Second recitation on statistical mechanics

Solution

1. A nanoparticle containing 6 atoms can be modeled approximately as an Einstein solid of 18 independent oscillators. The evenly spaced energy levels of each oscillator are \(4 \times 10^{-21}\) J apart.

   (a) When the nanoparticle’s energy is in the range \(5 \times 4 \times 10^{-21}\) J to \(6 \times 4 \times 10^{-21}\) J, what is the approximate temperature? (In order to keep precision for calculating the heat capacity, give the result to the nearest tenth of a Kelvin.)

   (b) When the nanoparticle’s energy is in the range \(8 \times 4 \times 10^{-21}\) J to \(9 \times 4 \times 10^{-21}\) J, what is the approximate temperature? (In order to keep precision for calculating the heat capacity, give the result to the nearest tenth of a degree.)

   (c) When the nanoparticle’s energy is in the range \(5 \times 4 \times 10^{-21}\) J to \(9 \times 4 \times 10^{-21}\) J, what is the approximate heat capacity per atom? For your convenience, the entropy-energy graph is also shown.

\[\begin{align*}
\text{Answer 1:} \\
&\text{We are given that,}\\
&\text{6 atoms in a nanoparticle} = 18 \text{ oscillators}\\
&\text{Energy of each quanta} = q = 4 \times 10^{-21} \text{ J.}
\end{align*}\]
Energy = \( q \times 4 \times 10^{-21} \text{ J} \)

(a) Approximate temperature \( T \) when energy is in between 5 and 6 quanta is \( \frac{1}{T} = \) slope of the entropy versus energy graph.

At \( q = 5 \):

To find the slope, we have

\[
\frac{1}{T} = \frac{\text{Change in entropy}}{\text{Change in energy}} = \frac{(0.159 - 0.141) \times 10^{-21} \text{ J/K}}{(6 - 5) \times 4 \times 10^{-21} \text{ J}} = 4.5 \times 10^{-3} \text{ 1/K}
\]

\( \Rightarrow T = 222.2 \text{ K} \).

(b)

\[
\frac{1}{T} = \frac{\text{Change in entropy}}{\text{Change in energy}} = \frac{(0.206 - 0.192) \times 10^{-21} \text{ J/K}}{(9 - 8) \times 4 \times 10^{-21} \text{ J}} = 4.5 \times 10^{-3} \text{ 1/K}
\]

\( \Rightarrow T = 285.7 \text{ K} \).
(c) The plot of the entropy versus energy (quanta) is shown in the question. To calculate the heat capacity per atom, one needs to find the energy difference between the points \( a \) and \( b \) and the corresponding change in temperature.

\[
\begin{align*}
T_a &\approx 222.2 \text{ K} \\
T_b &\approx 285.7 \text{ K} \\
\Delta T &= T_b - T_a \approx 63.5 \text{ K} \\
\text{Change in energy} &= 4 \times 10^{-21} \text{ J} \\
\Rightarrow C &= \frac{4 \times 4 \times 10^{-21} \text{ J}}{63.5 \text{ K}} \\
&= 4 \times 6.3 \times 10^{-23} \text{ J/K} \\
&= 25.2 \times 10^{-23} \text{ J/K}.
\end{align*}
\]

This is per atom.

2. For a certain metal the stiffness of the interatomic bond and the mass of one atom are such that the spacing of the quantum oscillator energy levels is \( 1.5 \times 10^{-23} \text{ J} \). A nanoparticle of this metal consisting of 10 atoms has a total thermal energy of \( 18 \times 10^{-23} \text{ J} \). Assume all the internal energy is of the disordered kind.

(a) What is the entropy of this nanoparticle?

(b) The temperature of the nanoparticle is 87 K. Next we add \( 18 \times 10^{-23} \text{ J} \) to the nanoparticle. By how much does the entropy increase?

**Answer 2:**

(a) We are given that,

\[
\begin{align*}
\text{Energy of one quanta} &= q \equiv 1.5 \times 10^{-23} \text{ J} \\
\text{Number of atoms} &= 10 \\
\text{Number of oscillators} &= 30 \\
\text{Thermal energy} &= 18 \times 10^{-23} \text{ J}.
\end{align*}
\]

In order to calculate the entropy of nanoparticle, firstly we should calculate number of microstates. Suppose all the energy is in the form of the thermal energy.

\[
\begin{align*}
\text{Number of Quanta} &= \frac{18 \times 10^{-23} \text{ J}}{1.5 \times 10^{-23} \text{ J}} \approx 12 \\
\text{Number of microstates} &= \Omega = \frac{(12 + 30 - 1)!}{12!(30 - 1)!} = \frac{41!}{12! \cdot 29!}
\end{align*}
\]
\[ \Omega = \frac{3.35 \times 10^{49}}{4.79 \times 10^8 \times 8.84 \times 10^{30}} = 7.91 \times 10^9. \]

Therefore entropy of the nanoparticle is,

\[ S = k_B \ln \Omega = 1.38 \times 10^{-23} \text{ J/K } \ln(7.91 \times 10^9) \]
\[ = 1.38 \times 10^{-23} \text{ J/K } \times 22.79 = 3.14 \times 10^{-22} \text{ J/K}. \]

(b) Now we are given that,

Temperature of nanoparticle = 87 K
Heat added to the nanoparticle = 18 \times 10^{-23} \text{ J}.

Slope \( dS/dE \) at this temperature is,

\[ \frac{dS}{dE} = \frac{1}{T} = \frac{1}{87} = 0.0115 \text{ K}^{-1}. \]

By adding 18 \times 10^{-23} \text{ J} of energy, entropy goes up by approximately,

\[ \text{Change in entropy} = 0.0115 \text{ K}^{-1} \times 18 \times 10^{-23} \text{ J} = 2.1 \times 10^{-24} \text{ J/K}. \]

3. A 50 gram block of copper (one mole has a mass of 63.5 grams) at a temperature of 35\(^\circ\) C is put in contact with a 100 gram block of aluminum (molar mass 27 grams) at a temperature of 20\(^\circ\) C. The blocks are inside an insulated enclosure, with little contact with the walls. At these temperatures, the high temperature limit is valid for the specific heat capacity, \( C_v = 3k_B \). Calculate the final temperature of the two blocks. Do NOT look up the specific heat capacities of aluminum and copper; these have been provided to you.

**Answer 3:**
We are given that,

- Mass of copper block = 50 g
- Molar mass of copper = 63.5 g
- Temperature of copper = 35°C = (35 + 273) K = 308 K

- Mass of Aluminium block = 100 g
- Molar mass of Aluminium = 27 g
- Temperature of Aluminium = 20°C = (20 + 273) K = 293 K
- Heat capacity = \( C_v = 3k_B \).

Final temperature of the blocks can be calculated by using the equation,

\[
Q = \int_{T_i}^{T_f} C_v dT.
\]

Let us first calculate the heat transferred from copper block to Aluminium block.

\[
E_{\text{int}}^{\text{Cu}} = 3k_B T = 3k_B \times 308 \text{ K} = 924k_B \text{ J/atom}
\]

\[
E_{\text{int}}^{\text{Al}} = 3k_B T = 3k_B \times 293 \text{ K} = 879k_B \text{ J/atom.}
\]

\( Q \) goes from Cu to Al, because average (or per atom) internal energy in Cu is higher, even though total internal energy in Al is higher because it has more atoms. If Avogadro’s number is represented by \( N_A \), then,

\[
E_{\text{int}}^{\text{Cu tot}} = \frac{50 \text{ g}}{63.5 \text{ g/mol}} \times 924k_B \text{ J/atom} \times N_A \text{ atoms} = 727.6k_BN_A \text{ Joules}
\]

\[
E_{\text{int}}^{\text{Al tot}} = \frac{100 \text{ g}}{27 \text{ g/mol}} \times 879k_B \text{ J/atom} \times N_A \text{ atoms} = 3255.6k_BN_A \text{ Joules}.
\]

A copper atom loses energy \( xk_B \) Joules, which is gained by an Al atom. Since energy is conserved,

\[
924k_B - xk_B = 879k_B + xk_B
\]

\[
\Rightarrow x = 22.5.
\]

Therefore 22.5 Joules of energy are transferred.

\[
\Rightarrow Q = -22.5k_B \text{ Joules}
\]

But \( Q = \int_{T_i}^{T_f} C_v dT. \)
Substituting the value of $Q$ and $C_v$, we obtained,

\[-22.5k_B = \int_{T_i}^{T_f} 3k_B dT = 3k_B \int_{T_i}^{T_f} dT\]
\[= 3k_B |T|_{T_i}^{T_f} = 3k_B (T_f - T_i)\]
\[= 3k_B (T_f - 308)\]
\[\Rightarrow T_f = 301.5 \, \text{K}\]
\[= 28.5^\circ \text{C}.\]