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:

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

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

Z is called the “partition function”.

On the importance of polymers…

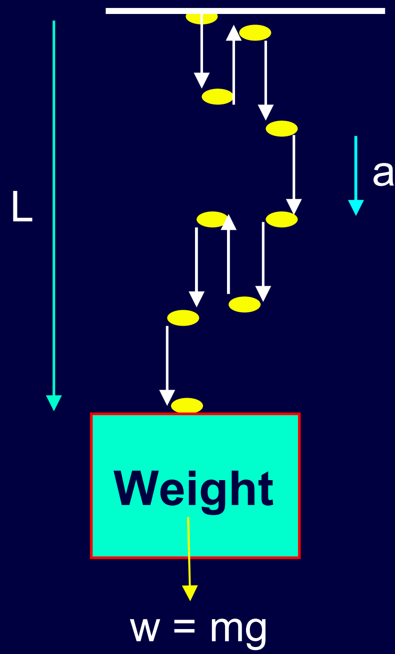
- Polymers play a major role in society.
- In 1930, Wallace Carothers (PhD UIUC, 1924) et. al at DuPont invent neoprene.
- In 1935 Carothers goes on to invent nylon – “the miracle fiber” (but commits suicide in 1937, just before it’s importance is realized). In WWII, nylon production was directed to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

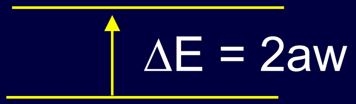
A polymer is a molecular chain (*e.g.*, rubber), consisting of many parts linked together. The joints are flexible.

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.



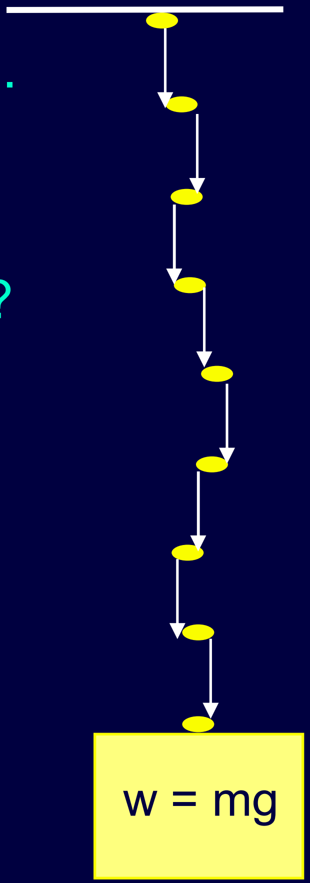
This is similar to the spin problem.
Each link has two energy states:



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.

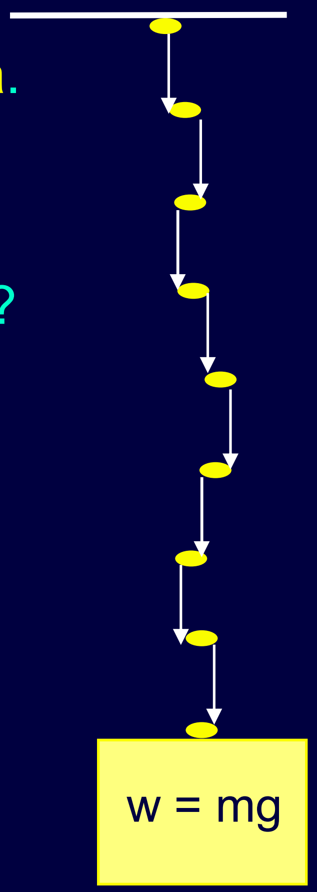
1) What is the chain length of the minimum entropy state?

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



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

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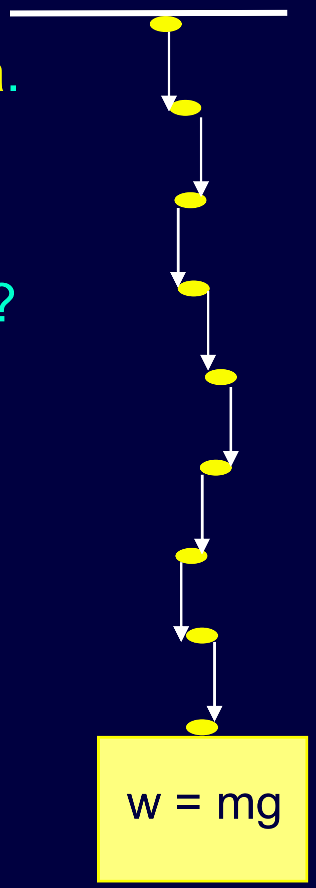

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2) What is the minimum entropy of the chain?

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

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

a) decrease b) remain the same c) increase

Solution

Suppose we rapidly stretch the rubber band.

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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:

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

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
→ 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

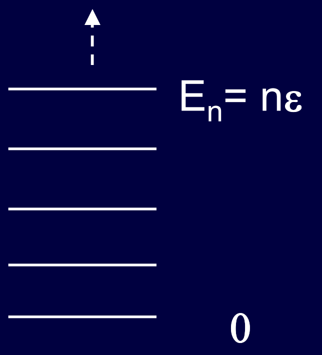
We can use the Boltzmann factor to calculate the average thermal energy, <E>, per particle and the internal energy, U, of a system. We will consider a collection of harmonic oscillators.

- 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:

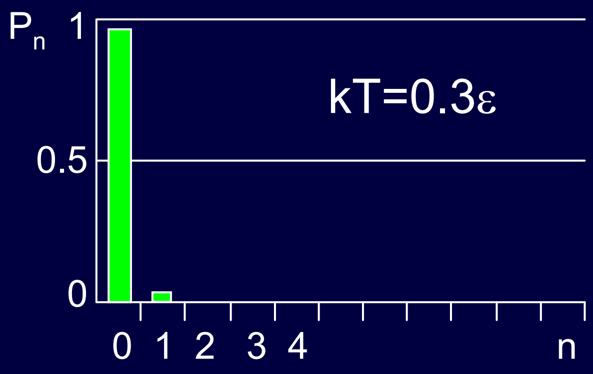
$$Z = \sum_{n=0}^{\infty} e^{-n\varepsilon/kT} = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

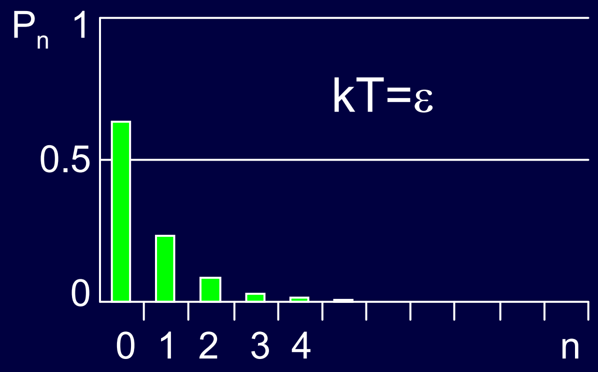
It's just a geometric series.

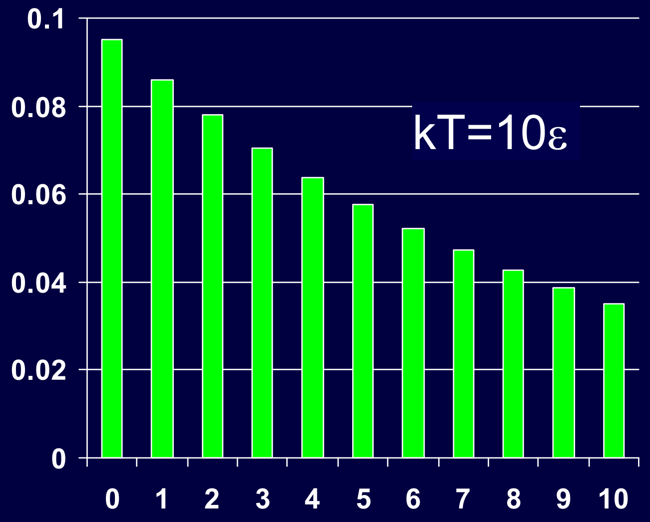
$$P_n = (1 - e^{-\varepsilon/kT})e^{-n\varepsilon/kT}$$

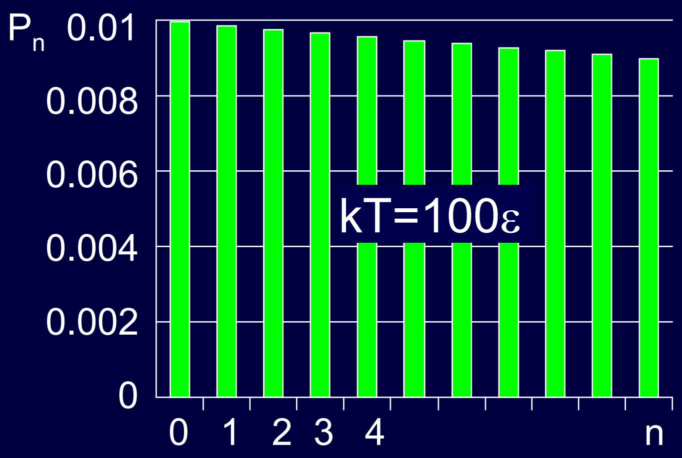
Heat Capacity & Harmonic Oscillators (2)

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.

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

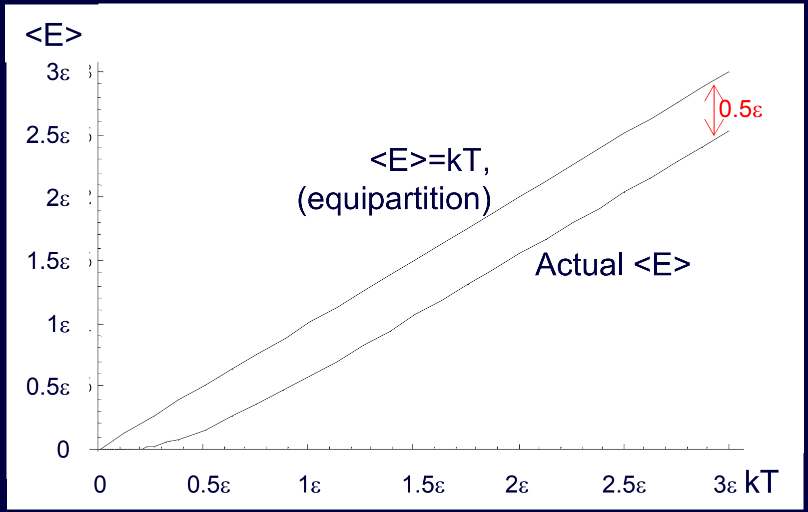
so $\langle E \rangle = \sum_{n=0}^{\infty} E_n P_n = \dfrac{\varepsilon}{e^{\varepsilon/kT} - 1}$ See supplemental slide for the algebra.

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

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

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.

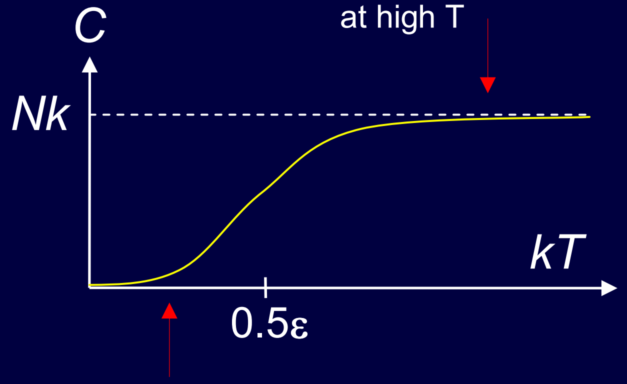
Heat Capacity & Harmonic Oscillators (4)

Calculate the heat capacity by taking the derivative :

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

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

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



Equipartition holds at high T

Vibrations are "frozen out" at low T

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

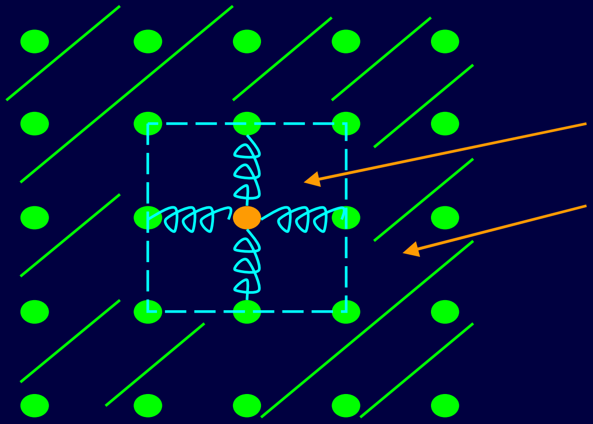
f is the oscillator frequency.

For typical vibrations in molecules and solids,

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

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

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

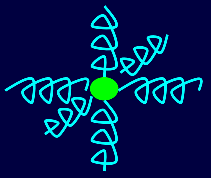


Small system (one atom)

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:

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

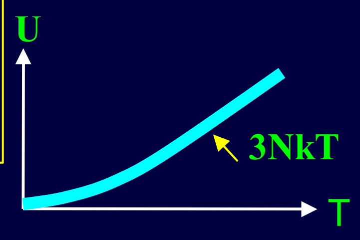
What about low temperatures? →

FYI: Heat Capacity of Einstein solid

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

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

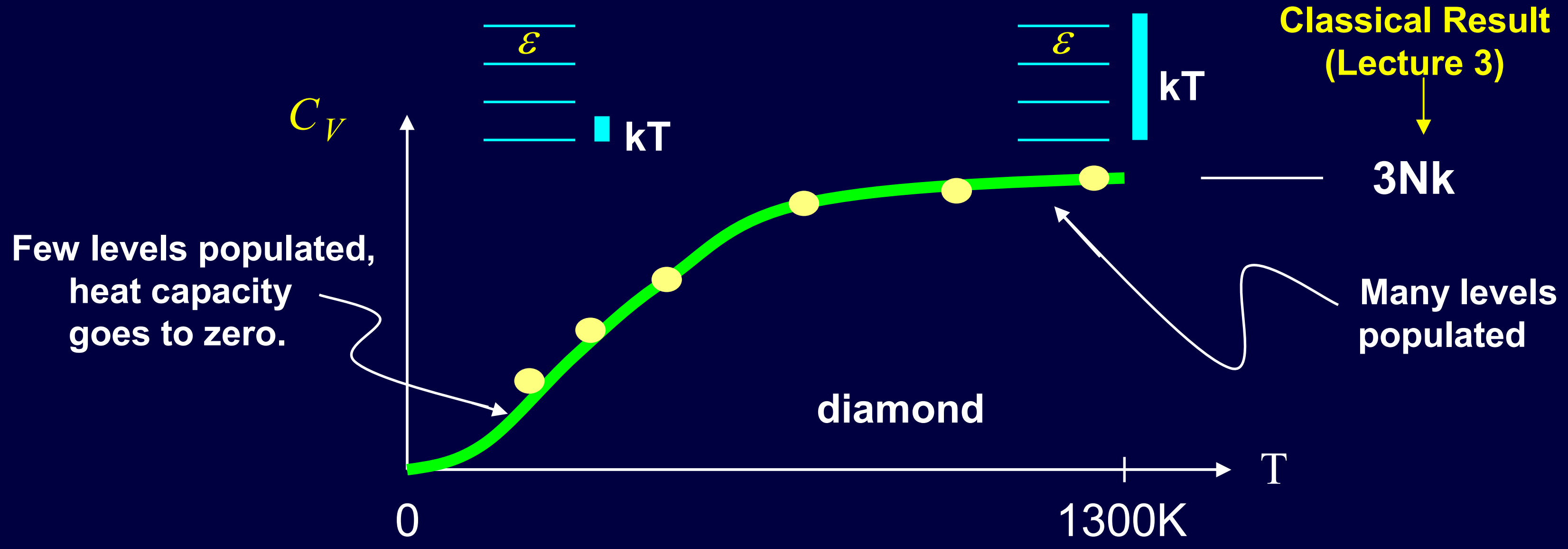
(3-D)



The heat capacity at
constant volume is:

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

Slope of this



Classical Result (Lecture 3)

3Nk

Few levels populated, heat capacity goes to zero.

Many levels populated

diamond

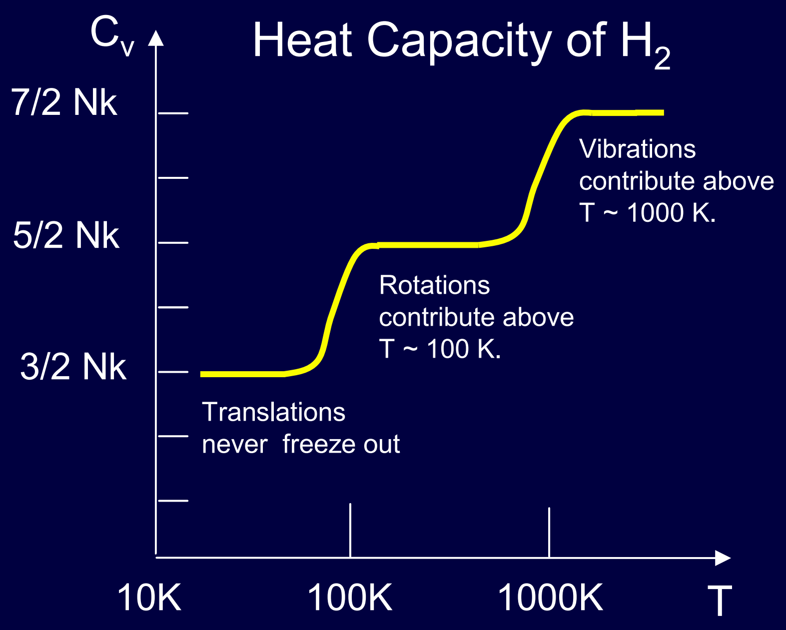
Many Modes of Motion ?

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

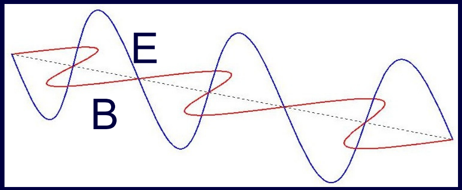
Consider a diatomic molecule (H_2).
It has three quadratic energy modes:

- Bond vibrations have a larger ε, corresponding to T ~ 1000 K.
- Rotations have 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 not bond vibrations.



Basics of Thermal Radiation



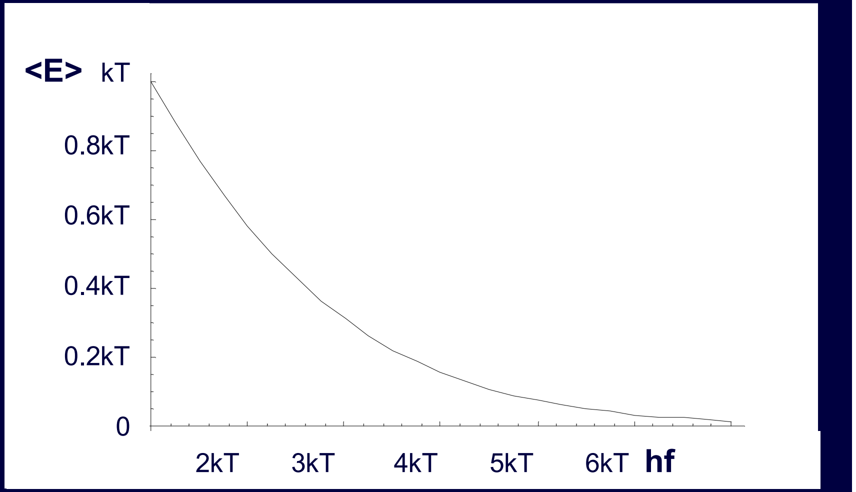
Every object in thermal equilibrium emits (and absorbs) electromagnetic (EM) waves from its surface. (It glows.) How much? What colors?

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 ε = hf, just like a mechanical oscillator.
Note: Each of these packets of energy ε=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 ε = hf << kT) satisfy equipartition. They have <E> = kT. High frequency modes do not.

Planck Radiation Law

“Black Body Radiation”

The calculation of <E> 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.

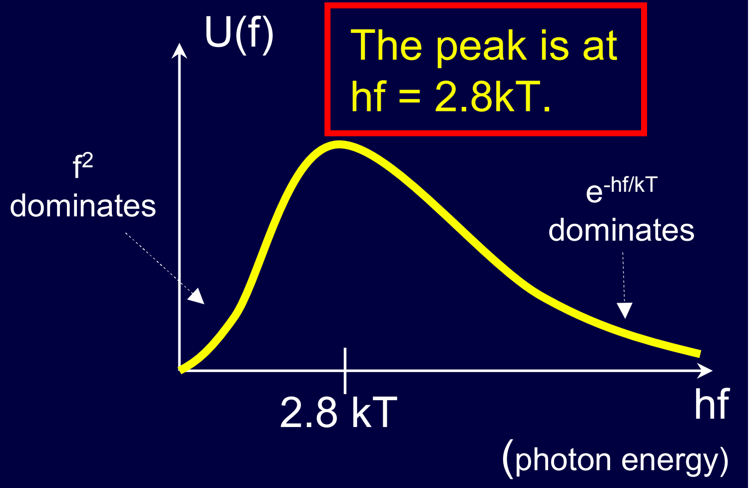
The density of frequency modes is proportional to f ^{2}. (See “Elements” for the derivation)
So, the EM radiation intensity as a function of frequency is:

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

Energy per frequency interval

Average energy per mode

Number of modes per frequency interval



The peak is at hf = 2.8kT.

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:

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

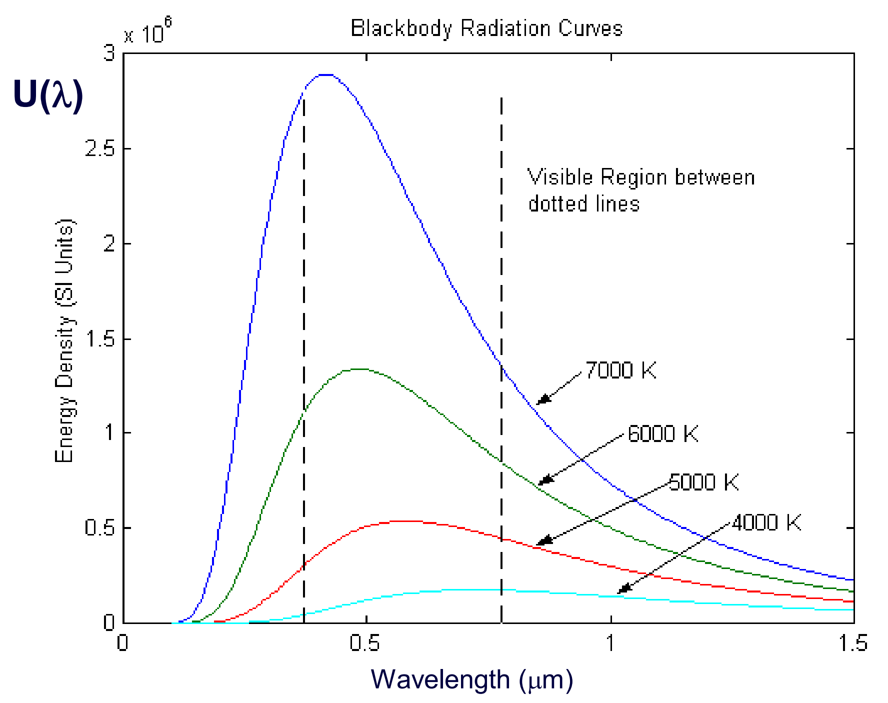
$f = c/\lambda \Rightarrow df \propto d\lambda/\lambda^2$

(The - sign doesn't matter.)

The peak wavelength:

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

This relation is known as Wien's Displacement law.



Act 3

Which of the following has a higher temperature?

a) a red-hot object b) a white-hot object c) a blue-hot object

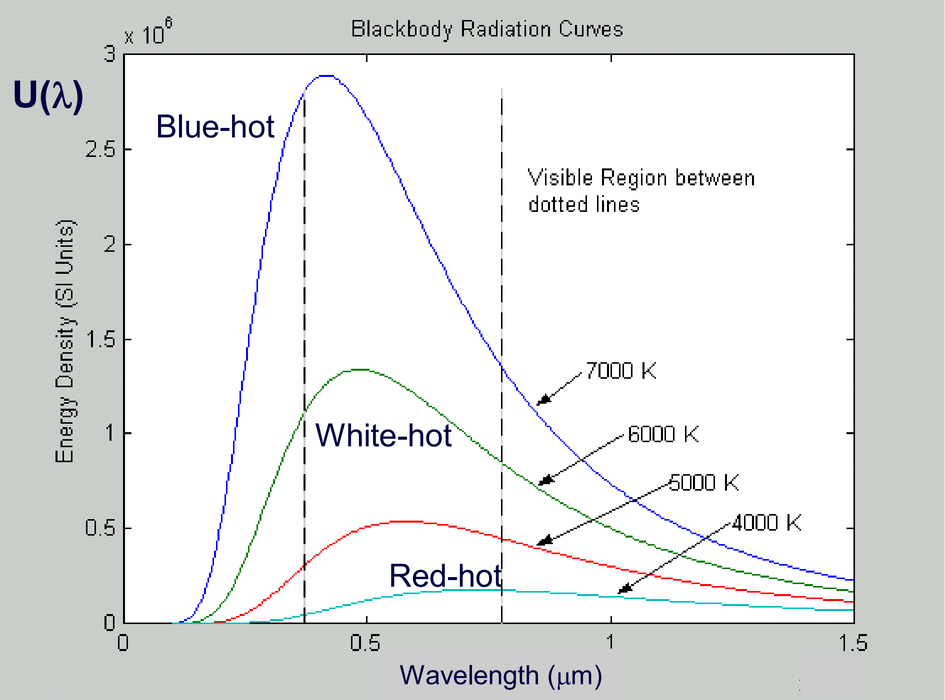
Solution

Which of the following has a higher temperature?

a) a red-hot object b) a white-hot object c) a blue-hot object

The peak moves to shorter wavelength as T increases.

Note: This is only applicable to thermal radiation, not colors due to pigments or other effects.

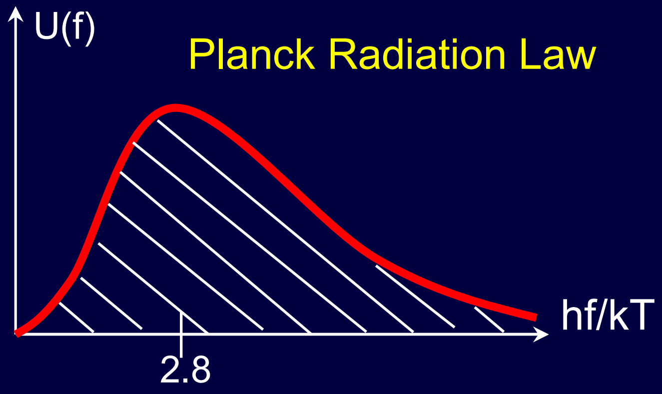


Where most burning is occurring, the fire is white, the hottest color possible for organic material in general, or yellow. Above the yellow region, the color changes to orange, which is cooler, then red, which is cooler still.

What is the Total Energy Radiated?

The Planck law gives the spectrum of electromagnetic energy contained in modes with frequencies between f and f + Δf:

$$U(f) \propto \frac{f^3}{e^{hf/kT} - 1}$$



Integrating over all frequencies gives
the total radiated energy per unit surface area:

$$\int_0^\infty U(f)\,df \propto \int_0^\infty \frac{f^3}{e^{hf/kT} - 1}\,df = \left(\frac{kT}{h}\right)^4 \boxed{\int_0^\infty \frac{x^3}{e^x - 1}\,dx} \qquad x = hf/kT$$

Just a number: $\pi^4/15$

The power radiated per unit surface area by a perfect radiator is:

$$\boxed{J = \sigma_{SB} T^4}$$

Stefan-Boltzmann Law of Radiation
$\sigma_{SB} = 5.670 \times 10^{-8}\ \mathrm{W\ m^{-2}\ K^{-4}}$ Stefan-Boltzmann constant

The total power radiated = J×Area

Not all Bodies are Black

Real materials are not truly "black" (*i.e.*, they don't completely absorb all wavelengths). The fraction absorbed is called absorbance, which is equal* to its emissivity, *e*, a dimensionless number $0 \le e \le 1$ that depends on the properties of the surface.

e = 1 for an ideal emitter (an ideal blackbody absorber).

e = 0 for something that doesn't emit (or absorb) at all, i.e., a perfect reflector.

Modified Stefan-Boltzmann Law of Radiation:

$$J = e\sigma_{SB} T^4$$

Typical emissivities (300 K):

gold, polished	0.02
aluminum, anodized	0.55
white paper	0.68
brick	0.93
soot	0.95
skin (!)	0.98

*If this equality didn't hold, we wouldn't have thermal equilibrium.

Next Class

- Law of Atmospheres
- Global Warming

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:

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

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

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

This is true for the harmonic oscillator:

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

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

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

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.*, ½mv^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 <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.