

Solutions to Pathria's Statistical Mechanics

Chapter 3

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March 17, 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 3.11

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:

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

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

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,

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

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

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

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 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 $E_n = -Z^2 k^2 e^4 m_e / 2\hbar^2 n^2$. 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

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

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:

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

So the canonical partition function of the system is:

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

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

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

So a list of quantities can be obtained:

$$Q_N = (1 + e^{-\varepsilon/kT})^N \quad (16)$$

$$A = -NkT \ln(1 + e^{-\varepsilon/kT}) \quad (17)$$

$$\mu = -kT \ln(1 + e^{-\varepsilon/kT}) \quad (18)$$

$$p = 0 \quad (19)$$

$$S = Nk \ln(1 + e^{-\varepsilon/kT}) + \frac{N\varepsilon}{T} \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \quad (20)$$

$$U = N\varepsilon \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \quad (21)$$

$$C_p = C_V = \frac{N\varepsilon^2 e^{-\varepsilon/kT}}{kT^2 (1 + e^{-\varepsilon/kT})^2} \quad (22)$$

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:

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

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:

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

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

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

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

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:

$$E = \mu_B H (N_\uparrow - N_\downarrow) \quad (26)$$

$$N = N_\uparrow + N_\downarrow \quad (27)$$

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:

$$\Omega(N, E) = C_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \quad (28)$$

So the entropy in micro canonical ensemble representation is:

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

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

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

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