# Solutions to Pathria's Statistical Mechanics
# Chapter 3

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## 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

## 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:

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

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

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

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

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

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

# 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 $\psi_n$ is the $n$-th Hermitian polynomial. Using the recursive relations, we have

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

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

(b) In Bohr-sommerfeld model, a quantized orbits are hypothesized, namely $m_evr = n\hbar$. 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

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

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:

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

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 3.31

"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:

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

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:

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

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

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

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

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 3.41

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:

$$\begin{aligned} E &= \mu_B H(N_\uparrow - N_\downarrow) && (26)\\ N &= N_\uparrow + N_\downarrow && (27) \end{aligned}$$

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:

$$\Omega(N,E) = \mathrm{C}_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{28}$$

So the entropy in micro canonical ensemble representation is:

$$\begin{aligned} S &= k \ln \Omega(E,N)\\ &= Nk\ln N - N_\uparrow k \ln N_\uparrow - N_\downarrow k \ln N_\downarrow\\ &= Nk\ln N - k\frac{N\mu_B H + E}{2\mu_B H}\ln\frac{N\mu_B H + E}{2\mu_B H} - k\frac{N\mu_B H - E}{2\mu_B H}\ln\frac{N\mu_B H - E}{2\mu_B H} && (29) \end{aligned}$$

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

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E}\\ &= -\frac{k}{2\mu_B H}\ln\frac{N\mu_B H + E}{2\mu_B H} - \frac{k}{2\mu_B H} + \frac{k}{2\mu_B H}\ln\frac{N\mu_B H - E}{2mu_B H} + \frac{k}{2\mu_B H}\\ &= \frac{k}{2\mu_B H}\ln\left(\frac{N\mu_B H - E}{N\mu_B H + E}\right) && (30) \end{aligned}$$

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