Problem #1

Show that the following relations for state functions hold:

a. In analogy to \(-\frac{\partial \ln Z}{\partial \beta} = U\) and \(\frac{\partial^2 \ln Z}{\partial \beta^2} = \delta U\) proved in class, what are \(\frac{\partial \ln \Xi}{\partial \beta\mu}\) and \(\frac{\partial^2 \ln \Xi}{\partial (\beta\mu)^2}\), where \(\Xi = e^{\beta PV}\) is the grand canonical partition function? Work in the Grand ensemble to derive this most easily by analogy of corresponding variables in the canonical ensemble.

b. For the ideal gas \(PV = nRT = N/\beta\) show that: i) \(\ln \Xi = N\); ii) \(\ln \Xi = e^{\beta\mu}\) [Hint: use the derivative \(\frac{\partial \ln \Xi}{\partial \beta\mu}\) from above, and remember that if \(\frac{\partial y}{\partial x} = y\), then \(y = e^x\).]; iii) \(N = \delta^2 N\) [Hint: the second derivative \(\frac{\partial^2 y}{\partial x^2} = y\) also if \(y = e^x\).]

c. Based on your answer in c-iii), what happens to the fluctuation of particle numbers \(\sqrt{\delta^2 N}\) when a system becomes macroscopic, i.e. \(N \gg 1\)?

Solutions #1

a. By analogy of corresponding variables, in the grand canonical ensemble

\[
\frac{\partial \ln \Xi}{\partial \beta\mu} = N \\
\frac{\partial^2 \ln \Xi}{\partial (\beta\mu)^2} = \delta N
\]

b. \(\Xi = e^{\beta\mu PV}\), therefore, \(\ln \Xi = \beta PV = N/\beta \cdot \beta = N\) (i)

Recall: \(\frac{\partial \ln \Xi}{\partial \beta\mu} = N\), therefore, \(\ln \Xi = e^{\beta\mu}\) (ii)

Recall: \(\frac{\partial^2 \ln \Xi}{\partial (\beta\mu)^2} = \delta N\) and \(\ln \Xi = e^{\beta\mu}\)

Therefore, \(\delta^2 N = e^{\beta\mu} = N\) (iii)

c. When the particle number \(N \gg 1\),

\[
\frac{\sqrt{\delta^2 N}}{N} = \frac{1}{\sqrt{N}} \ll 1
\]

Problem #2

Using the van der Waals equation of state, at what temperature \(T_c(a,b)\) is the critical point, where the two roots of \(P(V)\) disappear?

Solutions

We can solve it in two ways. The most common way is to use the criterier that the the first and second derivatives of van der Waals equation of state have to be zero. A second approach is to use the grand canonical partition function. The system destabilizes when particle fluctuation \(\delta^2 N\) become infinite.
(a) At the critical point the two points with first derivative equal to 0 coalesce, and therefore the first AND second derivative equals zero there:

\[
\left( \frac{\partial P}{\partial V} \right)_T = -\frac{N}{\beta (V - Nb)^2} + \frac{2aN^2}{V^3} = 0 \quad (1)
\]

and

\[
\left( \frac{\partial^2 P}{\partial V^2} \right)_T = \frac{2N}{\beta (V - Nb)^3} - \frac{6aN^2}{V^4} = 0 \quad (2)
\]

combine the two equations

\[3(V - Nb) = 2V\]

\[V_c = 3Nb\]

Therefore, from (1)

\[\frac{N}{\beta (V - Nb)^2} = \frac{2aN^2}{V^3} \rightarrow \]

\[\frac{N}{\beta (2Nb)^2} = \frac{2aN^2}{(3Nb)^3} \rightarrow \]

\[T_c = \frac{8a}{27k_b b}\]

(b) Let

\[P = \frac{N}{\beta (V - Nb)} - a\left(\frac{N}{V}\right)^2\]

We are assuming here for simplicity that \(N \approx 1\) and \(V >> Nb\), so only variations in \(N/V\) need to be considered. (The full solution would involve a more complicated \(y\) than the one below)

\[Z = e^{\beta PV} \quad \ln Z = \beta PV = \frac{NV}{(V - Nb)} - \beta a \frac{N^2}{V}, \text{ but} \]

\[N = \frac{\ln \Xi}{\beta \mu} \quad \ln \Xi = \frac{V}{(V - Nb)} - \frac{\beta a \ln \Xi}{\beta \mu}, \]

therefore

\[y = \ln \Xi, c_1 = \frac{V}{(V - Nb)}, c_2 = \frac{\beta a}{V}\]
\[ y = y'c_1 - y'^2c_2 \] (eq. 1)

whose roots are \[ y' = \frac{c_1}{2c_2} \pm \sqrt{\frac{c_1}{c_2} - 4\frac{y}{c_2}}^{1/2} \]

(b) Differentiating this equation (with respect to \( \beta \mu \)) yields
\[ y'' = y''c_1 - 2y'y''c_2 \]
\[ y'' = \delta^2 N = \frac{y'}{c_1 - 2c_2 y'} \]

(c) \( \delta^2 N \to \infty \) if \[ y' = \frac{c_1}{2c_2} \] which occurs when \( y = \frac{c_1^2}{4c_2} \)

\[ \ln Z = \frac{V^3}{4\beta a(V - Nb)^2} \] (critical point) This can happen if \( N \) is large.

**Problem #3**

\(|a>\) and \(|b>\) are one-particle states, “1” and “2” serve as labels for indistinguishable particles.

a. Show that \(|a_1>\mid b_2>\) is not an eigenfunction of the permutation operator \( P \).

b. Show that \((1/\sqrt{2}) \{|a_1>\mid b_2>\pm |b_1>\mid a_2>\}\) are eigenfunctions of \( P \) with eigenvalue \( \pm 1 \).

c. Show that two identical fermions cannot occupy the state \(|a>\) with non-zero probability.

**Solutions**

a. \( P|a_1>\mid b_2> = |a_2>\mid b_1> \neq |a_1>\mid b_2>\), \(|a_1>\mid b_2>\) is not an eigenfunction of the permutation operator \( P \).

b. \( P(1/\sqrt{2})\{|a_1>\mid b_2>\pm |b_1>\mid a_2>\} = (1/\sqrt{2})\{|a_2>\mid b_1>\pm |b_2>\mid a_1>\}\) and \( P(1/\sqrt{2})\{|a_1>\mid b_2>\pm |b_1>\mid a_2>\} = (1/\sqrt{2})\{|a_2>\mid b_1>\pm |b_2>\mid a_1>\}\) for \( \pm 1 \) eigenvalue of \( P \).

So \((1/\sqrt{2})\{|a_1>\mid b_2>\pm |b_1>\mid a_2>\}\) is an eigenfunction of \( P \). For two distinct particles, the wavefunction is \((1/\sqrt{2})\{|a_1>\mid b_2>\pm |b_1>\mid a_2>\}\). For two identical fermions trying to occupy the same state \(|a>\), the wavefunction can be written as

\[ (1/\sqrt{2})\{|a_1>\mid a_2>-|a_1>\mid a_2>\} = 0 \]

Therefore, two identical fermions cannot occupy the same state with non-zero probability.

**Problem #4**

If you have an unlimited supply of \$1, \$2 and \$5 bills, how many ways are there to make change for \$10? How many ways are there to make change for \$10 with exactly 6 bills?
Solutions

<table>
<thead>
<tr>
<th>$1$</th>
<th>$2$</th>
<th>$5$</th>
<th># of bills</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Eight ways to make change for $10$, and 2 ways to make change of $10$ with exactly 6 bills.

Problem #5

Let us derive the heat capacity for phonons. Like photons discussed in lecture, phonons can be annihilated and created in any number by anharmonic couplings in the potential energy, therefore $\mu=0$.

a. The dispersion relation for vibrations (=phonons) of a chain of atoms is $\omega k = a(\gamma/m)^{1/2}$ at low frequencies. What is the phase velocity $v$ of phonons? Plug in reasonable rough values for $a$, $\gamma$ and $m$ to estimate the velocity. (For example, $m=12$ amu $= 12 \times 1.66 \times 10^{-27}$ kg for a carbon.)

b. Using a and making the analogy to photons, write down $u(T, \omega)$, the energy per unit frequency and unit volume at temperature $T$ for a chain of atoms, in terms of $\omega$, $T$, and $v$. For the 3-D case, assume for simplicity that the velocity $v$ is the same for all types of modes in all directions, and note that phonons have 3 polarizations (2 transverse polarizations like photons, and 1 longitudinal polarization)

c. The lowest possible phonon frequency is close to 0, when the left half of atoms in the macroscopic crystal move left, and right half move right. To approximate the highest possible phonon frequency, what is the vibrational frequency $\omega_{max}$ of a single atom moving back and forth between two walls of fixed atoms?

d. Using d, write down $u(T)$, the energy per unit volume integrated from the lowest ($\approx 0$) to the highest frequency of the crystal lattice.

e. By Taylor-expanding the exponential in the denominator in d, show that at high temperature, $u(T) \sim T$. Therefore, what happens to the heat capacity $c_v$ at high $T$? Note that to get the correct constant value $c_v = 3k_B$ per atom in the lattice, the maximum frequency for a cubical crystal that goes into the integration limit would have to be determined accurately, instead of your rough estimate in c.

Solutions
a. Parameters for carbon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of the carbon atom (m)</td>
<td>$12 \times 1.66 \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>C-C bond length (a)</td>
<td>$1.5 \times 10^{-10}$ m</td>
</tr>
<tr>
<td>force constant ($\gamma$)</td>
<td>$4.5 \times 10^5$ dyne/cm = 500N/m</td>
</tr>
</tbody>
</table>

The phase velocity

$$V_p = \frac{\omega}{k} = 1.5 \times 10^{-10} \cdot \sqrt{\frac{450 \frac{N}{m}}{12 \times 1.66 \times 10^{-27} kg}} = 22500 \text{ m/s}$$

Note that the speed in a 1-D carbon chain somewhat overestimates the actual seed of sound in a diamond, which is 12000 m/s.

b. The number of microstates can be written just as for photons; instead of two transverse polarizations (photons) phonons can also be longitudinally polarized (compression wave), giving three polarizations (hence the factor of 3 below). As mentioned in the problem, the velocity is not usually isotropic, but we’ll assume it’s always the above $v_p$ for simplicity:

$$\frac{\omega}{k} = V_p$$

$$W(\omega) d\omega = \frac{V}{2\pi^2} \cdot \frac{3}{V_p^3} \cdot \omega^2 d\omega$$

$$\frac{U}{V} d\omega = u(T, \omega) d\omega = \frac{1}{2\pi^2} \cdot \frac{3}{V_p^3} \cdot \omega^2 \cdot \frac{h \omega}{e^{h \omega/k_B} - 1} d\omega$$

c. The minimum wavelength, corresponding to the maximum frequency, is $2a$.

$$\omega_{\text{max}} = \frac{V_p}{2a} \cdot 2\pi = \frac{\pi V_p}{a}$$

(You might also estimate a single atom vibrating against two springs of force constant $\gamma$ while the rest of the crystal is frozen, which has frequency

$$\omega = \sqrt{2\gamma/m} = \sqrt{2},$$

as an estimate of the upper frequency, but the above is more accurate.)
d. Energy per unit volume integrate from $\omega = 0$ to $\omega = c/2a$

$$u(T) = \int_{\omega=0}^{\omega=\frac{\pi V_E}{a}} \frac{3}{2\pi^2 V_p^3} \frac{1}{\frac{\hbar^2}{\beta^2} + 1} d\omega$$

e. Taylor expand the denominator

$$u(T) = \int_{\omega=0}^{\omega=\frac{\pi V_E}{a}} \frac{3}{2\pi^2 V_p^3} \frac{1}{\frac{\hbar^2}{\beta^2} + 1} d\omega$$

$$= \int_{\omega=0}^{\omega=\frac{\pi V_E}{a}} \frac{3}{2\pi^2 V_p^3} \frac{1}{\beta} \omega^3 d\omega$$

$$= \frac{3}{2\pi^2 V_p^3} \frac{1}{\beta} \left( \frac{\pi V_E}{a} \right)^3$$

At high temperature, $u(T) \sim k_B T$, so the heat capacity per unit volume $c_v = \left( \frac{\partial u}{\partial T} \right)_V$ is proportional to $k_B$ and independent of temperature.

Note that to get the heat capacity per mole correctly (it is $3AK_B=3R$ for any solid at high temperature because of equipartition of energy among all modes), we need to treat the crystal properly in 3D and divide by the volume per atom and multiply by Avogadro’s number. In his famous derivation, Debye fudged this by choosing a spherical integration volume ‘carefully’ to cancel all the factors and get $3R$!