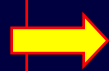


# Lecture 11

## Applying Boltzmann Statistics

- Elasticity of a Polymer
- Heat capacities
  - $C_V$  of molecules – for real !!
  - When equipartition fails

Not on  
midterm.



Planck Distribution of Electromagnetic Radiation

Reading for this Lecture:  
Elements Ch 9

Reading for Lecture 13:  
Elements Ch 4D-F

# Last time: Boltzmann Distribution

If we have a system that is coupled to a heat reservoir at temperature  $T$ :

- The entropy of the reservoir decreases when the small system extracts energy  $E_n$  from it.
- Therefore, this will be less likely (fewer microstates).
- The probability for the small system to be in a particular state with energy  $E_n$  is given by the Boltzmann factor:

$$P_n = \frac{e^{-E_n / kT}}{Z}$$

where,  $Z = \sum_n e^{-E_n / kT}$  to make  $P_{\text{tot}} = 1$ .

$Z$  is called the “partition function”.

## On the importance of polymers...

- Polymers play a major role in society.
- In 1930, Wallace Carothers (PhD UIUC, 1924) et. al at DuPont invent neoprene.
- In 1935 Carothers goes on to invent nylon – “the miracle fiber” (but commits suicide in 1937, just before it’s importance is realized). In WWII, nylon production was directed to making parachute canopies.
- Rubber also played a major role in WWII. You *need* rubber for tires, gas masks, plane gaskets, etc.
  - In 1941 our access to 90% of the rubber-producing countries was cut off by the Japanese attack on Pearl Harbor.
  - What to do? Make *synthetic* rubber. Who did it first?
  - Carl “Speed” Marvel, UIUC!
- Today, “plastics” are used for many, many, many things.
- Other polymers of note: cellulose, proteins, DNA, ...

# Statistical Mechanics of a Polymer

A polymer is a molecular chain (e.g., rubber), consisting of many parts linked together. The joints are flexible.

Here we consider a simple (i.e., crude) model of a polymer, to understand one aspect of some of them.

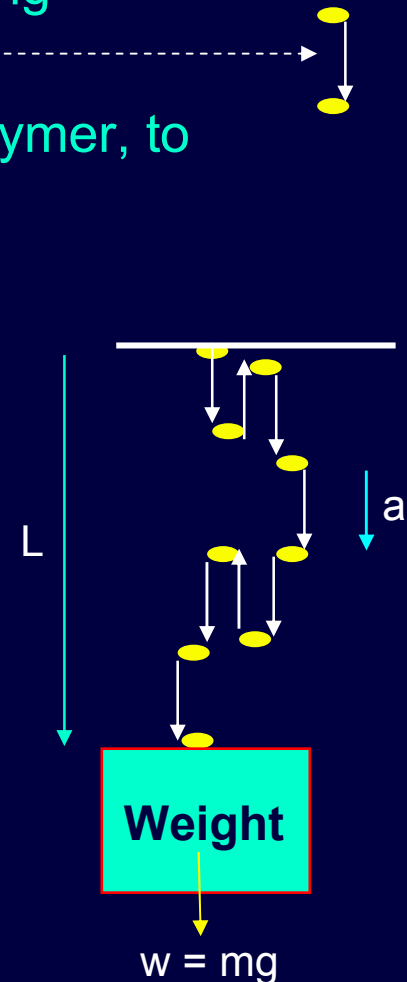
Consider a weight hanging from a chain. Each link has length  $a$ , and can only point up or down. Thus, it's a system containing "2-state" components.

This is similar to the spin problem. Each link has two energy states:



The reason is that when a link flips from down to up, the weight rises by  $2a$ . (We ignore the weight of the chain itself.)

In the molecular version of this experiment, the weight is replaced by an atomic force instrument.



# Act 1

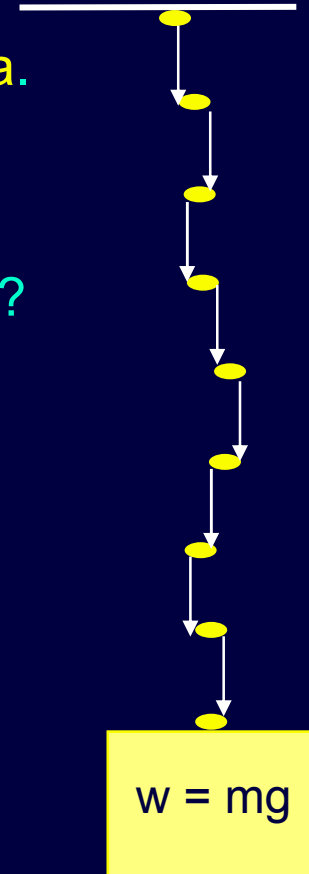
Suppose our polymer has 30 segments, each of length  $a$ . Each segment can be oriented up or down.

1) What is the chain length of the minimum entropy state?

a)  $L = 30a$    b)  $L = 0$    c)  $0 < L < 30a$

2) What is the minimum entropy of the chain?

a)  $\sigma_{\min} = 0$    b)  $\sigma_{\min} = 1$    c)  $\sigma_{\min} = \ln 30$



# Solution

Suppose our polymer has 30 segments, each of length  $a$ . Each segment can be oriented up or down.

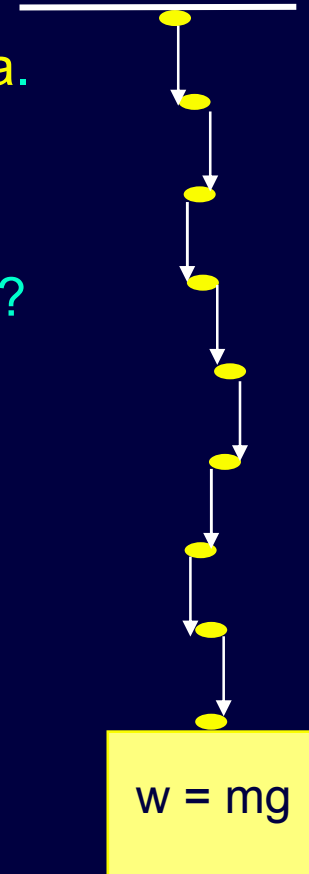
1) What is the chain length of the minimum entropy state?

- a)  $L = 30a$    b)  $L = 0$    c)  $0 < L < 30a$

The minimum entropy state has the fewest microstates or arrangements of the links.

2) What is the minimum entropy of the chain?

- a)  $\sigma_{\min} = 0$    b)  $\sigma_{\min} = 1$    c)  $\sigma_{\min} = \ln 30$



# Solution

Suppose our polymer has 30 segments, each of length  $a$ . Each segment can be oriented up or down.

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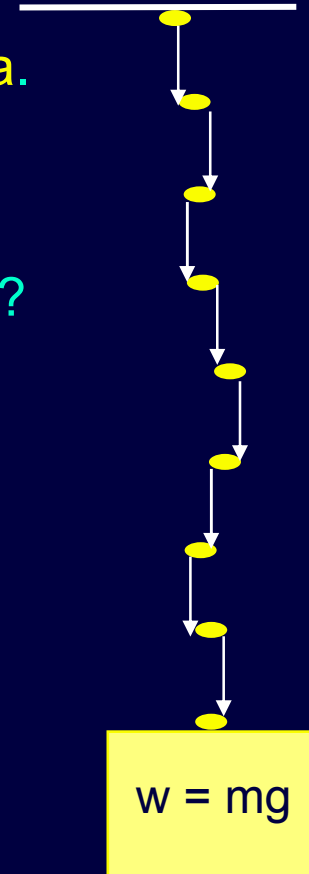
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The minimum entropy state has the fewest microstates or arrangements of the links.

2) What is the minimum entropy of the chain?

- a)  $\sigma_{\min} = 0$     b)  $\sigma_{\min} = 1$     c)  $\sigma_{\min} = \ln 30$

The minimum entropy state (with  $L=30a$ ) has only one microstate.



# The Equilibrium Length

The solution is mathematically the same as the spin system with the substitution  $\mu B \rightarrow wa$ .

The average length of the rubber band is (compare with magnetization result):

$$\langle L \rangle = Na \cdot \tanh\left(\frac{wa}{kT}\right)$$

The average energy is:

$$\langle E \rangle = -w \langle L \rangle$$

$N$  = # segments,  
 $a$  = segment length  
 $w$  =  $mg$

As the polymer stretches, its entropy decreases, and the reservoir's entropy increases (because  $U_R$  increases).

The maximum total entropy occurs at an intermediate length (not at  $L=0$  or  $L=Na$ ), where the two effects cancel.

Question: What happens when you heat the rubber band?



# Act 2

Suppose we rapidly stretch the rubber band.

1) The entropy of the segment configurations will

a) decrease   b) remain the same   c) increase



2) The temperature will

a) decrease   b) remain the same   c) increase

# Solution

Suppose we rapidly stretch the rubber band.

1) The entropy of the segment configurations will

a) decrease   b) remain the same   c) increase

The minimum entropy state has the fewest microstates or arrangements of the links, i.e., the extended chain.



2) The temperature will

a) decrease   b) remain the same   c) increase

# Solution

Suppose we rapidly stretch the rubber band.

1) The entropy of the segment configurations will

a) decrease   b) remain the same   c) increase

The minimum entropy state has the fewest microstates or arrangements of the links, i.e., the extended chain.



2) The temperature will

a) decrease   b) remain the same   c) increase

Why is that ???

# Act 2 Discussion

Because we are stretching the band rapidly, this is an example of an adiabatic process:

$$Q = 0 = \Delta U - W_{\text{on}} \rightarrow \Delta U = W_{\text{on}}$$

Stretching the band does work on it, so  $U$  increases.

The links themselves have no  $U$ , so

the energy goes into the usual kinetic energy (vibrational) modes

$\rightarrow T$  increases.

This is similar to adiabatically compressing an ideal gas (cf. 'firestarter' demo).

We often used  $dW_{\text{on}} = -pdV$ .

You could redo all the thermal physics, instead for elastic materials, using  $dW_{\text{on}} = +F dl$ .

Or for batteries, using  $dW_{\text{on}} = +V dq$ ,

Or for magnets ...

# Heat Capacity & Harmonic Oscillators

We can use the Boltzmann factor to calculate the average thermal energy,  $\langle E \rangle$ , per particle and the internal energy,  $U$ , of a system. We will consider a collection of harmonic oscillators.

- The math is simple (even I can do it!), and
- It's a good approximation to reality, not only for mechanical oscillations, but also for electromagnetic radiation.

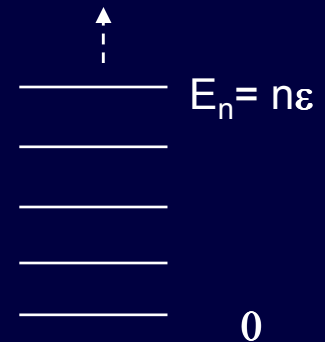
Start with the Boltzmann probability distribution:

$$P_n = \frac{e^{-E_n/kT}}{Z}$$

We need to calculate the partition function:

$$Z = \sum_n e^{-E_n/kT}$$

To do the sum, remember the energy levels of the harmonic oscillator:  $E_n = n\varepsilon$ . Equally spaced:



Define:  $x \equiv e^{-\varepsilon/kT}$

Then:

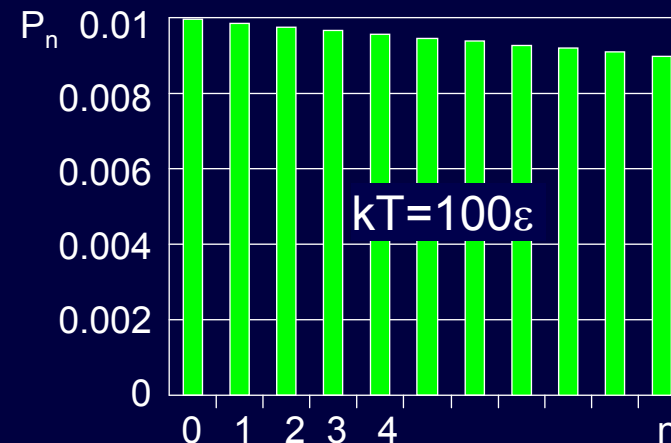
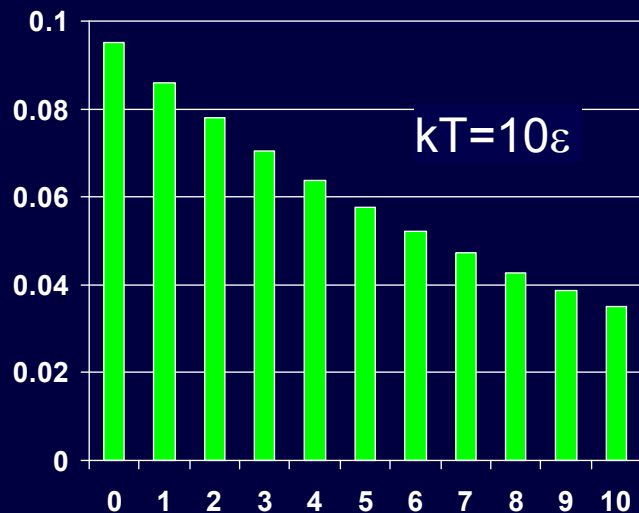
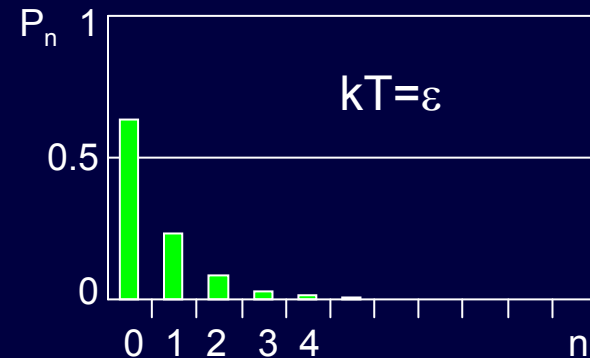
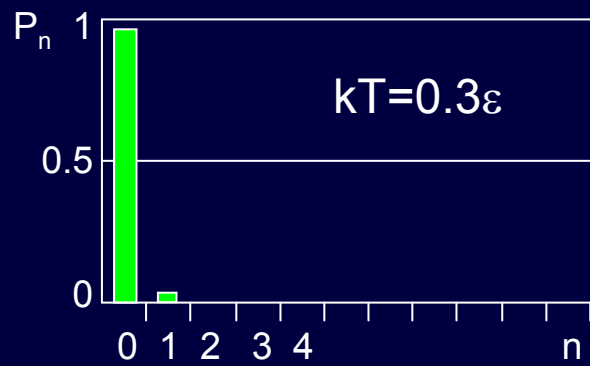
$$Z = \sum_{n=0}^{\infty} e^{-n\varepsilon/kT} = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

It's just a geometric series.

$$P_n = (1 - e^{-\varepsilon/kT}) e^{-n\varepsilon/kT}$$

# Heat Capacity & Harmonic Oscillators (2)

The ratio  $\varepsilon/kT$  is important. Let's look at the probability for an oscillator to have energy  $E_n$ , for various values of that ratio.



The important feature:  
At low temperatures, only a few states have significant probability.

# Heat Capacity & Harmonic Oscillators (3)

Let's calculate the average oscillator energy, and then the heat capacity.

$$E_n = n\varepsilon, \text{ and } P_n = (1 - e^{-\varepsilon/kT}) e^{-n\varepsilon/kT}$$

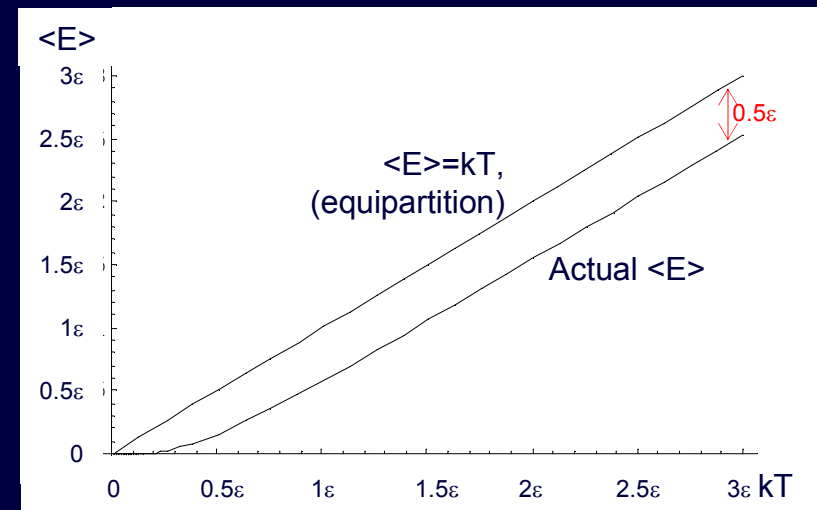
$$\text{so } \langle E \rangle = \sum_{n=0}^{\infty} E_n P_n = \frac{\varepsilon}{e^{\varepsilon/kT} - 1} \quad \text{See supplemental slide for the algebra.}$$

At high T (when  $kT \gg \varepsilon$ ),  $e^{\varepsilon/kT} \approx 1 + \varepsilon/kT$ :

$$\langle E \rangle \approx kT, \text{ equipartition !!}$$

At low T (when  $kT \ll \varepsilon$ ),  $e^{\varepsilon/kT} \gg 1$ :

$$\langle E \rangle \approx \varepsilon e^{-\varepsilon/kT} \ll kT.$$



Equipartition requires that  $kT$  is much larger than the energy level spacing, so that there are many states with  $E < kT$ .

# Heat Capacity & Harmonic Oscillators (4)

Calculate the heat capacity by taking the derivative :

$$C = N \frac{d\langle E \rangle}{dT} = Nk \left( \frac{\varepsilon}{kT} \right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2}$$

$\approx Nk$ , when  $kT \gg \varepsilon$

$\approx Nk \left( \frac{\varepsilon}{kT} \right)^2 e^{-\varepsilon/kT} \ll Nk$ , when  $kT \ll \varepsilon$

At what temperature is equipartition reached?

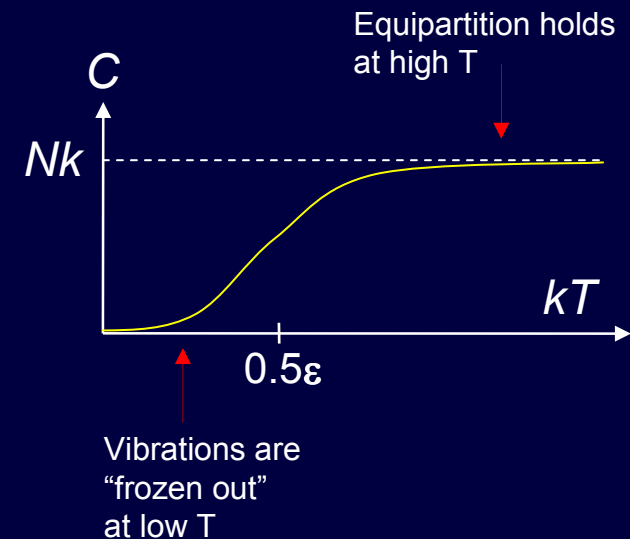
To answer this, we need to know how big  $\varepsilon$  is.

We use a fact from QM (P214):

$\varepsilon = hf$ , where  $h$  is Planck's constant =  $6.6 \cdot 10^{-34}$  J-s  
 $f$  is the oscillator frequency.

For typical vibrations in molecules and solids,

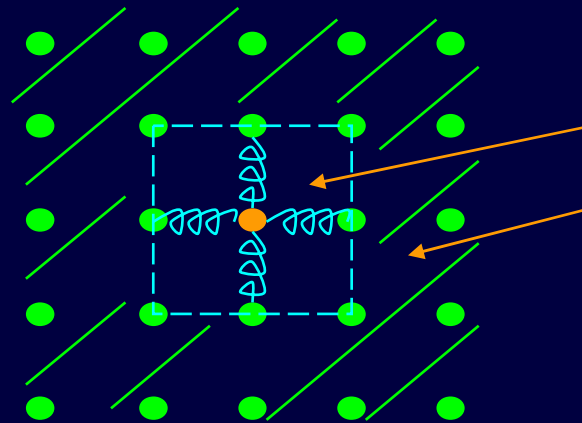
$kT = hf$  in the range 40 K to 4,000 K.





## FYI: Heat Capacity of an Einstein Solid $3N$ SHO's

- Consider a solid as atomic masses connected by springs (the atomic bonds):



Small system (one atom)

Einstein pretends it oscillates independently of other atoms.

For high  $T$ , Equipartition Theorem predicts  $\frac{1}{2} kT$  for each quadratic term in the energy:

$$\frac{1}{2} \langle (mv_x^2 + mv_y^2 + mv_z^2 + \kappa x^2 + \kappa y^2 + \kappa z^2) \rangle = 3kT$$



The energy and heat capacity of the entire solid ( $N$  atoms) is:

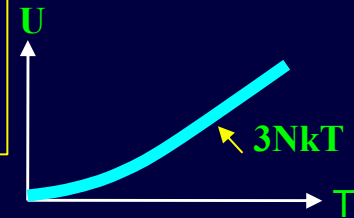
$$U = N \langle E \rangle = 3NkT \quad C_V = \frac{dU}{dT} = 3Nk$$

What about low temperatures?  $\longrightarrow$

# FYI: Heat Capacity of Einstein solid

For a solid with N atoms,  
total vibrational energy is:

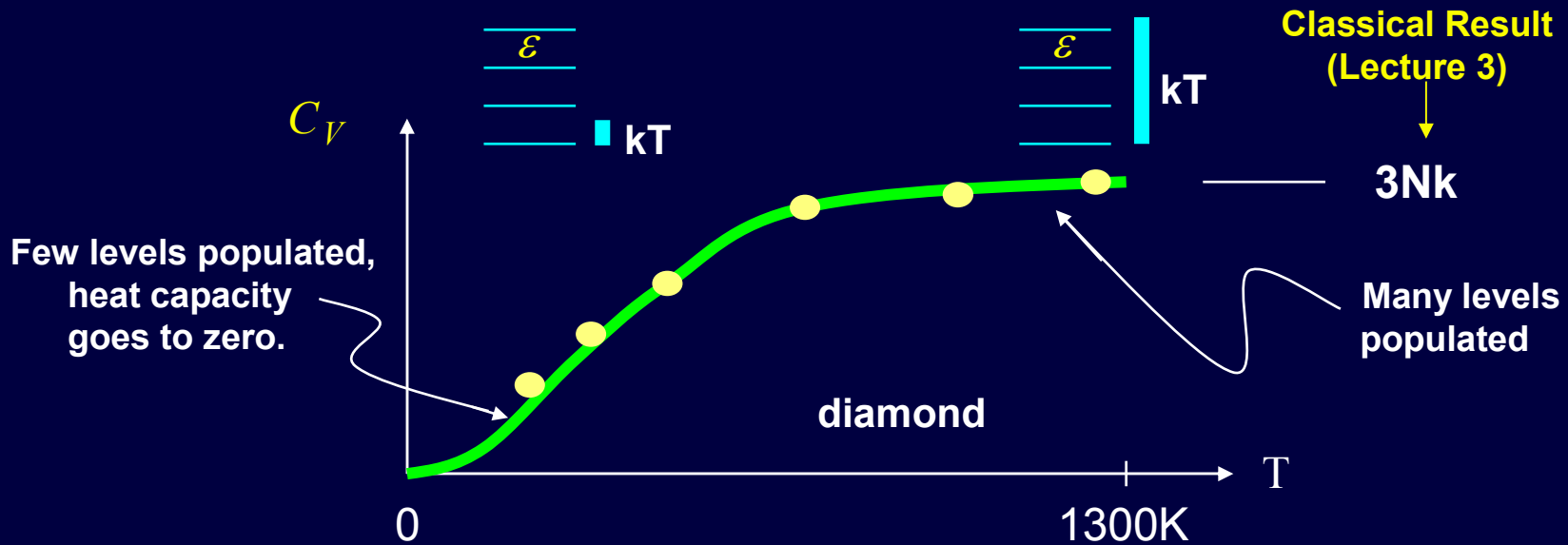
$$U = 3N \langle E \rangle = \frac{3N\varepsilon}{e^{\varepsilon/kT} - 1} \quad (3-D)$$



The heat capacity at  
constant volume is:

$$C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V$$

Slope of this



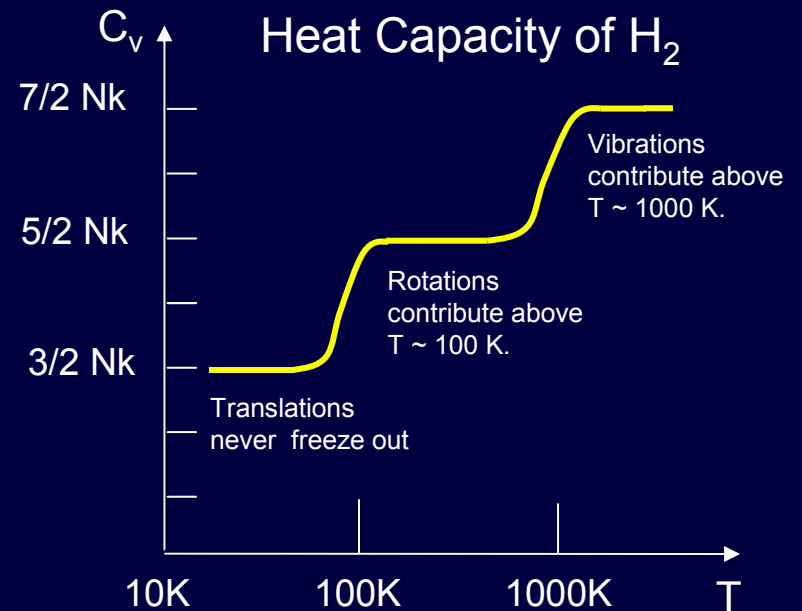
# Many Modes of Motion ?

If a molecule has several modes of motion, some may be in equipartition, while others may be “frozen out”.

Consider a diatomic molecule ( $H_2$ ).  
It has three quadratic energy modes:

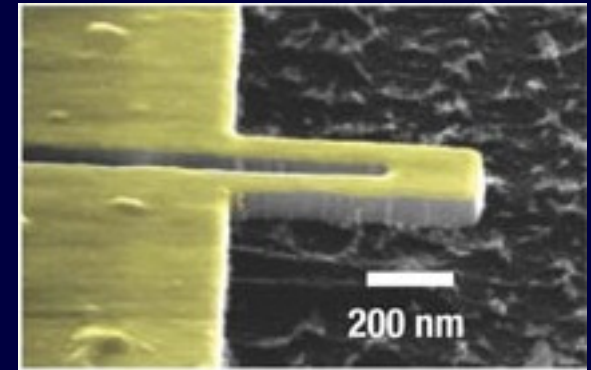
- Bond vibrations have a larger  $\varepsilon$ , corresponding to  $T \sim 1000$  K.
- Rotations have a moderate energy spacings, corresponding to  $T \sim 100$  K.
- Translations have a continuous range of energies  $\rightarrow$  never ‘frozen’ out

At  $T = 300$  K, translations and rotations contribute to the heat capacity, but not bond vibrations.



# Act 3

Very sensitive mass measurements ( $10^{-18}$  g sensitivity) can be made with nanocantilevers, like the one shown. This cantilever vibrates with a frequency,  $f = 127$  MHz. FYI:  $h = 6.6 \times 10^{-34}$  J-s and  $k = 1.38 \times 10^{-23}$  J/K



Li, *et al.*, Nature Nanotechnology 2, p114 (2007)

1) What is the spacing,  $\varepsilon$ , between this oscillator's energy levels?

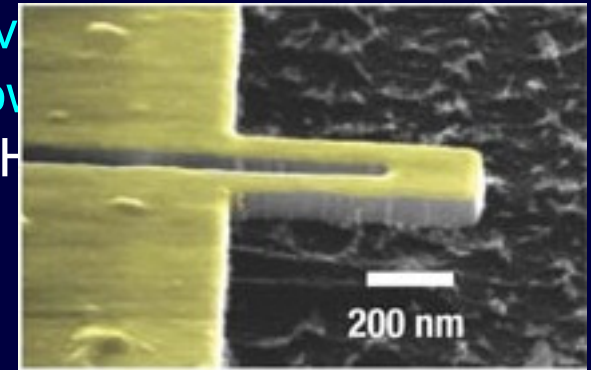
a)  $\varepsilon = 6.6 \times 10^{-34}$  J    b)  $\varepsilon = 8.4 \times 10^{-26}$  J    c)  $\varepsilon = 1.4 \times 10^{-23}$  J

2) At what approximate temperature,  $T$ , will equipartition fail for this oscillator?

a)  $T = 8.4 \times 10^{-26}$  K    b)  $T = 6.1 \times 10^{-3}$  K    c)  $T = 295$  K

# Solution

Very sensitive mass measurements ( $10^{-18}$  g sensitive) can be made with nanocantilevers, like the one shown. This cantilever vibrates with a frequency,  $f = 127$  MHz. FYI:  $h = 6.6 \times 10^{-34}$  J-s and  $k = 1.38 \times 10^{-23}$  J/K



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1) What is the spacing,  $\epsilon$ , between this oscillator's energy levels?



$$a) \epsilon = hf = (6.6 \times 10^{-34} \text{ J-s}) \times (127 \times 10^6 \text{ Hz}) = 8.4 \times 10^{-26} \text{ J}$$

2) At what approximate temperature,  $T$ , will equipartition fail for this oscillator?

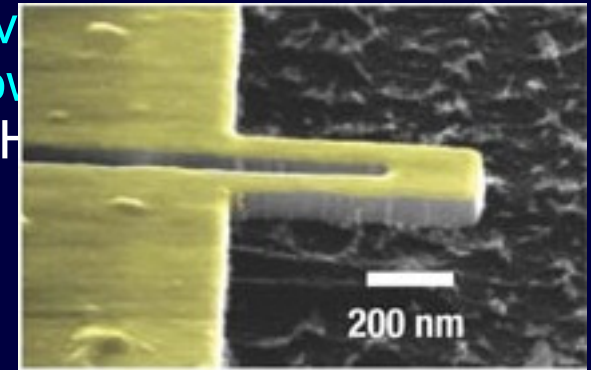
$$a) T = 8.4 \times 10^{-26} \text{ K}$$

$$b) T = 6.1 \times 10^{-3} \text{ K}$$

$$c) T = 295 \text{ K}$$

# Solution

Very sensitive mass measurements ( $10^{-18}$  g sensitive) can be made with nanocantilevers, like the one shown. This cantilever vibrates with a frequency,  $f = 127$  MHz. FYI:  $h = 6.6 \times 10^{-34}$  J-s and  $k = 1.38 \times 10^{-23}$  J/K



Li, et al., Nature Nanotechnology 2, p114 (2007)

1) What is the spacing,  $\epsilon$ , between this oscillator's energy levels?

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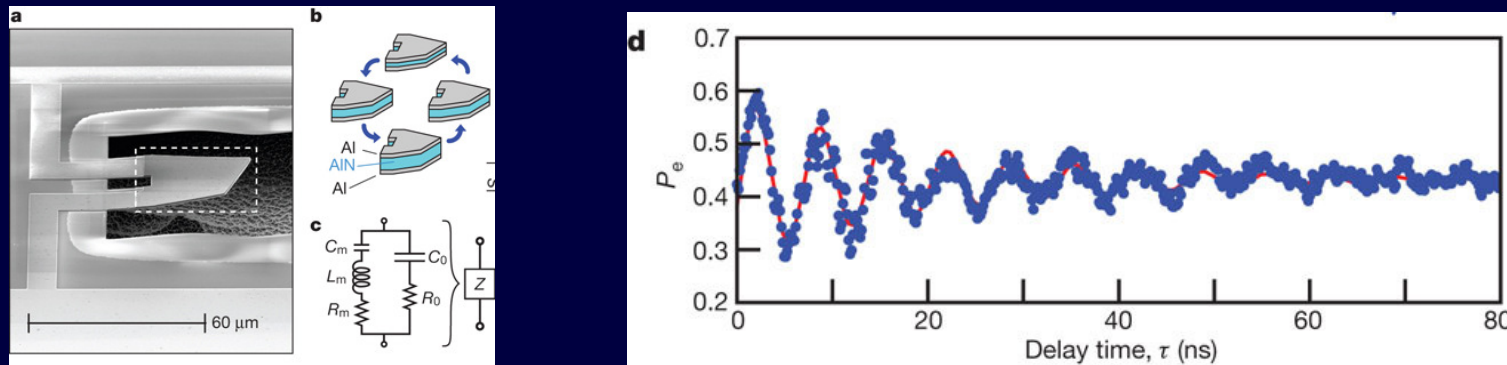
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2) At what approximate temperature,  $T$ , will equipartition fail for this oscillator?

a)  $T = \frac{\epsilon}{k} = \frac{(8.38 \times 10^{-26} \text{ J})}{(1.38 \times 10^{-23} \text{ J/K})} = 6.1 \times 10^{-3} \text{ K}$    b)  $T = 6.1 \times 10^{-3} \text{ K}$    c)  $T = 295 \text{ K}$

## FYI: Recent Physics Milestone!

There has been a race over the past ~20 years to put a ~macroscopic object into a quantum superposition. The first step is getting the object into the ground state, below all thermal excitations. This was achieved for the first time in 2010, using vibrations in a small “drum” :

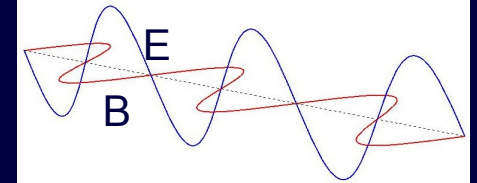


**“Quantum ground state and single-phonon control of a mechanical resonator”,**  
A. D. O’Connell, et al., *Nature* **464**, 697-703 (1 April 2010)

Quantum mechanics provides a highly accurate description of a wide variety of physical systems. However, a demonstration that quantum mechanics applies equally to macroscopic mechanical systems has been a long-standing challenge... Here, using conventional cryogenic refrigeration, we show that **we can cool a mechanical mode to its quantum ground state** by using a microwave-frequency mechanical oscillator—a ‘quantum drum’... We further show that **we can controllably create single quantum excitations (phonons) in the resonator**, thus taking the first steps to complete quantum control of a mechanical system.

# Basics of Thermal Radiation

Every object in thermal equilibrium emits (and absorbs) electromagnetic (EM) waves from its surface. (It glows.)  
How much? What colors?

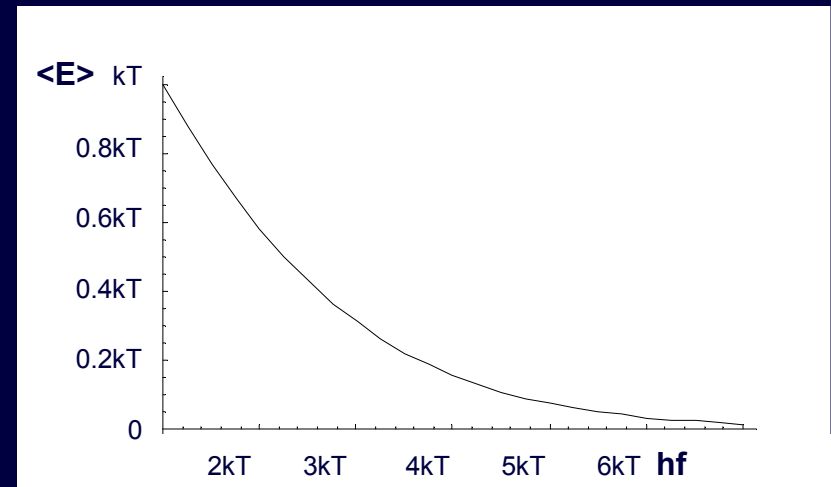


For our purposes, the important feature of EM waves is that they oscillate with a frequency,  $f$ , just like a mechanical oscillator. Therefore, the energy of an EM wave is a multiple of  $\varepsilon = hf$ , just like a mechanical oscillator.  
Note: Each of these packets of energy  $\varepsilon = hf$  is called a “photon”.

This means that in thermal equilibrium:

The average energy of an EM wave of frequency  $f$  is the same as the average energy of a mechanical oscillator with the same  $f$ :

$$\langle E \rangle = \frac{\varepsilon}{e^{\varepsilon/kT} - 1} = \frac{hf}{e^{hf/kT} - 1}$$



Low frequency modes (such that  $\varepsilon = hf \ll kT$ ) satisfy equipartition. They have  $\langle E \rangle = kT$ . High frequency modes do not.



# Planck Radiation Law

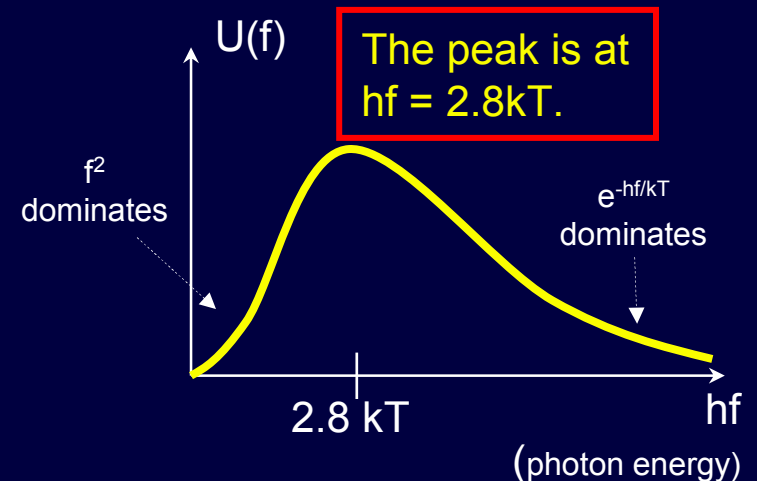
## “Black Body Radiation”

The calculation of  $\langle E \rangle$  on the previous slide is for each mode (specific  $f$ ). However, what we really want to know is how much energy there is per frequency interval. The more frequency modes there are near a particular frequency, the brighter the object is at that frequency. This is similar to the degeneracy effect from last lecture.

The density of frequency modes is proportional to  $f^2$ . (See “Elements” for the derivation)  
So, the EM radiation intensity as a function of frequency is:

$$U(f) \propto \frac{hf}{e^{hf/kT} - 1} f^2$$

Energy per frequency interval      Average energy per mode      Number of modes per frequency interval



This formula applies to almost any hot object, *i.e.*, it doesn't matter if it's hot gas on the sun, or the filament of a tungsten lamp.

# Dependence of Color on Temperature

You can also write the Planck distribution in terms of power/unit wavelength,  $U(\lambda)$ , instead of power/unit frequency,  $U(f)$ . The energy distribution varies as:

$$U(\lambda) \propto \frac{1}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

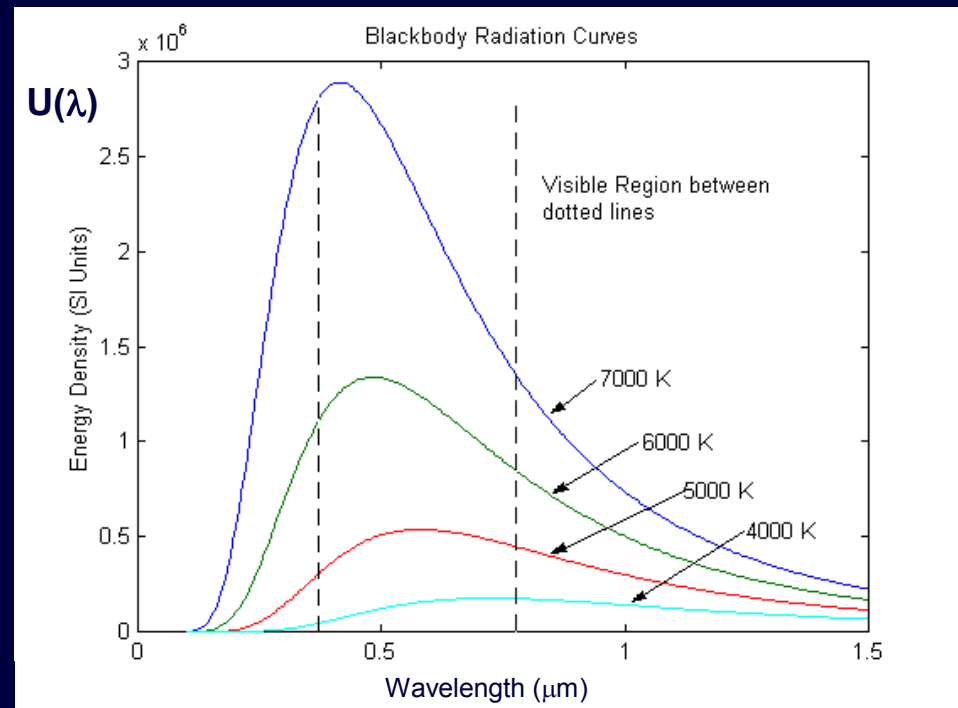
$$f = c/\lambda \Rightarrow df \propto d\lambda/\lambda^2$$

(The - sign doesn't matter.)

The peak wavelength:

$$\lambda_{\max} T = 0.0029 \text{ m-K}$$

This relation is known as Wien's Displacement law.





Where most burning is occurring, the fire is white, the hottest color possible for organic material in general, or yellow. Above the yellow region, the color changes to orange, which is cooler, then red, which is cooler still.

# Next Class

- Law of Atmospheres
- Global Warming

## Next Week: Heat Engines

- Thermodynamic processes and entropy
- Thermodynamic cycles
- Extracting work from heat

# Supplement:

## Derivation of $\langle E \rangle$ for the Harmonic Oscillator

This is always true:

$$Z = \sum_n e^{-E_n/kT} = \sum_n e^{-E_n\beta} \quad (\beta \equiv 1/kT)$$

$$\frac{dZ}{d\beta} = -\sum_n E_n e^{-E_n\beta}, \text{ so}$$

$$-\frac{1}{Z} \frac{dZ}{d\beta} = \sum_n E_n P_n = \langle E \rangle, \text{ because } P_n = \frac{e^{-E_n\beta}}{Z}$$

This is true for the harmonic oscillator:

$$Z = \frac{1}{1 - e^{-\epsilon\beta}}$$

$$\frac{dZ}{d\beta} = \frac{-1}{(1 - e^{-\epsilon\beta})^2} (-e^{-\epsilon\beta}) (-\epsilon) = \frac{-\epsilon e^{-\epsilon\beta}}{(1 - e^{-\epsilon\beta})^2}$$

$$\langle E \rangle = -\frac{1}{Z} \frac{dZ}{d\beta} = \frac{\epsilon}{e^{\epsilon\beta} - 1}$$

# Derivation of Equipartition

for quadratic degrees of freedom

To calculate  $\langle E \rangle$ , we must perform a sum:  $\langle E \rangle = \sum_{n=1}^{\infty} E_n P_n$

If  $kT \gg \varepsilon$  (the energy spacing), then we can turn this sum into an integral:

$$\langle E \rangle = \int_0^{\infty} E(q) P(q) \rho(q) dq$$

$q$  is the variable that determines  $E$  (e.g., speed).

The only subtle part is  $\rho(q)$ . This is the density of energy states per unit  $q$ , needed to do the counting right. For simplicity, we'll assume that  $\rho$  is constant.

Calculate  $\langle E \rangle$ , assuming that  $E = aq^2$ :

$$\langle E_q \rangle = \frac{\int aq^2 e^{-\frac{aq^2}{kT}} dq}{\int e^{-\frac{aq^2}{kT}} dq} = \frac{kT}{2}$$

So, equipartition follows naturally from simple assumptions, and we know when it fails.

See the supplement for the behavior of linear modes.

# Supplement: Equipartition for Linear Degrees of Freedom

When we talk about equipartition, ( $\langle E \rangle = \frac{1}{2}kT$  per mode) we say “quadratic”, to remind us that the energy is a quadratic function of the variable (e.g.,  $\frac{1}{2}mv^2$ ).

However, sometimes the energy is a linear function (e.g.,  $E = mgh$ ). How does equipartition work in that case?

**Boltzmann tells us the answer!**

Let's calculate  $\langle E \rangle$ , assuming that there are lots of states with  $E < kT$ , (necessary for equipartition), and that these states are uniformly spaced in  $y$  (to simplify the calculation). Suppose  $E(y) = ay$ .

$$\langle E \rangle = \int_0^{\infty} E(y) P dy = \frac{\int_0^{\infty} E(y) e^{-E(y)/kT} dy}{\int_0^{\infty} e^{-E(y)/kT} dy} = \frac{\int_0^{\infty} aye^{-ay/kT} dy}{\int_0^{\infty} e^{-ay/kT} dy} = \frac{(kT)^2/a}{kT/a} = kT$$

**So, each linear mode has twice as much energy,  $kT$ , as each quadratic mode.**