Notes for today

- Homework: due tomorrow at the beginning of class.
- I am still looking for a volunteer for problems 5 and 6.
- Lecture recordings etc.: Reminder again that you should let me know if you have a Covid quarantine (or other University excuse). I can share lecture recording or a zoom link to view the lecture in real time.
- Enable the microphone

Recall: $S \equiv k_B ln(\Omega)$ (Boltzmann)

$N_1 = 100$ ⟺ atoms $N_2 = 300$ 100 & 300 "bins"

$N = 5$ $N = 15$

20 total atoms, expected location of atoms?

- used $\Omega_i = \frac{N!}{n!(N-n)!}$
- independent configurations: multiply multiplicities.
- peak value based on maximum Ω

In[1]:= $N\left[\frac{100! \times 300!}{5! \times 95! \times 15! \times 285!}\right]$

Out[1]= 5.78801×10^{32} ⇐ Maximum entropy

In[2]:= $N\left[\frac{100! \times 300!}{4! \times 96! \times 16! \times 284!}\right]$

Out[2]= 5.36974×10^{32}

In[3]:= $N\left[\frac{100! \times 300!}{6! \times 94! \times 14! \times 286!}\right]$

Out[3]= 4.80648×10^{32}

Recall: $S \equiv k_B ln(\Omega)$ (Boltzmann)

$N_1 = 100$ ⇔ atoms $N_2 = 300$

100 & 300 "bins"

thermodynamic analysis for large N:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

Extremum for S: equalize $-\frac{\mu}{T} = \frac{\partial S}{\partial n_i}$

General conditions, $T_1 = T_2$ & $\mu_1 = \mu_2$ (chapter 2)

Can use Stirling approximation,

$\ln N! \cong N \ln N - N \ldots$

Find, $n_1/N_1 = n_2/N_2$ this situation

- used $\Omega_i = \frac{N!}{n!(N-n)!}$
- independent configurations: multiply multiplicities.
- peak value based on maximum Ω

Einstein oscillator problem:

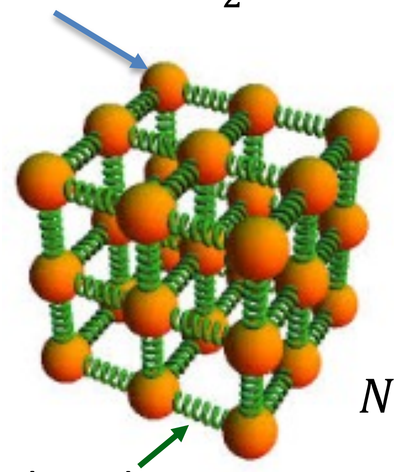
Vibrational energy for solid as a whole:

$$U = q\hbar\omega_o$$

Omitted zero-point energy (redefine zero of energy)

Solid contains q = total number of quanta of oscillation
>> Many equivalent ways to distribute this energy <<

$U = \hbar\omega_o(n + \frac{1}{2})$ each atom



N *atoms*

- Actual solid: bonds connect atoms, normal vibrational modes cover range of oscillation frequencies, determine vibrational energy & entropy.

- Einstein simplified model: Each atom acts as a 3D oscillator, with same frequency each site. With quantized oscillator energies, correctly models low-*T* downturn; qualitatively correct.

- Other crystal excitations may also contribute to entropy (e.g. conduction electrons in a metal) but vibrations are often the largest contribution

Einstein oscillator problem:

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solid as a whole:

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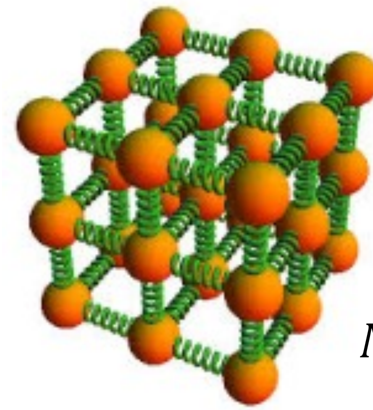
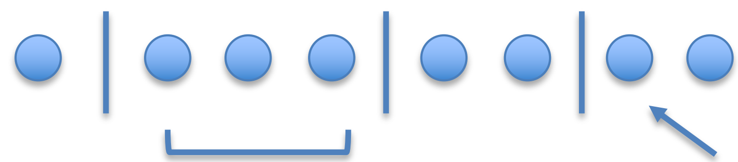


"trick" for solving:



$3N$ *modes for 3D case*

Einstein oscillator problem:

Vibrational energy for
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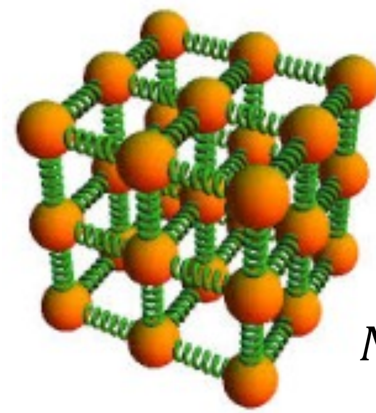
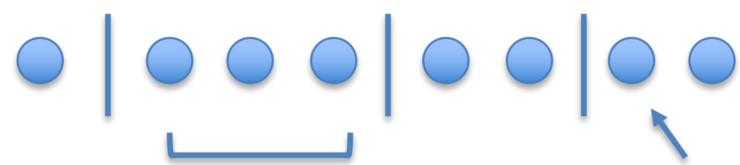


N atoms

binomial with q quanta, $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$

$$\& \;\; S = k_B ln(\Omega)$$



one vibrational mode

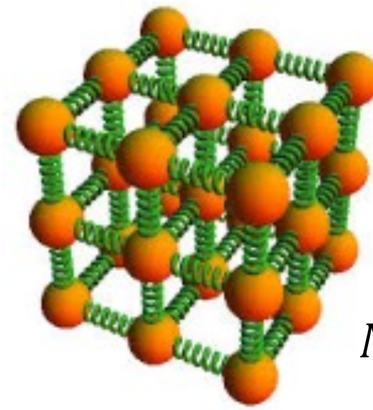
q quanta

3N modes for 3D case

Einstein oscillator problem:

binomial with q quanta, $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$



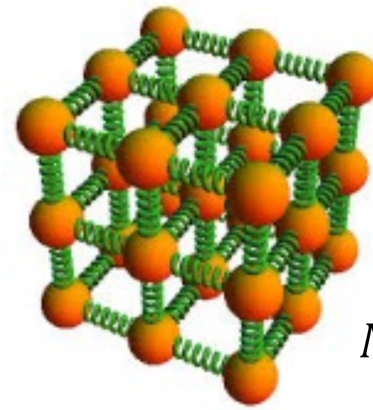
$N\ atoms$

$U/\hbar\omega_o$

Find, $S = k_B\left[3N\ln\left(1+\frac{q}{3N}\right) + q\ln\left(1+\frac{3N}{q}\right)\right]$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_o}\ln\left(1+\frac{3N}{q}\right)$$

Einstein oscillator problem:



$N\ atoms$

binomial with q quanta, $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$

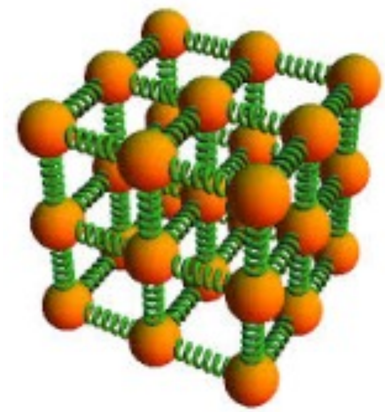
$U/\hbar\omega_o$

Find, $S = k_B\left[3N\ln\left(1+\frac{q}{3N}\right) + q\ln\left(1+\frac{3N}{q}\right)\right]$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_o}\ln\left(1+\frac{3N}{q}\right)$$

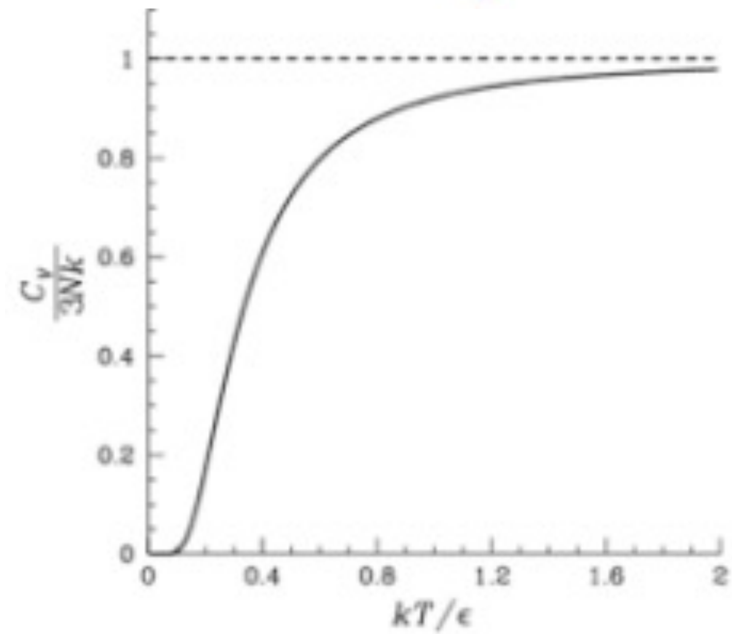
$$U = \frac{3N\hbar\omega_o}{e^{\hbar\omega_o/k_BT}-1}$$

Einstein oscillator problem:



binomial with q quanta, $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$



$$U = \frac{3N\hbar\omega_o}{e^{\hbar\omega_o/k_BT} - 1} \equiv 3N\hbar\omega_o\langle n\rangle$$

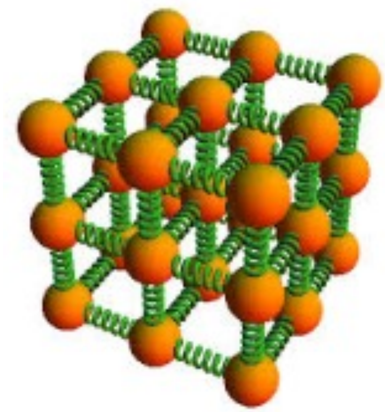
"Bose-Einstein distribution for undermined particle number"
(with particles = quanta ≈ "phonons")

$U \sim e^{-\hbar\omega_o/k_BT}$ low-T (activated form)

$U = 3Nk_BT$ high-T (correct classical limit)

Equipartition theorem

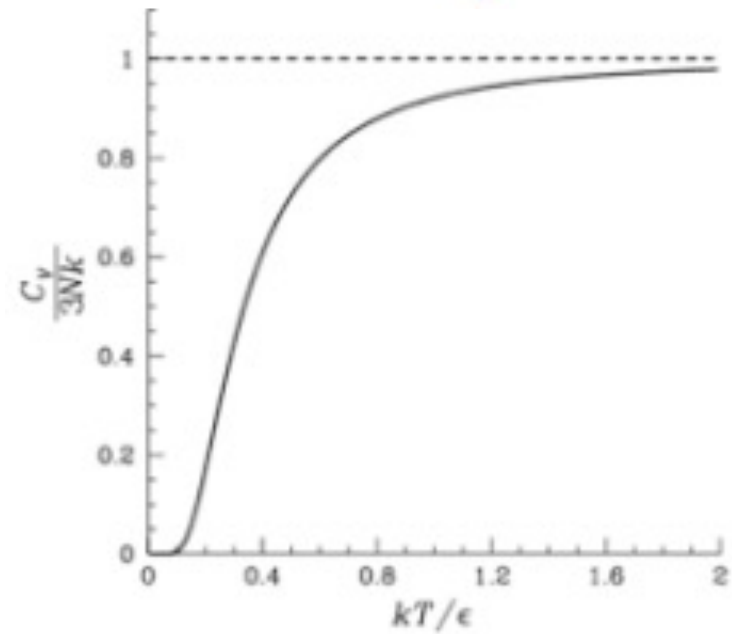
Einstein oscillator problem:



$$U = \frac{3N\hbar\omega_o}{e^{\hbar\omega_o/k_BT} - 1} \equiv 3N\hbar\omega_o\langle n\rangle$$

$$U \sim e^{-\hbar\omega_o/k_BT} \quad \text{low-}T$$

$$U = 3Nk_BT \quad \text{high-}T$$



- Correct classical limit helps validate the choice, $S = k_B ln(\Omega)$
- Actually, vibrational normal modes have *different* frequencies, not all identical (low-T details not correct)
- In high T limit, magnitude of $\hbar\omega_o$ becomes irrelevant, result is exact.