2/8.

(0)

Quiz 2 today

Quiz 3 2/22 in two weeks

Reading. Sections 2.1 – 2.4

Appendix. B, 2

Slides and videos:

simplest sustained nonequilibrium system
Rayleigh-Benard convection

show some static states: stripes, hexagons
dynamical states: spirals, spatiotemporal chaos
pattern formation

no broad powerful formalism yet known to
understand, predict, control patterns

Last lecture:

existence of entropy $S(U,V,N)$ that is additive over subsystems, $dS/dt \geq 0$ for isolated nonequilibrium system, explains why T defined by $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ is equal for all subsystems when isolated system in equilibrium

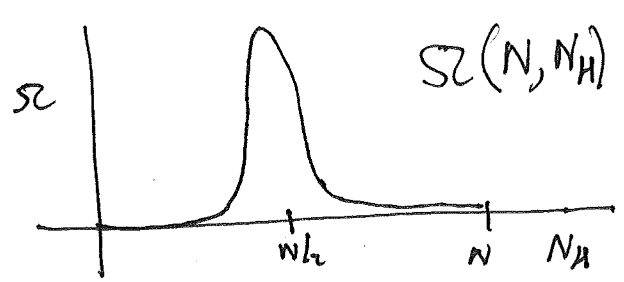
$T_1 > T_2 \Rightarrow$ energy flows from subsystem 1 $\rightarrow$ subsystem 2

Will discover and understand S by first studying a related concept: multiplicity $\Omega(U,V,N)$ which counts how many microstates are "accessible" or "compatible" or "consistent" with given macroscopic state defined by given values of U, V, N

Looked at N coins   # macrostates $= N+1$ state = # heads N_H

microstates $= 2^N$

$$\Omega(N, N_H) = \binom{N}{N_H} = \frac{N!}{N_H!\,(N-N_H)!}$$



$$\text{prob} = \frac{\binom{N}{N_H}}{2^N}$$

Calculate Ω for three different systems

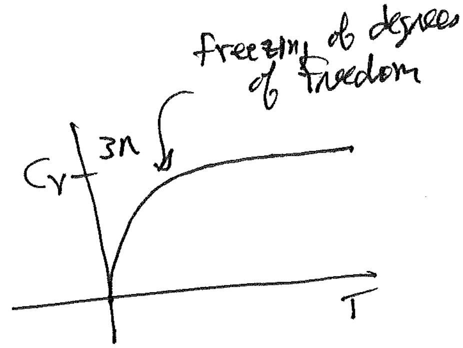
(1) Einstein "solid": N identical quantum harmonic oscillators, e.g. diatomic molecules and vibration modes

(2) ideal gas of atoms

(3) spin-1/2 paramagnet: no equipartition theorem relevant
no motion, so what is T?

Will give us valuable sense of Ω and hence entropy in several cases

$$C_V = 3Nk \frac{\left(\frac{\epsilon}{kT}\right)^2 e^{\epsilon/kT}}{\left(e^{\epsilon/kT}-1\right)^2}$$



$$C_V = \frac{3Nk}{2}$$ atomic gas, no internal structure

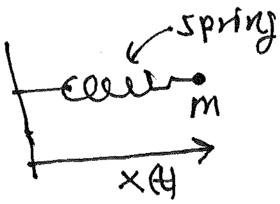
$$C_V = Nk \frac{(\mu B/kT)^2}{\cosh^2\left(\frac{\mu B}{kT}\right)}$$

Einstein solid

What is Ω? What is S? What is $\frac{1}{T} = \frac{\partial S}{\partial U}$

What is C_V?

Begin with some observations of classical harmonic oscillator



$$m \cdot a = \vec{F}$$

$$m \cdot \frac{d^2x}{dt^2} = -k(x - x_0)$$

$$x(t) - x(0) = A\cos(\omega t) + B\sin\omega t$$ periodic behavior

$$\omega = \sqrt{k/m}$$ angular frequency

$$\text{Energy} = \frac{1}{2}mv^2 + \frac{1}{2}k(x - x_0)^2$$

lowest value: $v = 0, \; x = x_0 \Rightarrow E = 0$

E can take on any values $E \geq 0$

Where Does Spring Constant Come From?

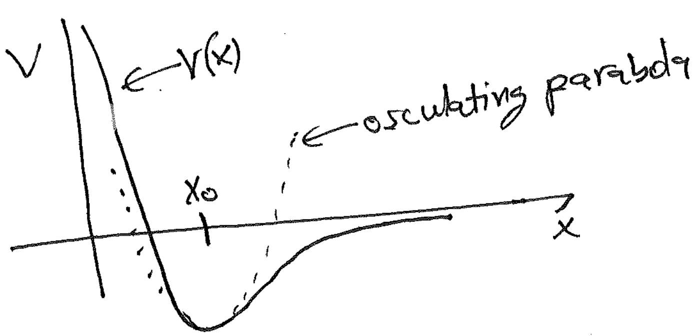
Intro physics: forces come from potential energies

$$F = -\frac{dV}{dx} \qquad V = \text{pot energy} = V(x)$$

$$\vec{F} = -\nabla V \qquad V = V(x,y,z)$$

Consider 1d case, say potential for atoms in diatomic molecule

x_0 = equilibrium value at minimum



Taylor expand $V(x)$ around $x = x_0$

$$V(x) = V(x_0) + \underbrace{V'(x_0)}_{=0 \text{ at minimum}}(x-x_0) + \frac{1}{2!}V''(x_0)(x-x_0)^2 + \overbrace{\frac{1}{3!}V'''(x_0)(x-x_0)^3}^{\text{anharmonic term}} + \frac{1}{4!}\cdots$$

x close to x_0

$$\simeq V_0 + \underbrace{\frac{1}{2}V''(x_0)(x-x_0)^2}_{\text{spring-like term}} + \cdots$$

Conclude: spring constant ~~be~~ $\boxed{k = V''(x_0)}$

if $|x-x_0|$ becomes large, get anharmonic behavior, need to keep high-order terms

$$m\ddot{x} = -kx - k_2 x^3 \quad \text{Duffing eq}$$

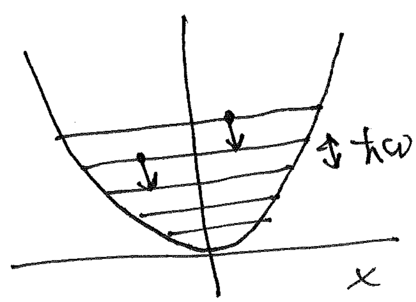
Quantum Mechanic Harmonic Oscillator

given mass m, Frequency $= \sqrt{\frac{k}{m}} = \sqrt{\frac{V''(x_0)}{m}} = \omega$

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

Quantum mechanics predicts that energy levels of particle are discrete and equally spaced:

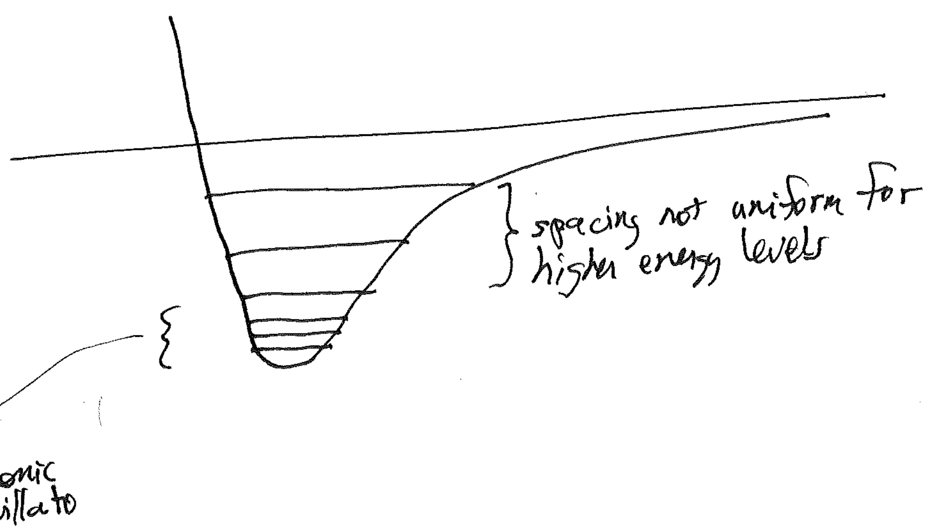
$$\boxed{E = \frac{\hbar\omega}{2} + (\hbar\omega)n} \qquad n = 0, 1, 2, \ldots$$



Can deduce freq ω from spectroscopy:
emitted photon has energy

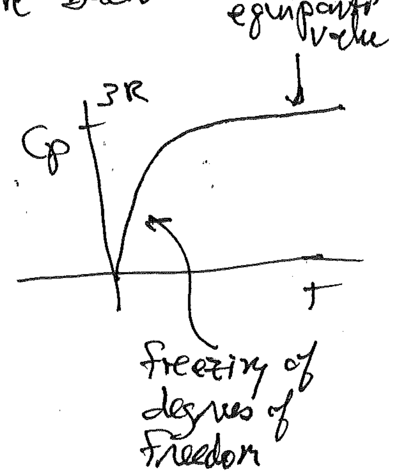
$$\Delta E = \hbar\omega = hf$$

~~Real~~ Perfect harmonic oscillators don't exist, molecules become anharmonic at higher energies



Einstein Solid: N Identical Quantum Harmonic Oscillator With Frequency f

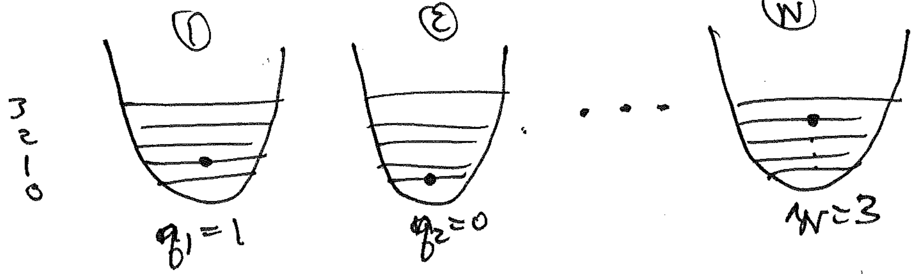
Far away from melting point, solid of $N/3$ atoms consist of atoms oscillating about equil point. Einstein in ~1907 approximated vibrations of solid as arising from <u>N</u> identical independent quantum osillators. Real solid has continuous range of frequencies, will come back and study Debye theory later.



Einstein able to explain experimental data: especially that $C_p(T) \to 0$ as $T \to 0$

First successful application of QM to solids

Multiplicity $\Omega(N, q)$ of Einstein Solid with N Oscillators, Total Energy q



<u>microstate</u> given by integers $q_1, q_2, \ldots, q_N$ giving amount of energy in system $\quad q_1 \geq 0 \ \cdots \ q_N \geq 0$

<u>macrostate</u>: $E_{total} = E_1 + E_2 + \cdots + E_N$

$$= \left(\frac{\hbar\omega}{2} + \hbar\omega q_1\right) + \left(\frac{\hbar\omega}{2} + \hbar\omega q_2\right) + \cdots$$

$$E_{total} = \underbrace{N\frac{\hbar\omega}{2}}_{\downarrow} + \hbar\omega(q_1 + q_2 + \cdots + q_N)$$

The so-called <u>ground-state energy</u> $N\frac{\hbar\omega}{2}$ not involved with thermal energy U of system so ignore

For given ~~macrosc~~ macroscopic state with energy $q \geq 0$ (this is abbreviation for $E = \hbar\omega q$), how many microstates? $\quad \Omega(N, q) = ?$

claim: $\boxed{\Omega(N, q) = \binom{N+q-1}{q}}$

Multiplicity For N=3 Oscillators In Einstein Solid

<table>
<tr><th>q</th><th>Etotal = ħωq</th><th>q1</th><th>q2</th><th>q3</th><th>Ω</th></tr>
<tr><td>0</td><td>||</td><td>0</td><td>0</td><td>0</td><td>1</td></tr>
<tr><td>1</td><td>|•|</td><td>0</td><td>1</td><td>0</td><td>3</td></tr>
<tr><td></td><td>||•</td><td>0</td><td>0</td><td>1</td><td></td></tr>
<tr><td></td><td>•||</td><td>1</td><td>0</td><td>0</td><td></td></tr>
<tr><td>2</td><td>•|•|</td><td>1</td><td>1</td><td>0</td><td>6</td></tr>
<tr><td></td><td>•||•</td><td>1</td><td>0</td><td>1</td><td></td></tr>
<tr><td></td><td>|•|•</td><td>0</td><td>1</td><td>1</td><td></td></tr>
<tr><td></td><td>|••|</td><td>0</td><td>2</td><td>0</td><td></td></tr>
<tr><td></td><td>||••</td><td>0</td><td>0</td><td>2</td><td></td></tr>
<tr><td></td><td>••||</td><td>2</td><td>0</td><td>0</td><td></td></tr>
<tr><td>3</td><td>•|•|•</td><td>1</td><td>1</td><td>1</td><td>10</td></tr>
<tr><td></td><td>•|••|</td><td>1</td><td>2</td><td>0</td><td></td></tr>
<tr><td></td><td>•||••</td><td>1</td><td>0</td><td>2</td><td></td></tr>
<tr><td></td><td>••|•|</td><td>2</td><td>1</td><td>0</td><td></td></tr>
<tr><td></td><td>••||•</td><td>2</td><td>0</td><td>1</td><td></td></tr>
<tr><td></td><td>|•|••</td><td>0</td><td>1</td><td>2</td><td></td></tr>
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<tr><td></td><td>|•••|</td><td>0</td><td>3</td><td>0</td><td></td></tr>
<tr><td></td><td>||•••</td><td>0</td><td>0</td><td>3</td><td></td></tr>
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$\Omega(4) = ?$

Derivation $\Omega(N,q) = \binom{N+q-1}{q}$

Clever trick to count microstates for N oscillators with total energy q

Represent q by q dots, e.g. $q=3$ • • •

represent oscillators by $N-1$ vertical lines | | |

microstate then corresponds to arbitrary linear ordering of dots and bars, e.g.:

$N=3$
$q=3$

$\underbrace{\bullet\,\bullet}_{q_1=2}\;|\;\underbrace{\bullet}_{q_2=0}\;|$ $\quad q_3=0$

$\bullet\;|\;\bullet\;|\;\bullet$ $\quad q_1=q_2=q_3=$

$\bullet\;|\;|\;\bullet\,\bullet$

$q_1=1 \quad q_2=0 \quad q_3=2$

But I have $N-1+q$ symbols so # microstates # of ways I can place q dots in $N-1+q$ slots, with bars occupying other slots

$$\Omega(N,q) = \binom{N-1+q}{q} \checkmark$$

check:

$$\Omega(3,1) = \binom{2+1}{1} = \binom{3}{1} = 3$$

$$\Omega(3,3) = \binom{5}{3} = \frac{5\cdot 4}{1\cdot 2} = 10 \checkmark$$

$$\Omega(8,3) = \binom{10}{8} = \binom{10}{2} = \frac{10\cdot 9}{1\cdot 2} = 45$$ tedious!