

T3M8

Consider an Einstein solid having $N=200$ atoms

a) What's the solid's temp when it has an energy of $10E$,
 assuming $E = \hbar\omega \approx 0.02 \text{ eV}$? Calculate this directly from definition
 Of temp by finding sum $10E$ over $N\epsilon$, computing $\frac{\partial S}{\partial U} \approx \left(\frac{\partial S}{\partial U}\right)_E - \text{second}$,
 and then applying the definition of temp?

We define temperature T by $\frac{\partial S}{\partial U} = \frac{1}{T}$, where $\frac{\partial S}{\partial U}$ is 1st derivative
 of entropy with respect to thermal energy.

We can approximate $\frac{\partial S}{\partial U}$ by $\frac{\Delta S}{\Delta U} = \frac{S(11E) - S(10E)}{E}$ in this case.

$$\text{From equation T3.2, } S(U,N) = k_B \cdot \ln\left(\frac{(3N+U-1)!}{(3N-1)!(U-1)!}\right)$$

Plugging this into our approximation, we get:

$$\begin{aligned} \frac{\Delta S}{\Delta U} &= \frac{S(11E, 20) - S(10E, 20)}{E} = \frac{k_B \cdot \left(\ln\left(\frac{(60+11-1)!}{(60-1)!(11-1)!}\right) - \ln\left(\frac{(60+10-1)!}{(60-1)!(10-1)!}\right)\right)}{E} \\ &\Rightarrow \frac{\Delta S}{\Delta U} = \frac{k_B \cdot \ln\left(\frac{70 \cdot 89 \cdot 10}{59 \cdot 60 \cdot 69}\right)}{E} = \frac{k_B}{E} \cdot \ln\left(\frac{70 \cdot 10 \cdot 10}{11 \cdot 10 \cdot 69}\right) \end{aligned}$$

$$\text{So } \frac{\Delta S}{\Delta U} = \frac{k_B}{E} \cdot \ln\left(\frac{70}{11}\right) = \frac{8.617 \cdot 10^{-21} \text{ J/K}}{0.02 \text{ eV}} \cdot \ln\left(\frac{70}{11}\right) = 0.00797 \text{ K}^{-1} = \frac{1}{125 \text{ K}}$$

$$\text{So } T = \frac{1}{0.00797 \text{ K}^{-1}} = 125 \text{ K}$$

b) How does this compare with the result from the formula $U = 3Nk_B T$, which
 is only accurate if N is large and $\frac{U}{3Nk_B} \gg 1$?

$$\text{If we compute } T = \frac{U}{3Nk_B}, \text{ we get } T = \frac{10.002 \text{ eV}}{3 \cdot 20 \cdot 8.617 \cdot 10^{-21} \text{ J/K}} = 39 \text{ K}$$

We see that this is very different from our result ($\approx 125 \text{ K}$)!

Note that N here is small, and $\frac{U}{3Nk_B} = \frac{10E}{3 \cdot 20E} = \frac{1}{6}$. This is subcritical, so
 the conditions for accuracy in the use of $U = 3Nk_B T$ are not met,
 which is why our answers are so different.

c) Repeat for $N=200$, $U=100E$

$$\text{we can use same trick: } \frac{\Delta S}{\Delta U} = \frac{S(100E, 200) - S(100E, 200)}{E} = \frac{k_B}{E} \cdot \ln\left(\frac{(600+100-1)! \cdot (600-1)! \cdot 100!}{(600+100-1)! \cdot (600-1)! \cdot 100!}\right)$$

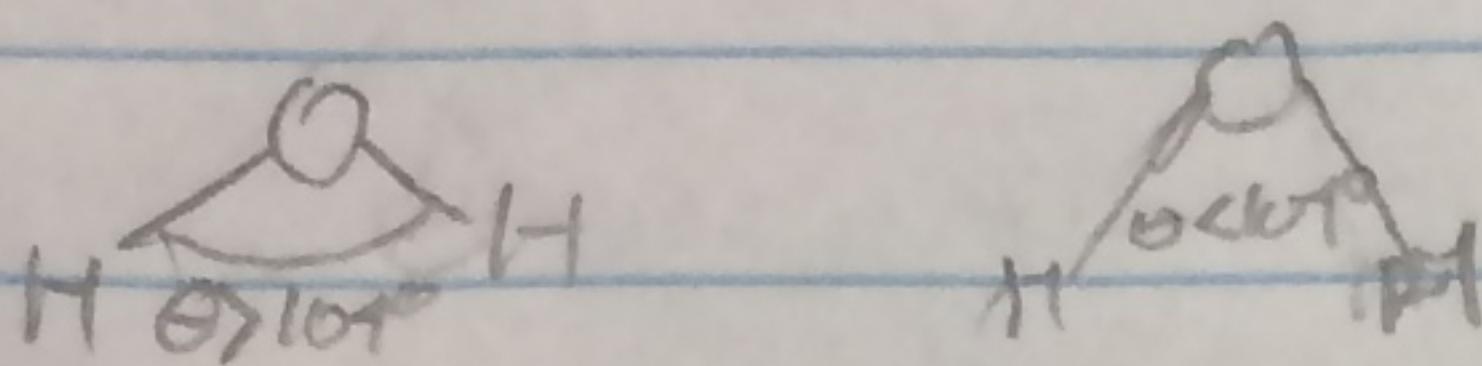
$$\Rightarrow \frac{k_B}{E} \cdot \ln\left(\frac{700 \cdot 699 \cdot 100!}{699 \cdot 101 \cdot 100!}\right) = \frac{k_B}{E} \cdot \ln\left(\frac{700}{101}\right) = \frac{8.617 \cdot 10^{-21} \text{ J/K}}{0.02 \text{ eV}} \cdot \ln\left(\frac{700}{101}\right) = 0.00234 \text{ K}^{-1}$$

$$T = \frac{1}{0.00234 \text{ K}^{-1}} = 120 \text{ K}$$

Comparing this to $T = \frac{U}{3Nk_B} = \frac{100 \cdot 0.02 \text{ eV}}{3 \cdot 200 \cdot 8.617 \cdot 10^{-21} \text{ J/K}} = 39 \text{ K}$. As in, we see that N is large, $\frac{U}{3Nk_B} = \frac{100E}{3 \cdot 200E} = \frac{1}{6}$
 which makes the value of $T = \frac{U}{3Nk_B}$ increase.

RM.1

A water molecule can vibrate in many ways, but the "flexing" mode, where the angle between the OH bonds oscillates about its central value of 105° , is the vibrational mode whose excited energies are the greatest.



near room temp Vmax fits the formula $\nu_0 \approx 13 \text{ cm}^{-1}$

Assumption Q, the energy levels are $(n+1)k_B T$, $n=0, 1, 2, \dots$

This mode's natural freq of ω is $3.0 \cdot 10^{11} \text{ s}^{-1}$. Calculate the absolute probabilities that a water molecule at room temp will be in its flexing ground state or its first two excited states.

The transition energy of the vibratory water molecule will be very small, even the "room" that the molecule is in should cancel with can be found as the room is so big.

So equation 7.4.8 applies:

$$Pr(E) = \frac{1}{Z} e^{-E/k_B T} = \frac{e^{-E/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}} \quad n = \text{number of states}$$

$$Pr(E_0) = \frac{e^{-E_0/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}} = \left(e^{\frac{E_0}{k_B T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{(n+1)k_B T}{k_B T}} \right)^{-1} = \left(e^{\frac{E_0}{k_B T}} \cdot \sum_{n=0}^{\infty} X^{2n+1} \right)^{-1}, \quad X = e^{-\frac{k_B T}{2k_B T}}$$

$$\text{Notice that } \sum_{n=0}^{\infty} X^{2n+1} = X + X^3 + X^5 + \dots$$

$$\text{Multiply both sides by } (1+X) \text{ gives } (1+X) \cdot \sum_{n=0}^{\infty} X^{2n+1} = X + X^3 + X^5 + \dots = \left(\sum_{n=0}^{\infty} X^n \right)^2 - 1, \text{ hence } X^2$$

$$\therefore (1+X) \sum_{n=0}^{\infty} X^{2n+1} = \frac{1+X}{1-X} = \frac{X}{1-X} \Rightarrow \sum_{n=0}^{\infty} X^{2n+1} = \frac{1}{(1-X)(1+X)} = \frac{X}{1-X^2}$$

$$\text{so } \sum_{n=0}^{\infty} X^{2n+1} = \frac{X}{1-X^2} = \frac{e^{-\frac{k_B T}{2k_B T}}}{1-e^{-\frac{3.0 \cdot 10^{11} \text{ s}^{-1} \cdot k_B T}{2k_B T}}}$$

$$\text{so } Pr(E_0) = \left(e^{\frac{E_0}{k_B T}} \cdot e^{\frac{E_0}{k_B T}} / \left(1 - e^{\frac{E_0}{k_B T}} \right) \right)^{-1} = \left(e^{\frac{E_0}{k_B T}} / \left(1 - e^{\frac{E_0}{k_B T}} \right) \right)^{-1}$$

$$\Rightarrow \left(1 - e^{\frac{E_0}{k_B T}} \right) / e^{\frac{E_0}{k_B T}} = \frac{e^{\frac{E_0}{k_B T}} - 1}{e^{\frac{E_0}{k_B T}} + e^{\frac{E_0}{k_B T}}} = e^{\frac{E_0}{k_B T}} - e^{\frac{2E_0}{k_B T}}$$

$$\text{so } Pr(E_0) = e^{\frac{E_0}{k_B T}} - e^{\frac{2E_0}{k_B T}} \quad \text{In this case, } \frac{E_0}{k_B T} = \frac{1.0526 \cdot 10^{-33} \text{ J} \cdot 3.0 \cdot 10^{11} \text{ s}^{-1}}{1.38 \cdot 10^{-23} \text{ J} \cdot 2.9515 \text{ K}} \approx 7.7676$$

$$Pr(E_0) = e^0 - e^{-7.7676} = 99.98767749\%$$

$$Pr(E_1) = e^{-7.7676} - e^{-2 \cdot 7.7676} = 0.012304645\%$$

$$Pr(E_2) = e^{-2 \cdot 7.7676} - e^{-3 \cdot 7.7676} = 0.0001790440709\%$$

Evaluation: RM.2: ordered magnitude score reasonable, right on it
RM.1: reasonable orders of magnitude, right on it