Solutions to Pathria's Statistical Mechanics
Chapter 3

SM-at-THU

March 18, 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 λ 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

Problem 3.9

For an ideal monaomic gas,its heat capacity C would be 3R/2.While asume the whole progress 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

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

The energy difference is given by

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

Therefore, the heat absorbed is

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

Problem 3.12

The Hamiltonian of the classical system can be written as:

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

So the partition function of the system is:

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

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

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

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 $\overline{U} = 0$, so the free volume is

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

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

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

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.

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

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

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

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

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

$\therefore$for N molecules,

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

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

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

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 $m\omega^2A^2\cos^2\omega t/2$ and $m\omega^2A^2\sin^2\omega t/2$ respectively. Average them it's easy to see that $\bar{K} = \bar{U} = m\omega^2A^2/4$.

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

$$\bar{K} = -\frac{\hbar^2}{2m}\sum_n |c_n|^2 \int \psi^* \frac{d^2}{dx^2}\psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{9}$$

$$\bar{U} = \frac{m\omega^2}{2}\sum_n |c_n|^2 \int \psi^* x^2 \psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{10}$$

(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 $E_n = -Z^2k^2e^4m_e/2\hbar^2n^2$. The radius of which is $r_n = n^2\hbar^2/Zke^2m_e$. By a naive calculation $\bar{U} = -Z^2k^2e^4m_e/\hbar^2n^2$ and $\bar{T} = Z^2k^2e^4m_e/2\hbar^2n^2$.
In the Schroedinger hydrogen atom, $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$. The kinetic energy is given by

$$\begin{aligned}
\bar{T} &= \frac{\hbar^2}{2m}\int \psi^*_{nlm}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2})\psi_{nlm} r^2 \sin\theta dr d\theta d\phi \\
&= \frac{\hbar^2}{2m}\int R_{nl}(r)(\frac{1}{n^2a^2})R_{nl}(r) r^2 dr \\
&= \frac{e^2}{2an^2}
\end{aligned} \tag{11}$$

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:

$$Q = \frac{1}{h}\int dp dx\, e^{-\beta\left(\frac{p^2}{2m} + \frac{1}{4}kx^4\right)} \tag{12}$$

Use the "equipartition theorem", we can get the following result:

$$\left\langle x\frac{\partial H}{\partial x}\right\rangle = kT \tag{13}$$

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:

$$\langle K\rangle = \frac{1}{2}\left\langle p\frac{\partial H}{\partial p}\right\rangle = \frac{kT}{2} \tag{14}$$

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

Problem 3.23

According to the equation 3.7.15

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

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

$$\boldsymbol{\nu_0} = -3NkT$$

So we can infer that

$$\boldsymbol{\nu_0} = -3PV$$

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

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

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

Problem 3.29

I can't solve this problem.The intergral of the unharnomic terms in the partition fuction is infinite.

Problem 3.31

"Partition function" for single particle is

$$Q_1 = 1 + e^{-\varepsilon/kT}. \tag{15}$$

So a list of quatities can be obtained:

$$Q_N = (1 + e^{-\varepsilon/kT})^N \tag{16}$$
$$A = -NkT \ln(1 + e^{-\varepsilon/kT}) \tag{17}$$
$$\mu = -kT \ln(1 + e^{-\varepsilon/kT}) \tag{18}$$
$$p = 0 \tag{19}$$
$$S = Nk \ln(1 + e^{-\varepsilon/kT}) + \frac{N\varepsilon}{T} \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \tag{20}$$
$$U = N\varepsilon \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \tag{21}$$
$$C_p = C_V = \frac{N\varepsilon^2 e^{-\varepsilon/kT}}{kT^2(1 + e^{-\varepsilon/kT})^2} \tag{22}$$

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:

$$\begin{aligned}
S &= -k\left[p_1 \ln(p_1/g_1) + p_2 \ln(p_2/g_2)\right] \\
&= -k\left[\frac{g_1 e^{-\beta\epsilon_1}}{Q}\ln\frac{e^{-\beta\epsilon_1}}{Q} + \frac{g_2 e^{-\beta\epsilon_2}}{Q}\ln\frac{e^{-\beta\epsilon_2}}{Q}\right] \\
&= k\ln Q + \frac{1}{T}\frac{g_1\epsilon_1 e^{-\beta\epsilon_1} + g_2\epsilon_2 e^{-\beta\epsilon_2}}{Q} \\
&= k\ln g_1 + k\ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{1}{T}\frac{g_2(\epsilon_2-\epsilon_1)e^{-\beta\epsilon_2}}{Q} \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{g_2 e^{-\beta\epsilon_2} x}{Q}\right] \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1 + \frac{g_1}{g_2}e^{x}}\right] \qquad (23)
\end{aligned}$$

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:

$$\begin{aligned}
S &= -\frac{\partial A}{\partial T} \\
&= \frac{\partial}{\partial T}\{kT\ln Q\} \\
&= k\ln Q + \frac{1}{T}\frac{g_1\epsilon_1 e^{-\beta\epsilon_1} + g_2\epsilon_2 e^{-\beta\epsilon_2}}{Q} \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1 + \frac{g_1}{g_2}e^{x}}\right] \qquad (24)
\end{aligned}$$

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

(c) Clearly from equation (23), when temperature is $T = 0$, the entropy will be:

$$S = \lim_{x\to+\infty} k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1 + \frac{g_1}{g_2}e^{x}}\right] = k\ln g_1 \qquad (25)$$

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 3.39

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

$$\begin{cases} \dot{N}_+ + N_- = N \\ (N_+ - N_-) g \mu_b J = M \\ J = 1/2 \end{cases} \tag{26}$$

So we could get the answer

$$\begin{cases} \dot{N}_+/N = \dfrac{1}{1 + \exp(-\beta g \mu_b H)} \\ N_-/N = \dfrac{\exp(-\beta g \mu_b H)}{1 + \exp(-\beta g \mu_b H)} \end{cases} \tag{27}$$

Acoording to the given situation,flux density 0.1 $weber/m^2$ and temperature of 1000K,the respective fractions are

$$\begin{cases} \dot{N}_+/N = 50.00168\% \\ N_-/N = 49.99832\% \end{cases} \tag{28}$$

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:

$$E = \mu_B H (N_\uparrow - N_\downarrow) \tag{29}$$
$$N = N_\uparrow + N_\downarrow \tag{30}$$

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:

$$\Omega(N, E) = \mathrm{C}_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{31}$$

So the entropy in micro canonical ensemble representation is:

$$
\begin{aligned}
S &= k \ln \Omega(E, N) \\
&= Nk \ln N - N_\uparrow k \ln N_\uparrow - N_\downarrow k \ln N_\downarrow \\
&= Nk \ln N - k \frac{N\mu_B H + E}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - k \frac{N\mu_B H - E}{2\mu_B H} \ln \frac{N\mu_B H - E}{2\mu_B H}
\end{aligned}
\tag{32}
$$

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

$$
\begin{aligned}
\frac{1}{T} &= \frac{\partial S}{\partial E} \\
&= -\frac{k}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - \frac{k}{2\mu_B H} + \frac{k}{2\mu_B H} \ln \frac{N\mu_B H - E}{2mu_B H} + \frac{k}{2\mu_B H} \\
&= \frac{k}{2\mu_B H} \ln \left(\frac{N\mu_B H - E}{N\mu_B H + E} \right)
\end{aligned}
\tag{33}
$$

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

Problem 3.43

The hamiltonian of the system is :

$$
\boldsymbol{H} = e\phi(\boldsymbol{q}) + \frac{1}{2m_e} \sum_{i=1}^{N} (\boldsymbol{P_i} - \frac{e}{c} \boldsymbol{A_i})^2
$$

$$
\dot{q}_i = -\frac{\partial H}{\partial p_i} \propto p_i
$$

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.

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

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