wall, which gives a  $1/2$  coefficient to the probability. Hence the pressure on the wall satisfies

$$\left\langle \sum_N \frac{1}{2} \frac{\dot{q}_i \Delta S \Delta t}{V} \cdot 2p_i \right\rangle = P \Delta S \Delta t$$

$$i.e., \left\langle \sum_i p_i \dot{q}_i \right\rangle = 3PV, i = 1, \dots, 3N$$

From the equipartition theorem,  $\langle \sum_i p_i \dot{q}_i \rangle = 3NkT$ , hence

$$PV = NkT$$

for noninteracting systems.

### Problem 3.26

To calculate the multiplicity of an  $s$ -dimensional oscillator, we can write the energy eigenvalues in this form:

$$\epsilon_j = (j + s/2)\hbar\omega = \left( \sum_{i=1}^s n_i + s/2 \right) \hbar\omega \quad (20)$$

Where  $n_i$  is the “eigenvalues” of each dimension. And  $n_i$  can be a integer between 0 to  $j$ , just have to obey  $\sum_{i=1}^s n_i = j$ . So this problem is equivalent to putting  $s - 1$  “clapboards” between  $N$  particles. Hence we can get the multiplicity:

$$m_j = \frac{(j + s - 1)!}{j!(s - 1)!} \quad (21)$$

Then we can get the partition function of a single oscillator:

$$\begin{aligned} Q_1 &= \sum_j m_j \exp(-\beta \epsilon_j) \\ &= \frac{(j + s - 1)!}{j!(s - 1)!} \exp[-\beta(j + s/2)\hbar\omega] \\ &= \left[ \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \right]^s \end{aligned} \quad (22)$$

The partition function of a system of  $N$  oscillators is:

$$Q_N = Q_1^N = \left[ \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \right]^{sN} \quad (23)$$

We can study the thermodynamics of this system from equation.(23): And we can study the thermodynamics of this system:

$$\begin{aligned} U &= -\frac{\partial \ln Q_N}{\partial \beta} = sN \left[ \frac{1}{2} + \frac{1}{1 - \exp(-\beta\hbar\omega)} \right] \hbar\omega \\ \mu_s &= -\frac{1}{\beta} \frac{\partial \ln Q_N}{\partial N} = s \left[ \frac{\hbar\omega}{2} + \frac{\ln[1 - \exp(-\beta\hbar\omega)]}{\beta} \right] \end{aligned}$$

For a system of  $sN$  one-dimensional oscillators:

$$Q_{sN} = Q_1^s N = \left[ \frac{\exp(-\beta \hbar \omega / 2)}{1 - \exp(-\beta \hbar \omega)} \right]^{sN}$$

$$U = -\frac{\partial \ln Q_N}{\partial \beta} = sN \left[ \frac{1}{2} + \frac{1}{1 - \exp(-\beta \hbar \omega)} \right] \hbar \omega$$

$$\mu_1 = -\frac{1}{\beta} \frac{\partial \ln Q_N}{\partial sN} = \left[ \frac{\hbar \omega}{2} + \frac{\ln[1 - \exp(-\beta \hbar \omega)]}{\beta} \right]$$

And we have:

$$\mu_s = s\mu_1$$

### Problem 3.27

$$\begin{aligned} g(E) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{(\beta+i\gamma)(E-(N/2)\hbar\omega)} (1 - e^{-\hbar\omega(\beta+i\gamma)})^{-N} d\gamma \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{(\beta+i\gamma)(E-(N/2)\hbar\omega)} (1 + C_N^1 e^{-\hbar\omega(\beta+i\gamma)} + C_{N+1}^2 e^{-2\hbar\omega(\beta+i\gamma)} + C_{N+2}^3 e^{-3\hbar\omega(\beta+i\gamma)} + \dots) d\gamma \\ &= \sum_{k=0}^{\infty} \delta(E - (N/2)\hbar\omega - k\hbar\omega) C_{N+k-1}^k \end{aligned}$$

The above result is the same as that derived from direct state counting for  $N$  distinguishable quantum SHOs. Assume  $E = (m + N/2)\hbar\omega$ , then we have:

$$S = k \ln(g(E)dE) = k \ln(C_{N+m-1}^m)$$

while  $m \gg 1$ ,  $N \gg 1$ , using the Stirling formula we can find:

$$S \approx k(m \ln \frac{N+m-1}{m} + (N-1) \ln \frac{N+m-1}{N-1}) \approx Nk(\frac{m+N}{N} \ln \frac{m+N}{N} - \frac{m}{N} \ln \frac{m}{N})$$

which is the desired formula.

### Problem 3.28

a)

Define

$$R = \left( E - \frac{1}{2}N\hbar\omega \right) / \hbar\omega$$

Number of states available for the whole system is

$$m_0 = \frac{(R+N-1)!}{R!(N-1)!}$$

Number of states available for a particular oscillator in state  $n$

$$m = \frac{(R+N-1-n-1)!}{(R-n)!(N-1)!}$$

Probability

$$p_n = \frac{m}{m_0} = \frac{R(R-1) \cdots (R-n+1)(N-1)}{(R+N-1) \cdots (R+N-1-n-1)}$$

for  $N \gg 1$  and  $R \gg n$

$$p_n \approx \frac{(\bar{n})^n}{(\bar{n}+1)^{n+1}}$$

where  $\bar{n} = R/N$

**b)**

The number of states available for total energy  $E$  and  $N$  particles are

$$g(E, N) = \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \frac{(2\pi m)^{3N/2}}{(3N/2-1)!} E^{3N/2-1}$$

Probability

$$p = \frac{g(E-\epsilon, N-1)}{g(E, N)}$$

For  $N \ll 1$  and  $E \ll \epsilon$

$$p \propto \left( \frac{E-\epsilon}{E} \right)^{3N/2} \approx \exp(-\beta\epsilon)$$

where  $\beta = 3N/2E$ .

## Problem 3.29

I can't solve this problem. The integral of the unharmonic terms in the partition function is infinite.

## Problem 3.31

"Partition function" for single particle is

$$Q_1 = 1 + e^{-\epsilon/kT}. \quad (24)$$

So a list of quantities can be obtained:

$$Q_N = (1 + e^{-\epsilon/kT})^N \quad (25)$$

$$A = -NkT \ln(1 + e^{-\epsilon/kT}) \quad (26)$$

$$\mu = -kT \ln(1 + e^{-\epsilon/kT}) \quad (27)$$

$$p = 0 \quad (28)$$

$$S = Nk \ln(1 + e^{-\epsilon/kT}) + \frac{N\epsilon}{T} \frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \quad (29)$$

$$U = N\epsilon \frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}} \quad (30)$$

$$C_p = C_V = \frac{N\epsilon^2 e^{-\epsilon/kT}}{kT^2 (1 + e^{-\epsilon/kT})^2} \quad (31)$$

This specific heat is sometimes referred to *Schottky anomaly*.

### Problem 3.32

(a) Since the distribution is given by canonical distribution, the probabilities are:

$$p_i = Q^{-1} g_i e^{-\beta \epsilon_i}$$

and the entropy should be:

$$\begin{aligned}
 S &= -k [p_1 \ln(p_1/g_1) + p_2 \ln(p_2/g_2)] \\
 &= -k \left[ \frac{g_1 e^{-\beta \epsilon_1}}{Q} \ln \frac{e^{-\beta \epsilon_1}}{Q} + \frac{g_2 e^{-\beta \epsilon_2}}{Q} \ln \frac{e^{-\beta \epsilon_2}}{Q} \right] \\
 &= k \ln Q + \frac{1}{T} \frac{g_1 \epsilon_1 e^{-\beta \epsilon_1} + g_2 \epsilon_2 e^{-\beta \epsilon_2}}{Q} \\
 &= k \ln g_1 + k \ln \left( 1 + \frac{g_2}{g_1} e^{-x} \right) + \frac{1}{T} \frac{g_2 (\epsilon_2 - \epsilon_1) e^{-\beta \epsilon_2}}{Q} \\
 &= k \left[ \ln g_1 + \ln \left( 1 + \frac{g_2}{g_1} e^{-x} \right) + \frac{g_2 e^{-\beta \epsilon_2} x}{Q} \right] \\
 &= k \left[ \ln g_1 + \ln \left( 1 + \frac{g_2}{g_1} e^{-x} \right) + \frac{x}{1 + \frac{g_1}{g_2} e^x} \right]
 \end{aligned} \tag{32}$$

When  $g_1 = g_2 = 1$ , the situation is the same as Fermi oscillator with energy 0 and  $\epsilon_2 - \epsilon_1$ .

(b) The entropy is the derivative of the free energy, so we can get the entropy by the following process:

$$\begin{aligned}
 S &= -\frac{\partial A}{\partial T} \\
 &= \frac{\partial}{\partial T} \{kT \ln Q\} \\
 &= k \ln Q + \frac{1}{T} \frac{g_1 \epsilon_1 e^{-\beta \epsilon_1} + g_2 \epsilon_2 e^{-\beta \epsilon_2}}{Q} \\
 &= k \left[ \ln g_1 + \ln \left( 1 + \frac{g_2}{g_1} e^{-x} \right) + \frac{x}{1 + \frac{g_1}{g_2} e^x} \right]
 \end{aligned} \tag{33}$$

which is the same as we get in (a).

(c) Clearly from equation (32), when temperature is  $T = 0$ , the entropy will be:

$$S = \lim_{x \rightarrow +\infty} k \left[ \ln g_1 + \ln \left( 1 + \frac{g_2}{g_1} e^{-x} \right) + \frac{x}{1 + \frac{g_1}{g_2} e^x} \right] = k \ln g_1 \tag{34}$$

From the distribution of canonical ensemble, we know that when the temperature is  $T = 0$ , the system will stay on the ground state. Since the ground is  $g$ -fold degenerate, there are  $g_1$  possible states. So the entropy is  $S = k \ln g_1$ .

### Problem 3.33

Let's consider parameter  $\frac{\mu H}{kT}$ .

If you plot the Langevin's function:

$$L(x) = \coth(x) - \frac{1}{x}$$

You will find when  $\frac{\mu H}{kT} = 5.12$  magnetic moment is saturated.

### Problem 3.35

For  $\epsilon = \frac{p^2}{2m} + \left\{ \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right\} - \mu E \cos \theta$ , just calculate

$$\begin{aligned}
 Q &= \frac{1}{h^3} \int e^{-\beta \epsilon} d^3 p d^3 q \\
 &= \int_0^\infty \exp\left(-\frac{\beta p^2}{2m}\right) dp \int_0^\infty \exp\left(-\frac{\beta p_\theta^2}{2I}\right) dp_\theta \int_0^\infty \exp\left(-\frac{\beta p_\phi^2}{2I \sin^2 \theta}\right) dp_\phi \int \exp(-\mu E \cos \theta) dr d\theta d\phi \\
 &= \frac{2\pi I}{\beta} \sqrt{\frac{2\pi m}{\beta}} \int_0^R dr \int_0^\pi \sin \theta \exp(-\mu E \cos \theta) d\theta \int_0^{2\pi} d\phi \\
 &= \frac{4\pi^2 I R}{\beta} \sqrt{\frac{2\pi m}{\beta}} \frac{e^{\mu E} - e^{-\mu E}}{\mu E}
 \end{aligned}$$

$$\therefore Q_N = \frac{1}{N!} Q^N$$

Once  $Q_N$  is obtained, all thermodynamics of the system can be obtained. I forget the definition of electric polarization, etc. I hope you can obtain them from  $Q_N$  by yourself.

### Problem 3.37

Prof.Ni's ppt has given a detailed and complete solution to this problem. If someone regards it worthwhile I will renew this text later.

### Problem 3.38

As defined in the problem, we examine the partition function

$$\begin{aligned}
 Q_1(\beta) &= \int_{-J}^J \exp(\beta g \mu_B m H) \\
 &= \frac{1}{\beta g \mu_B H} (\exp(\beta g \mu_B J H) - \exp(-\beta g \mu_B J H))
 \end{aligned}$$

Choose  $x = \beta g \mu_B J H$

Thermal dynamic properties

$$\begin{aligned}
 \bar{\mu}_z &= \frac{1}{\beta} \frac{\partial}{\partial H} \ln Q_1(\beta) \\
 &= J^2 g \mu_B (\coth(x) - \frac{1}{x})
 \end{aligned}$$

### Problem 3.39

By using equation (3.9.18) we could get

$$Q = \sum_{m=-1/2}^{1/2} \exp(\beta g \mu_b m H) = \exp(-\beta g \mu_b H/2) (1 + \exp(\beta g \mu_b H))$$

The mean magnetic moment is

$$M = \frac{N}{\beta} \frac{\partial}{\partial H} \ln Q = \frac{1}{2} N \mu_b g \frac{1 - \exp(-\beta g \mu_b H)}{1 + \exp(-\beta g \mu_b H)}$$

While the number of parallel atoms  $N_+$  and antiparallel  $N_-$  satisfied that

$$\begin{cases} N_+ + N_- = N \\ (N_+ - N_-)g\mu_b J = M \\ J = 1/2 \end{cases} \quad (35)$$

So we could get the answer

$$\begin{cases} N_+/N = \frac{1}{1 + \exp(-\beta g \mu_b H)} \\ N_-/N = \frac{\exp(-\beta g \mu_b H)}{1 + \exp(-\beta g \mu_b H)} \end{cases} \quad (36)$$

According to the given situation, flux density 0.1 weber/m<sup>2</sup> and temperature of 1000K, the respective fractions are

$$\begin{cases} N_+/N = 50.00168\% \\ N_-/N = 49.99832\% \end{cases} \quad (37)$$

### Problem 3.41

The equilibrium temperature will be positive, since the energy of the whole system is not bounded from above. This case is a bit like the spin and lattice case. For the subsystem of spins, its energy is bounded from above, so it is possible to attain a negative temperature. While the subsystem of lattice, i.e. ideal gas in this problem, only has positive temperature. The whole system doesn't have a energy limit, so the temperature will only be positive. And energy may flow from the spin subsystem to the ideal gas.

### Problem 3.42

Paramagnetic system.

For a given energy  $E$ , we can know that:

$$E = \mu_B H (N_\uparrow - N_\downarrow) \quad (38)$$

$$N = N_\uparrow + N_\downarrow \quad (39)$$

So the occupying number of up(down)-spin is

$$N_\uparrow = \frac{1}{2} \left( N + \frac{E}{\mu_B H} \right) \quad N_\downarrow = \frac{1}{2} \left( N - \frac{E}{\mu_B H} \right)$$

And the number of the possible states will be:

$$\Omega(N, E) = C_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \quad (40)$$

So the entropy in micro canonical ensemble representation is:

$$\begin{aligned} S &= k \ln \Omega(E, N) \\ &= Nk \ln N - N_\uparrow k \ln N_\uparrow - N_\downarrow k \ln N_\downarrow \\ &= Nk \ln N - k \frac{N\mu_B H + E}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - k \frac{N\mu_B H - E}{2\mu_B H} \ln \frac{N\mu_B H - E}{2\mu_B H} \end{aligned} \quad (41)$$

This result is the same as (3.10.9) in Pathria's Book. Then the temperature:

$$\begin{aligned}
\frac{1}{T} &= \frac{\partial S}{\partial E} \\
&= -\frac{k}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - \frac{k}{2\mu_B H} + \frac{k}{2\mu_B H} \ln \frac{N\mu_B H - E}{2\mu_B H} + \frac{k}{2\mu_B H} \\
&= \frac{k}{2\mu_B H} \ln \left( \frac{N\mu_B H - E}{N\mu_B H + E} \right)
\end{aligned} \tag{42}$$

And this result is also the same as equation (3.10.8).

### Problem 3.43

The hamiltonian of the system is :

$$\begin{aligned}
H &= e\phi(\mathbf{q}) + \frac{1}{2m_e} \sum_{i=1}^N (\mathbf{P}_i - \frac{e}{c} \mathbf{A}_i)^2 \\
\dot{q}_i &= -\frac{\partial H}{\partial p_i} \propto p_i
\end{aligned}$$

On the other hand

$$\vec{\mu} = \frac{e}{2c} \vec{r} \times \vec{v} = \sum_{i=1}^N \vec{a}_i \cdot \dot{q}_i$$

$a_i$  are vector coefficients depending on the position coordinates.

$$\bar{\mu} = \frac{\int \mu * d\omega}{\int d\omega} \propto \int_{-\infty}^{+\infty} p * dp = 0$$

The integrand is an odd function of  $p$ , so it vanishes.