Lecture 11

Applying Boltzmann Statistics

- Elasticity of a Polymer
- Heat capacities

  C_V of molecules – for real !!

  When equipartition fails

Reading for this Lecture:
Elements Ch 8

Reading for Lecture 12:
Elements Ch 9

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:

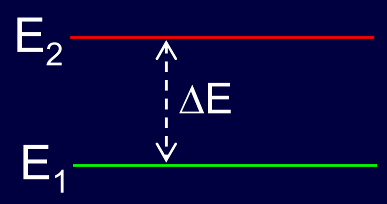
$$P_n = \frac{e^{-E_n/kT}}{Z}$$

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

Z is called the “partition function”.

Two-state Systems in General

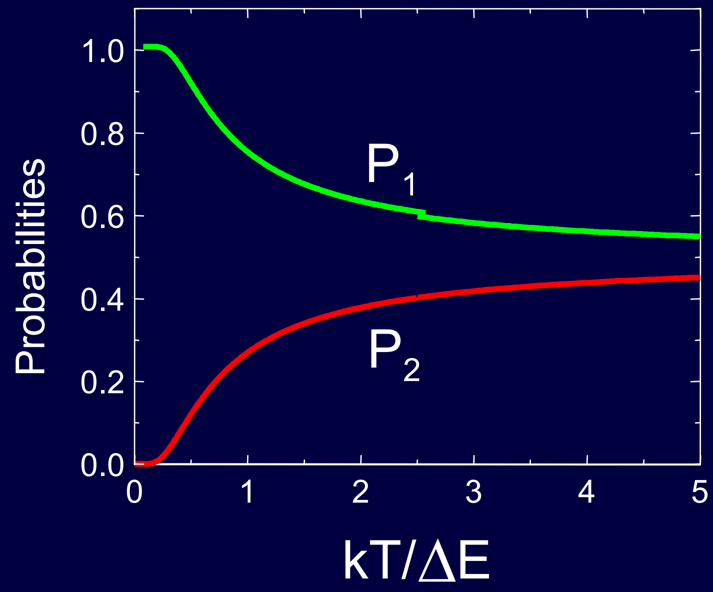
Consider a two-state system with an energy difference ΔE between the two states.



How do the occupation probabilities of the states vary with T?

$$P_1 = \frac{1}{1 + e^{-\Delta E/kT}} \qquad P_2 = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$$

The low energy state is preferentially occupied at low T, but the states approach equal occupancy at high T.



This behavior will be exactly the same for every "two-state system" with the same ΔE.

Summary: Collection of Spins

We used the Boltzmann factor (and remembering that the sum of the probabilities is always 1) to tell us the probabilities of each of the two energy states of a single magnetic moment in a magnetic field.

$$P_{up} = \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}}; \quad P_{down} = \frac{e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}}$$

In a collection, the average number pointing up (or down) is just N times the probability:

$$N_{up} = NP_{up}, \text{ and } N_{down} = NP_{down}$$

$$M = \mu\left(N_{up} - N_{down}\right) = N\mu(P_{up} - P_{down})$$

$$= N\mu \frac{e^{\mu B/kT} - e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}}$$

$$= N\mu \tanh\left(\mu B/kT\right)$$

Using these averages, we can calculate macroscopic properties:

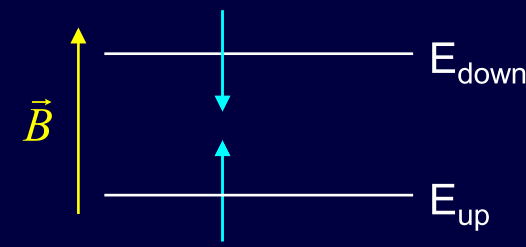
- total magnetic moment, *M*
- internal energy, *U*
- heat capacity, C_B
- entropy, *S*

Supplement: Internal Energy of a Collection of Spins

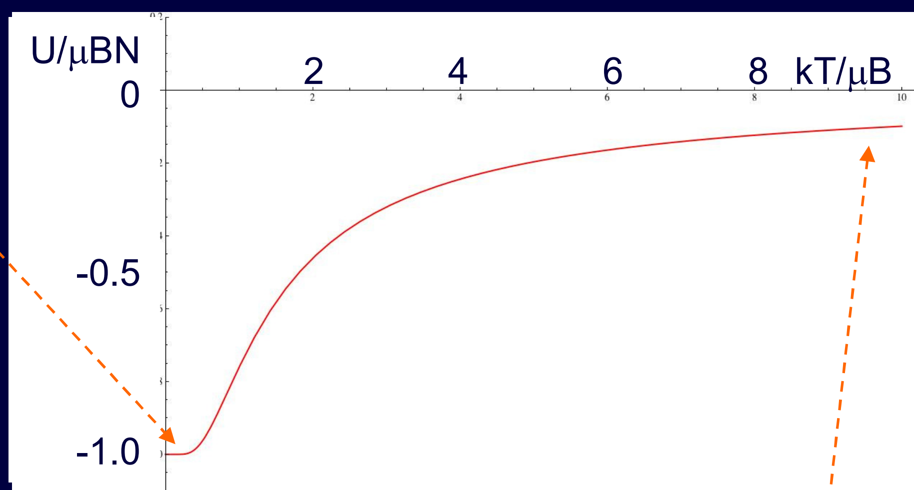
Recall how to calculate the internal energy U:

$U = N_u E_u + N_d E_d = -(N_u - N_d)\mu B$
$\quad = -N\mu B \tanh(\mu B/kT)$

What does this look like as a function of T?



$E_{up} = -E_{down} = -\mu B$



Low T ($kT \ll \mu B$):
Boltzmann factor ~ 0.
All spins are stuck in low energy state.
$U = NE_{up} = -\mu BN$, independent of T

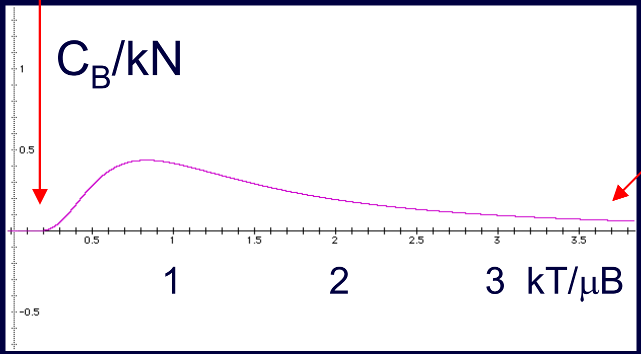
High T ($kT \gg \mu B$):
Boltzmann factor approaches 1.
Almost equal numbers in the up and down states.
$U \approx (N/2)(E_{up}+E_{down}) = 0$, independent of T

Supplement: Heat Capacity of a Collection of Spins

We now have U(T), for fixed B, so we can get the heat capacity, C_B (at constant B), by taking $\partial U/\partial T$.

$$C_B = \left[\frac{\partial U}{\partial T}\right]_{B=const} = Nk\left(\frac{\mu B}{kT}\right)^2 \mathrm{sech}^2(\mu B/kT)$$

For $kT \ll \mu B$, C_B vanishes, because all are stuck in "ground state".



For $kT \gg \mu B$, C vanishes, because the probabilities of the two states each approach 0.5, and cease to depend on T.

A collection of 2-state spins does not behave anything like an ideal gas.

On the importance of polymers…

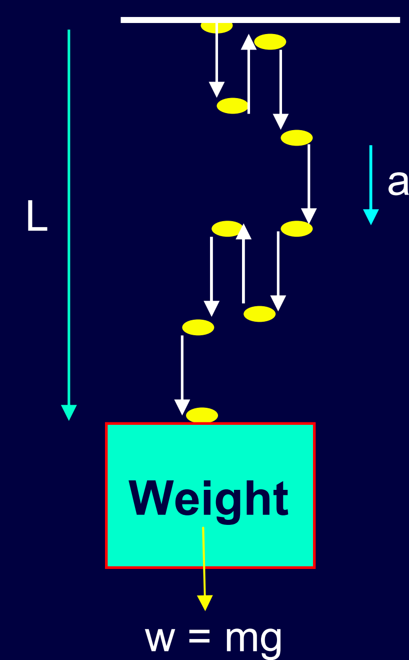
- Polymers play a major role in society.
- In 1930, Wallace Carothers (PhD UIUC, 1924) et. al at DuPont invent neoprene.
- In 1935 Carothers goes on to invent nylon – "the miracle fiber" (but commits suicide in 1937, just before it's importance is realized). In WWII, nylon production was directed to 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.



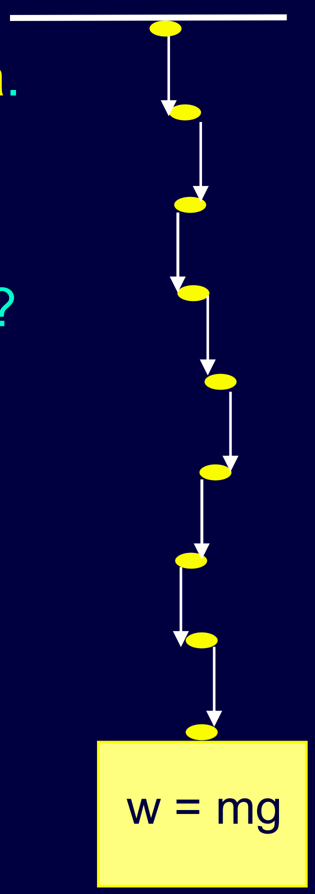
This is similar to the spin problem. Each link has two energy states:

The reason is that when a link flips from down to up, the weight rises by 2*a*.
(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?

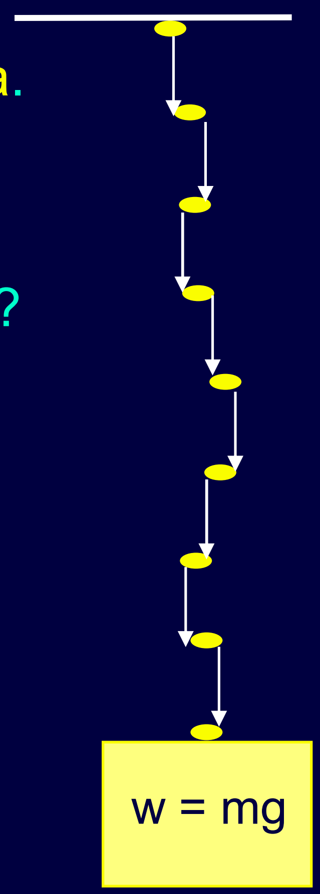
a) L = 30a b) L = 0 c) 0 < L < 30a

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) $\sigma_{min} = \ln 30$

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):

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

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

The average energy is:

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

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

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Suppose we rapidly stretch the rubber band.

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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:

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

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 $dW_{on} = -pdV$.

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

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

Or for magnets …

Heat Capacity & Harmonic Oscillators

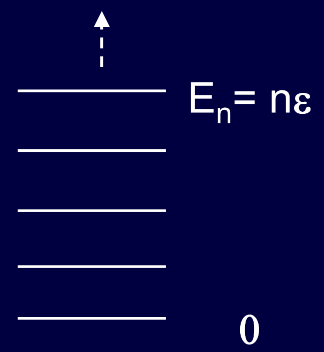
We can use the Boltzmann factor to calculate the average thermal energy, <E>, per particle and the internal energy, U, of a system. We will consider a collection of harmonic oscillators.

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

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:

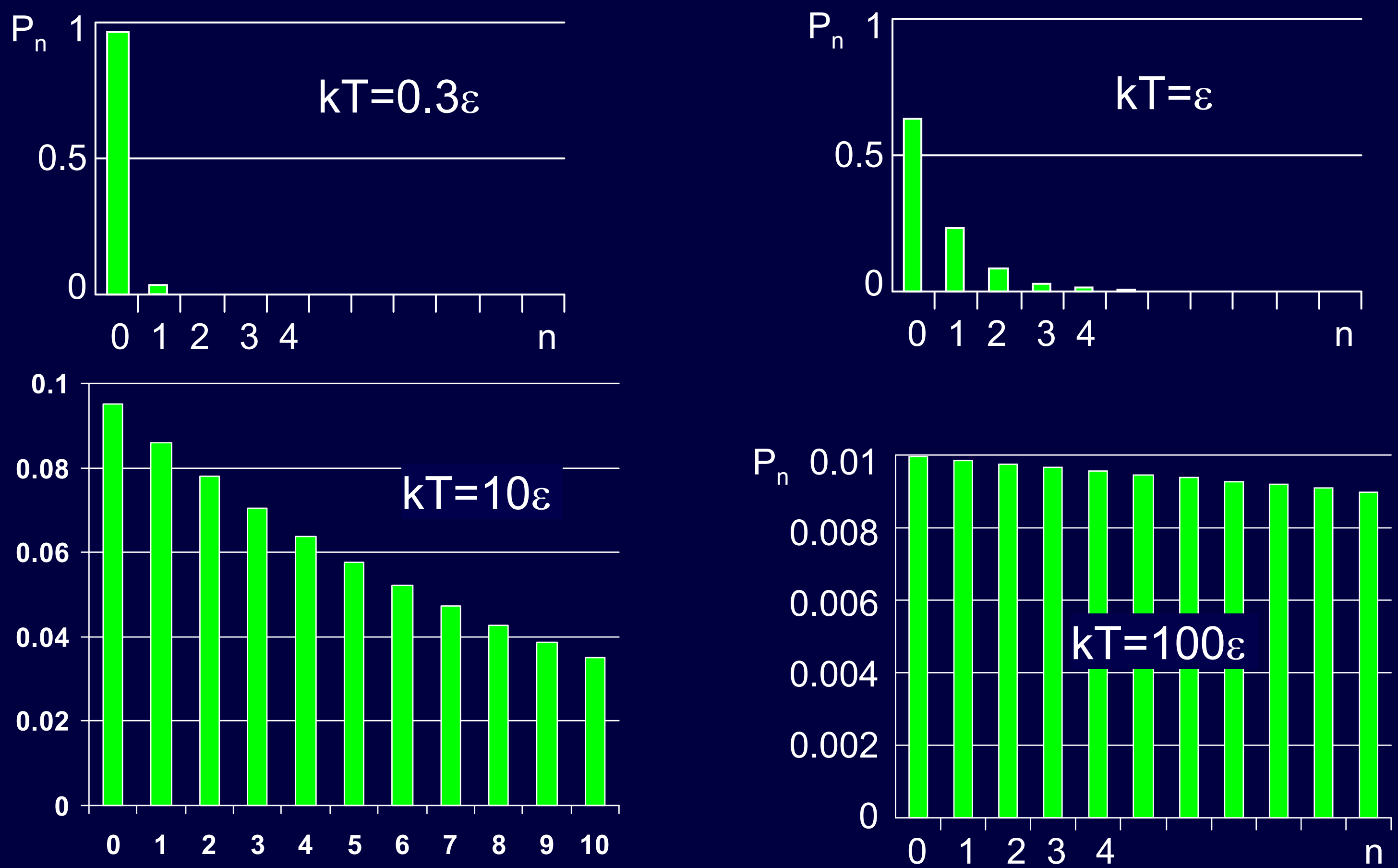
$$Z = \sum_{n=0}^{\infty} e^{-n\varepsilon/kT} = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

It's just a geometric series.

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

Heat Capacity & Harmonic Oscillators (2)

The ratio ε/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.

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

$$\text{so } \langle E \rangle = \sum_{n=0}^{\infty} E_n P_n = \frac{\varepsilon}{e^{\varepsilon/kT} - 1}$$

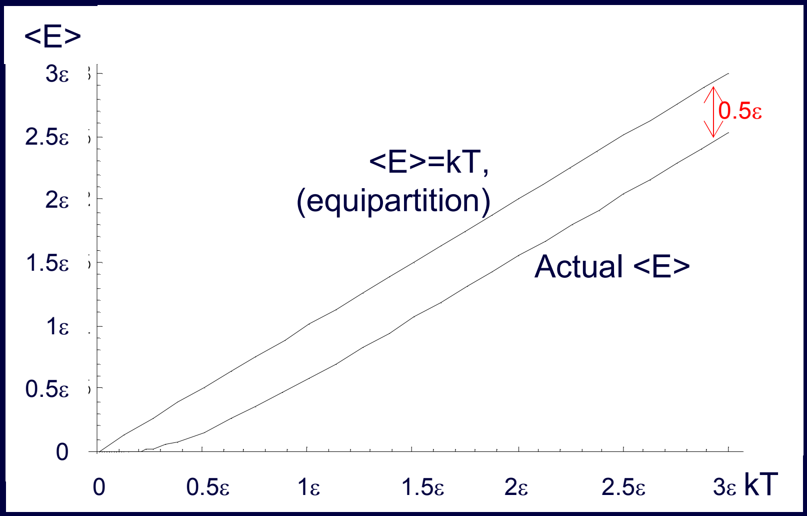
See supplemental slide for the algebra.

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

<E> ≈ kT, equipartition !!

At low T (when kT << ε), $e^{\varepsilon/kT} >> 1$:

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



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

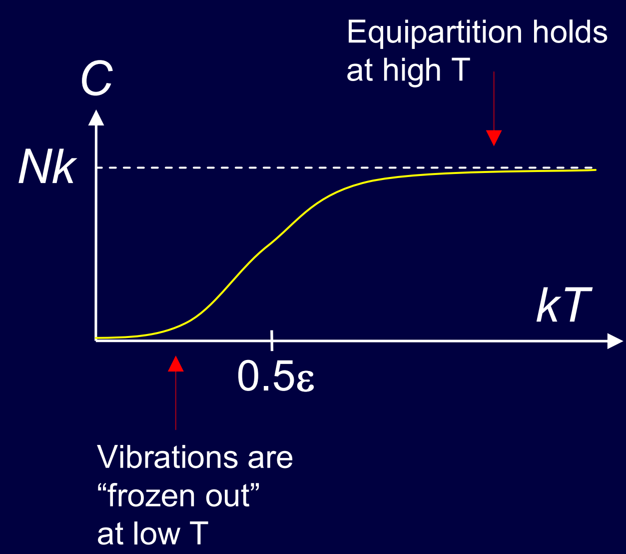
Heat Capacity & Harmonic Oscillators (4)

Calculate the heat capacity by taking the derivative :

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

$$\approx Nk, \text{ when } kT \gg \varepsilon$$

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



At what temperature is equipartition reached?

To answer this, we need to know how big ε is.

We use a fact from QM (P214):

ε = hf, where h is Planck's constant = $6.6\ 10^{-34}$ J-s

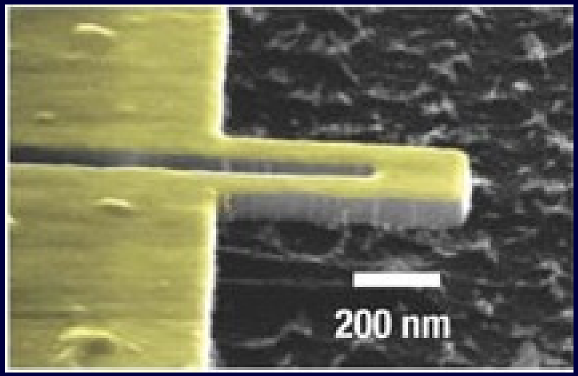
f is the oscillator frequency.

For typical vibrations in molecules and solids,

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

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: $h = 6.6\times10^{-34}$ J-s and $k = 1.38\times10^{-23}$ J/K



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

1) What is the spacing, ε, between this oscillator's energy levels?

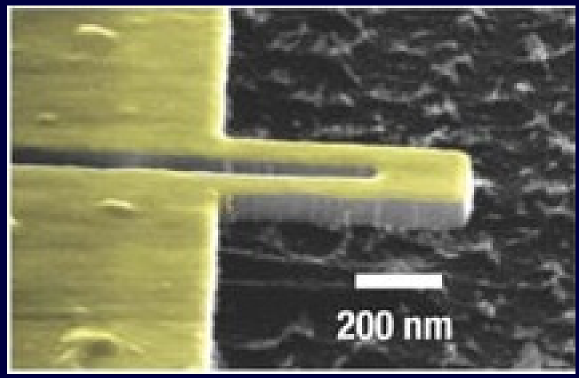
a) $\varepsilon = 6.6\times10^{-34}$ J b) $\varepsilon = 8.4\times10^{-26}$ J c) $\varepsilon = 1.4\times10^{-23}$ J

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

a) $T = 8.4\times10^{-26}$ K b) $T = 6.1\times10^{-3}$ K c) T = 295 K

Solution

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: $h = 6.6\times10^{-34}$ J-s and $k = 1.38\times10^{-23}$ J/K



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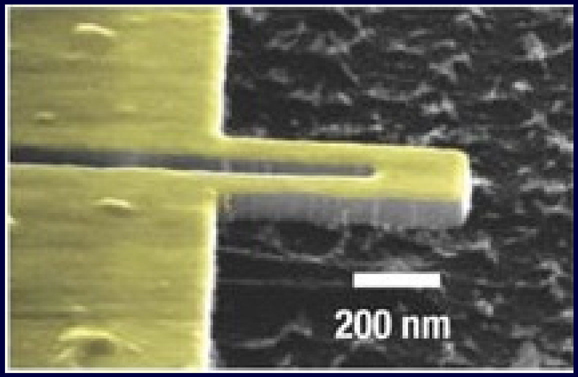

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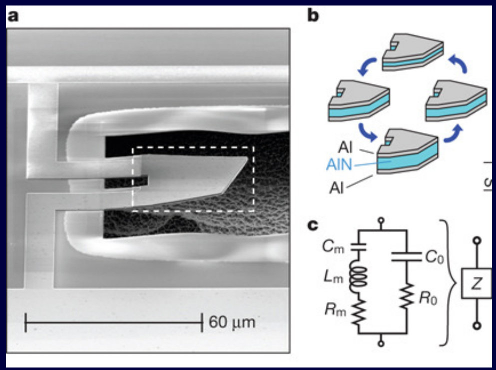
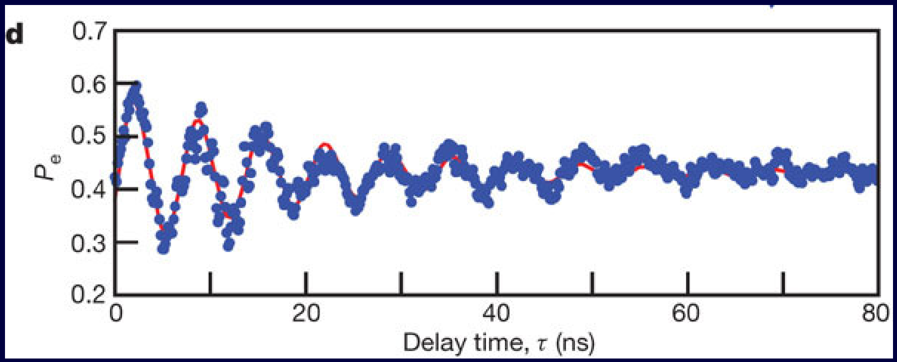
a) $T = 8.4\times10^{-26}$ K   **b) $T = 6.1\times10^{-3}$ K**   c) T = 295 K

$$T = \varepsilon/k = (8.38\times10^{-26}\ \text{J})/(1.38\times10^{-23}\ \text{J/K}) = 6.1\times10^{-3}\ \text{K}$$

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" :

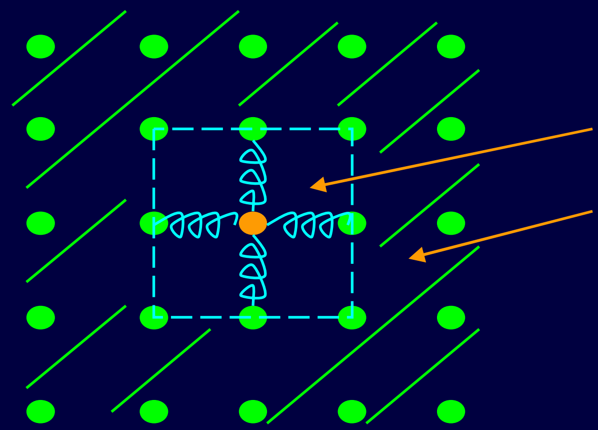




"Quantum ground state and single-phonon control of a mechanical resonator",
A. D. O'Connell, et al., *Nature* **464**, 697-703 (1 April 2010)
Quantum mechanics provides a highly accurate description of a wide variety of physical systems. However, a demonstration that quantum mechanics applies equally 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.

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

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

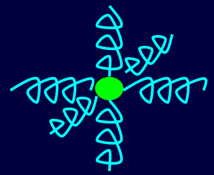


Small system (one atom)

Einstein pretends it oscillates independently of other atoms.

For high T, Equipartition Theorem predicts ½ kT for each quadratic term in the energy:

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



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

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

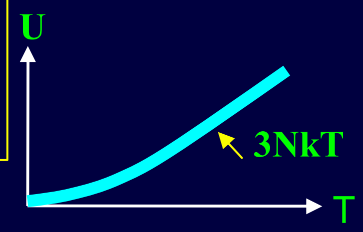
What about low temperatures? →

FYI: Heat Capacity of Einstein solid

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

$$U = 3N < E > \quad = \frac{3N\varepsilon}{e^{\varepsilon/kT} - 1}$$

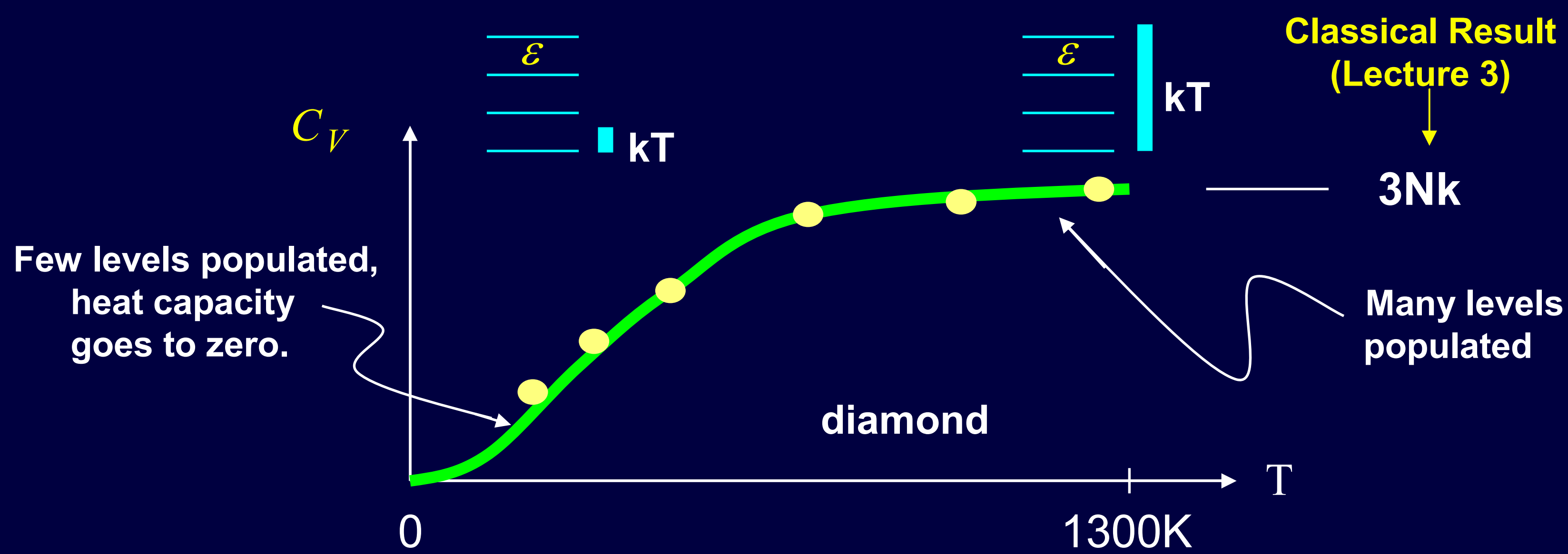
(3-D)



The heat capacity at constant volume is:

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

Slope of this

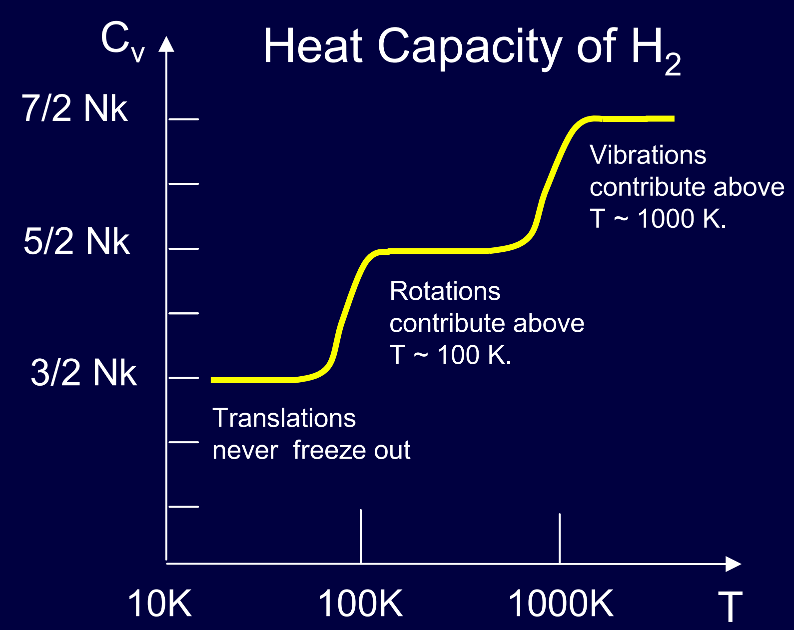


Many Modes of Motion ?

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 ε, corresponding to T ~ 1000 K.
- Rotations have a moderate energy spacings,corresponding to T ~ 100 K.
- Translations have a continuous range of energies → never ‘frozen’ out



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

Next Class

- Law of Atmospheres
- Thermal Radiation

Next Week: Heat Engines

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

Supplement:

Derivation of <E> for the Harmonic Oscillator

This is always true:

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

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

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

This is true for the harmonic oscillator:

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

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

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

Derivation of Equipartition

for quadratic degrees of freedom

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

If kT >> ε (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 ρ is constant.

Calculate <E>, 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, (<E> = ½kT per mode) we say "quadratic", to remind us that the energy is a quadratic function of the variable (*e.g.*, ½mv²).

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 <E>, 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.

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

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