

Answers C

Problem 2.17

Since the derivation uses Stirling's approximation, we are assuming that $N \gg 1$ and $q \gg 1$. Therefore equation (2.17) applies, which says that

$$\Omega(N, q) \approx \frac{(q + N)!}{q!N!}. \quad (1)$$

If we further assume that $q \gg N$, the derivation in Schroeder shows that

$$\Omega(N, q) \approx \frac{(q + N)!}{q!N!} \approx \left(\frac{eq}{N}\right)^N, \quad (\text{when } q \gg N), \quad (2)$$

where $e \equiv \exp(1)$. Note, however, that (1) is unchanged if $N \rightarrow q$ and $q \rightarrow N$, so pretending that q is N and N is q does not make a difference. Doing this transformation on (2), we obtain

$$\Omega(N, q) \approx \frac{(q + N)!}{q!N!} \approx \left(\frac{eN}{q}\right)^q, \quad (\text{when } N \gg q), \quad (3)$$

which is the desired result.

Problem 2.30

- a) $S/k = 4N \ln(2) - \frac{1}{2} \ln(8\pi N) = 2.77 \cdot 10^{23}$
- b) $S/k = 4N \ln(2) - \ln(4\pi N) = 2.77 \cdot 10^{23}$
- c) The issue of time scales is not really relevant to the entropy of this system.
- d) The violation is not significant. We should (in any case) not lose sleep over it (since that would only reduce our ability to think).

Problem 2.34

For the monatomic ideal gas, $U = \frac{3}{2}NkT$, so for an isothermal process, U is fixed. Therefore $\Delta U = W + Q = 0$, and hence $W = -Q$. We have

$$W = - \int_{V_i}^{V_f} P dV = -NkT \int_{V_i}^{V_f} \frac{1}{V} dV = -NkT \ln\left(\frac{V_f}{V_i}\right) = -T\Delta S,$$

where the last equality follows from equation (2.51) in Schroeder. We hence have $-Q = -T\Delta S$, so $\Delta S = Q/T$.

For the free expansion process, $Q = 0$ while S is given by equation (2.51). Therefore $\Delta S \neq Q/T$.

Problem 3.5

We start from the multiplicity

$$\Omega = \left(\frac{eN}{q}\right)^q \quad \text{for } N \gg q \gg 1.$$

The entropy is then

$$S = k \ln(\Omega) = kq \ln(eN/q).$$

The total energy is

$$U = q\epsilon,$$

where ϵ is the energy unit of the harmonic oscillators. We have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{\epsilon} \left(\frac{\partial S}{\partial q} \right)_{V,N} = \epsilon^{-1} (k \ln(eN/q) - k) = k\epsilon^{-1} \ln(N/q)$$

Rearranging this, we obtain

$$T = \frac{\epsilon}{k \ln(N/q)} = \frac{\epsilon}{k \ln(\epsilon N/U)}$$

and

$$U = N\epsilon e^{-\epsilon/(kT)}.$$

Note also that

$$q = N e^{-\epsilon/(kT)},$$

so the condition $q \ll N$ means $kT \ll \epsilon$.

Problem 3.8

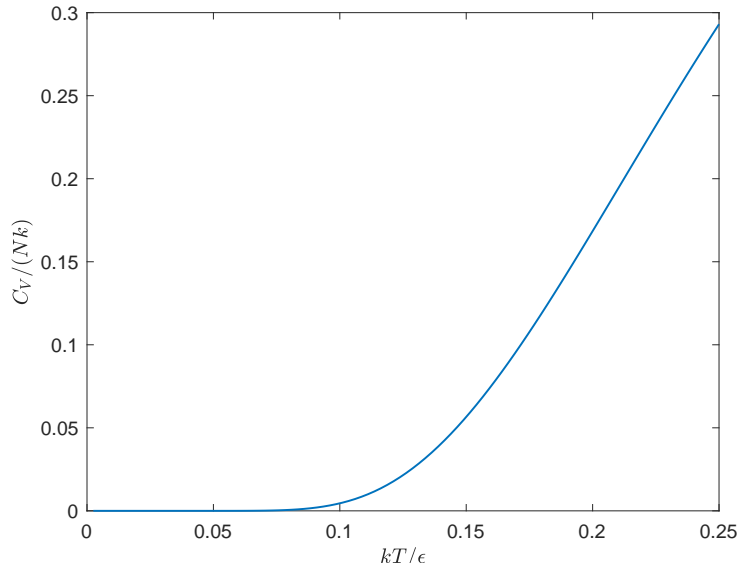
Using the result from problem 3.5, we find that the heat capacity for $kT \ll \epsilon$ is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{N\epsilon^2}{kT^2} e^{-\epsilon/(kT)}.$$

This can also be written as

$$\frac{C_V}{Nk} = \frac{1}{(kT/\epsilon)^2} e^{-1/(kT/\epsilon)}.$$

Plot of the heat capacity



Problem 3.23

We start from

$$\frac{S}{k} = \ln \left(\frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!} \right) \approx N \ln(N) - N_{\uparrow} \ln(N_{\uparrow}) - (N - N_{\uparrow}) \ln(N - N_{\uparrow})$$

and

$$U = \mu B(N - 2N_{\uparrow}) \quad \Leftrightarrow \quad N_{\uparrow} = \frac{1}{2} \left(N - \frac{U}{\mu B} \right) \quad \Leftrightarrow \quad N - N_{\uparrow} = \frac{1}{2} \left(N + \frac{U}{\mu B} \right).$$

We have

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial U} \right)_{N,B} = -\frac{1}{2\mu B} \left(\frac{\partial S}{\partial N_{\uparrow}} \right)_{N,B} = -\frac{k}{2\mu B} (-\ln(N_{\uparrow}) - 1 + \ln(N - N_{\uparrow}) + 1) \\ &= \frac{k}{2\mu B} \ln \left(\frac{N_{\uparrow}}{N - N_{\uparrow}} \right) = \frac{k}{2\mu B} \ln \left(\frac{N - \frac{U}{\mu B}}{N + \frac{U}{\mu B}} \right) \end{aligned}$$

Defining $x \equiv \mu B/(kT)$ and rearranging, we obtain

$$\begin{aligned} \left(N + \frac{U}{\mu B} \right) e^{2x} &= N - \frac{U}{\mu B} \quad \Leftrightarrow \quad \frac{U}{\mu B} e^{2x} + \frac{U}{\mu B} = N - N e^{2x} \quad \Leftrightarrow \\ U &= -N\mu B \frac{e^{2x} - 1}{e^{2x} + 1} = -N\mu B \frac{e^x - e^{-x}}{e^x + e^{-x}} = -N\mu B \tanh(x). \end{aligned}$$

It follows that

$$N_{\uparrow} = \frac{N}{2} (1 + \tanh(x)) = \frac{N e^x}{e^x + e^{-x}} \quad \Leftrightarrow \quad N - N_{\uparrow} = \frac{N}{2} (1 - \tanh(x)) = \frac{N e^{-x}}{e^x + e^{-x}},$$

which we insert into the expression for the entropy

$$\begin{aligned} \frac{S}{Nk} &= \ln(N) - \frac{e^x}{e^x + e^{-x}} \ln \left(\frac{N e^x}{e^x + e^{-x}} \right) - \frac{e^{-x}}{e^x + e^{-x}} \ln \left(\frac{N e^{-x}}{e^x + e^{-x}} \right) \\ &= \ln(e^x + e^{-x}) - \frac{x e^x}{e^x + e^{-x}} + \frac{x e^{-x}}{e^x + e^{-x}} \\ &= \ln(2 \cosh(x)) - x \tanh(x). \end{aligned}$$

We hence conclude that

$$S = Nk [\ln(2 \cosh(x)) - x \tanh(x)], \quad x \equiv \frac{\mu B}{kT}.$$

The low temperature limit is

$$\begin{aligned} \lim_{T \rightarrow 0} S &= Nk \lim_{x \rightarrow \infty} [\ln(2 \cosh(x)) - x \tanh(x)] = Nk \lim_{x \rightarrow \infty} \left[\ln(e^x + e^{-x}) - x \frac{e^x - e^{-x}}{e^x + e^{-x}} \right] \\ &= Nk \lim_{x \rightarrow \infty} \left[x + \ln(1 + e^{-2x}) - x \frac{1 - e^{-2x}}{1 + e^{-2x}} \right] = Nk \lim_{x \rightarrow \infty} \left[\ln(1 + e^{-2x}) + \frac{2x e^{-2x}}{1 + e^{-2x}} \right] = 0 \end{aligned}$$

This agrees with the third law of thermodynamics, since the ground state is nondegenerate.

The high temperature limit is

$$\lim_{T \rightarrow \infty} S = Nk \lim_{x \rightarrow 0} [\ln(2 \cosh(x)) - x \tanh(x)] = Nk \lim_{x \rightarrow 0} [\ln(2) + \ln(\cosh(x)) - x \tanh(x)] = Nk \ln(2).$$

For infinite temperature, we should have that half of the particles are in the up state and half of them are in the down state, since this maximizes the entropy of the system. This gives the multiplicity $\Omega = N!/((N/2)!(N/2)!)$, and hence the entropy $S = k \ln(N!/((N/2)!(N/2)!))$. Using Stirling's approximation in the form $\ln(N!) \approx N \ln(N) - N$, we find

$$S = k(N \ln(N) - N - 2(N/2) \ln(N/2) + 2(N/2)) = kN(\ln(N) - \ln(N/2)) = kN \ln(2).$$

The result $S = kN \ln(2)$ for the high temperature limit is hence as expected.

Problem 3.25(a-e)

a) The entropy is

$$S = k \ln(\Omega) = k[(q + N) \ln(q + N) - q \ln(q) - N \ln(N)].$$

The factor omitted would add $-k \ln(\sqrt{2\pi q(q + N)/N})$ to the entropy. Here q and N are large. Taking \ln of a large number gives a small number, and since S itself is a large number, the extra term does not make a significant difference.

b) We have $U = q\epsilon$ and

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{\epsilon} \left(\frac{\partial S}{\partial q} \right)_{V,N} = \frac{k}{\epsilon} [\ln(q + N) + 1 - \ln(q) - 1] = \frac{k}{\epsilon} \ln \left(1 + \frac{N}{q} \right),$$

so

$$T = \frac{\epsilon}{k \ln(1 + \epsilon N/U)}.$$

c) Rearranging, we obtain

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

It follows that

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{N\epsilon^2}{kT^2} \frac{e^{\epsilon/(kT)}}{(e^{\epsilon/(kT)} - 1)^2}.$$

d) The high temperature limit of the heat capacity is

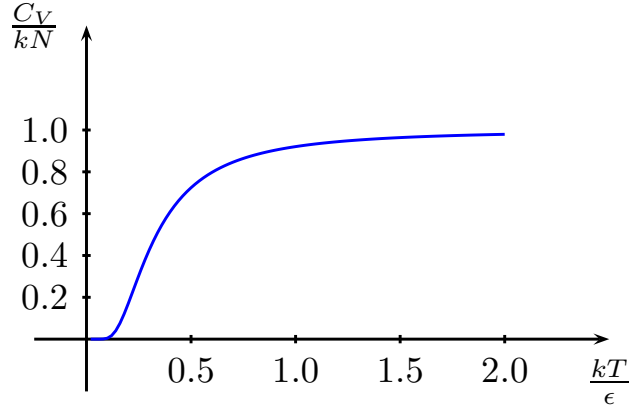
$$\lim_{T \rightarrow \infty} C_V = \lim_{T \rightarrow \infty} \frac{N\epsilon^2}{kT^2} \frac{1}{(\epsilon/(kT))^2} = Nk.$$

The Einstein solid consists of N oscillators. Each of these has two quadratic degrees of freedom. The equipartition theorem therefore predicts that the heat capacity is $N \cdot 2 \cdot \frac{k}{2} = Nk$, when the temperature is high enough. The result is hence as expected.

e) The heat capacity is

$$\frac{C_V}{Nk} = \frac{1}{t^2} \frac{e^{1/t}}{(e^{1/t} - 1)^2}, \quad t \equiv kT/\epsilon.$$

Plot of the heat capacity



The Einstein solid predicts a too low value for the heat capacity at low T .

The heat capacity takes the value $C_V = \frac{1}{2}Nk$ for $t \approx 0.335$. Let $T_{1/2}$ be the corresponding value of the temperature, that is $\epsilon \approx kT_{1/2}/0.335$. Reading off $T_{1/2}$ for lead, aluminum, and diamond from figure 1.14 in Schroeder, we obtain the following rough estimates for the energy units:

Lead: $T_{1/2} \approx 22 \text{ K} \Rightarrow \epsilon \approx 0.006 \text{ eV}$

Aluminum: $T_{1/2} \approx 90 \text{ K} \Rightarrow \epsilon \approx 0.02 \text{ eV}$

Diamond: $T_{1/2} \approx 430 \text{ K} \Rightarrow \epsilon \approx 0.1 \text{ eV}$

Problem Hand-in C

a)

$$\Omega(n_A, n_B) = \frac{N_A!}{n_A!(N_A - n_A)!} \cdot \frac{N_C!}{n_C!(N_C - n_C)!}$$

By using Stirling's approximation one obtains (2).

b) S is maximal in equilibrium, that is

$$\frac{\partial S}{\partial n_A} + \frac{\partial S}{\partial n_C} \frac{\partial n_C}{\partial n_A} = 0.$$

From equation (1) we have

$$\frac{\partial n_C}{\partial n_A} = -\frac{E_A}{E_C},$$

and using equation (2) one obtains equation (3) with $\gamma = E_A/E_C$.

c) We have $n_A = n_C = E/(2E_A)$ when $N_A = N_C$ and $E_A = E_C$. Inserting this into equation (2), one obtains

$$S = 2k \left[N_A \ln(N_A) - \frac{E}{2E_A} \ln\left(\frac{E}{2E_A}\right) - \left(N_A - \frac{E}{2E_A}\right) \ln\left(N_A - \frac{E}{2E_A}\right) \right].$$

Using

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

one obtains

$$E = \frac{2N_A E_A}{e^{\beta E_A} + 1}.$$

The limits are

$$\lim_{T \rightarrow 0} E = 0 \quad \text{and} \quad \lim_{T \rightarrow \infty} E = N_A E_A.$$

For $T = 0$, no base pairs are broken, and the system is in the ground state. For $T \rightarrow \infty$, half of the $2N_A$ base pairs are broken.