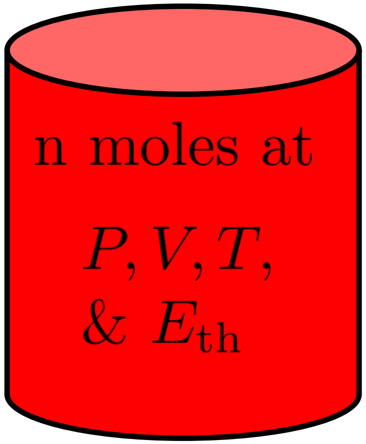
20-1: Micro – Macro Connection

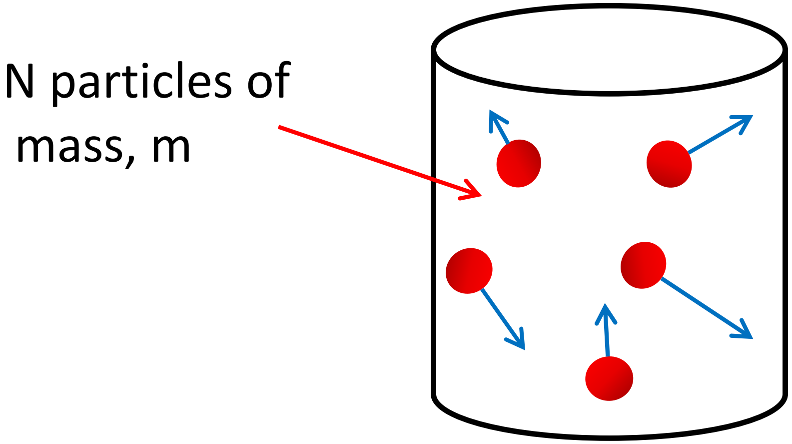
Here, we follow in the steps of Ludwig Boltzmann from the video, The Story of Energy, and address the following question:

For a gas, we have two descriptions:

Macroscopic description



Microscopic description



Laws:

$$PV = nRT$$

$$\Delta E_{\rm th} = Q + W$$

Particles move randomly, but obey Newton's laws

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Question: **Can we relate the microscopic behavior of the gas particles to the macroscopic thermodynamic state variables and laws?**

(or, what do the state variables really mean?)

Difficulty: **For a macroscopic sample of gas, N is a huge number, so we can't track all of the particles.**

Solution: **As Boltzmann did, we analyze the motion statistically, this is called "Statistical Mechanics" or "Kinetic Theory"**

Speed Distributions in a Gas

Consider this collection of N gas particles (atoms or molecules):

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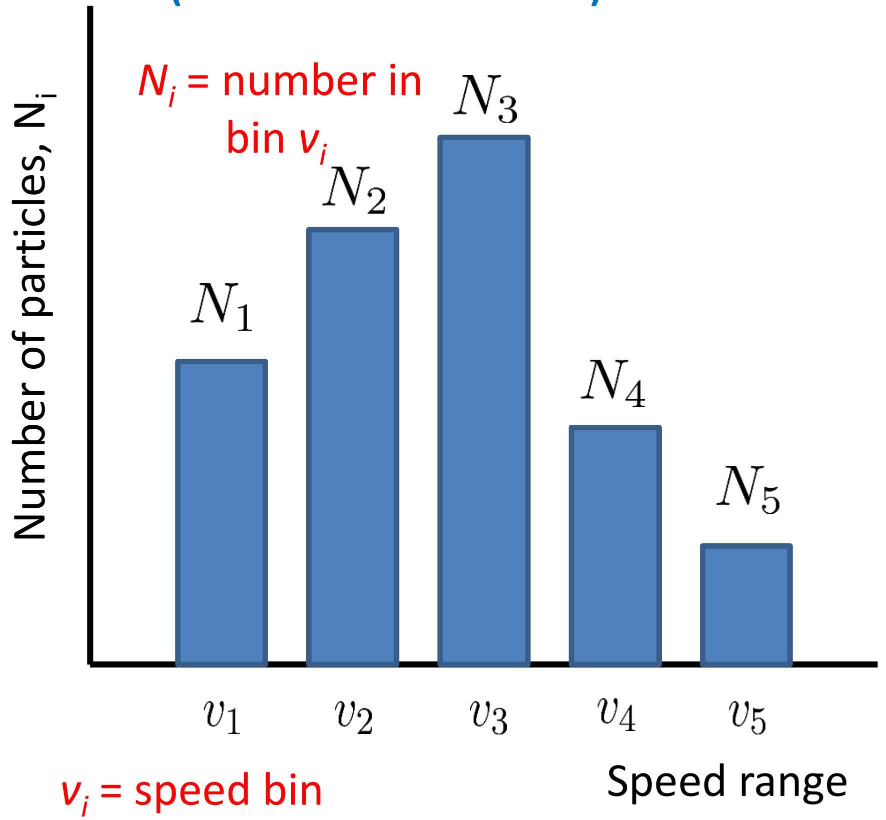
Velocity directions are random, and **at any instant in time**, some of the particles have low speed, some high speed, and most are in between. **How would you describe this?**

A Speed Distribution:

(at some instant in time)



N_i = number in bin v_i

v_i = speed bin

Statistically Important Speeds:

Most Probable Speed: speed you would obtain most of the time if you made random measurements of speeds.

From distribution: The maximum

Average Speed: measure a bunch of speeds and take the average.

From distribution:

$$v_{\mathrm{avg}} = \frac{1}{N} \sum_{i=1}^{n_{\mathrm{bins}}} v_i N_i$$

(N = total number of particles; n_{bins} = number of speed bins)

Root-mean-square Speed: square root of the average of the square.

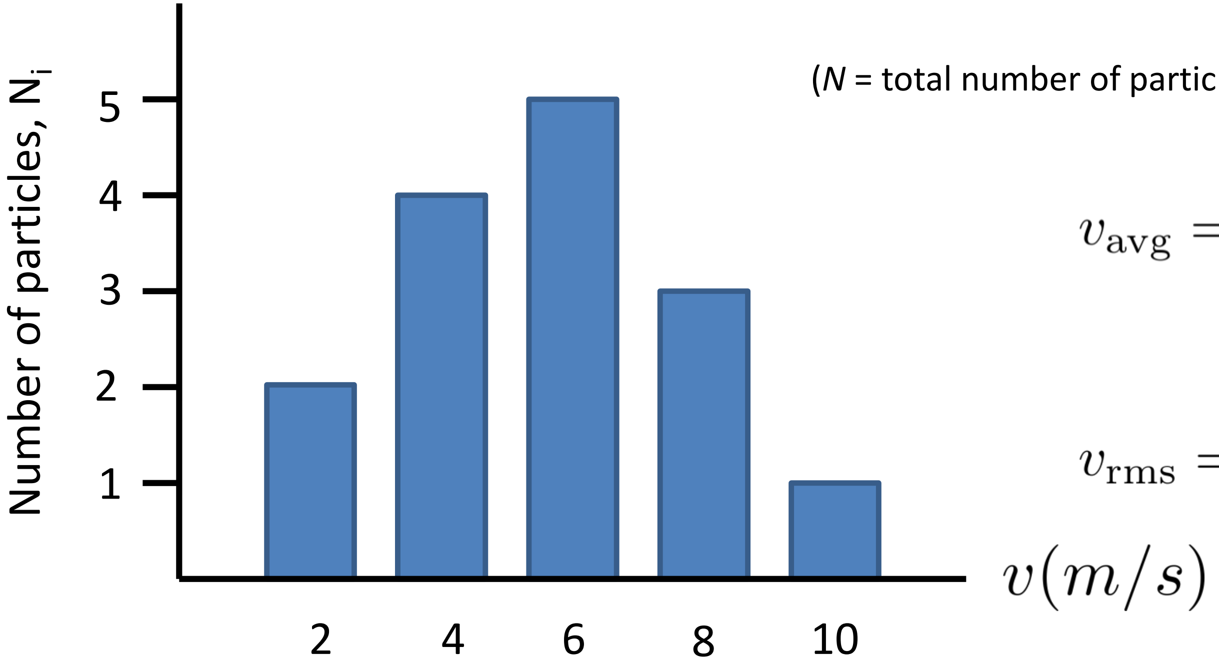
From distribution:

$$v_{\mathrm{rms}} = \left[\frac{1}{N} \sum_{i=1}^{n_{\mathrm{bins}}} v_i^2 N_i \right]^{1/2}$$

Whiteboard Problem 20-1: Speeds from a Distribution

The plot below shows the distribution of speeds of the molecules in a small sample of gas molecules.

What are: **a) The Most Probable Speed, v_{mp}? (LC)**
b) The Average Speed, v_{avg}? (LC)
c) The Root Mean Square Speed, v_{rms}? (LC)



(*N* = total number of particles; n_{bins} = number of speed bins)

$$v_{\rm avg} = \frac{1}{N}\sum_{i=1}^{n_{\rm bins}} v_i N_i$$

$$v_{\rm rms} = \left[\frac{1}{N}\sum_{i=1}^{n_{\rm bins}} v_i^2 N_i\right]^{1/2}$$

The Maxwell-Boltzmann Distribution

In a real sample of gas with N ~ Avagadro's Number of particles, the equilibrium distribution of speeds becomes a continuous function called the Maxwell Boltzmann Distribution:

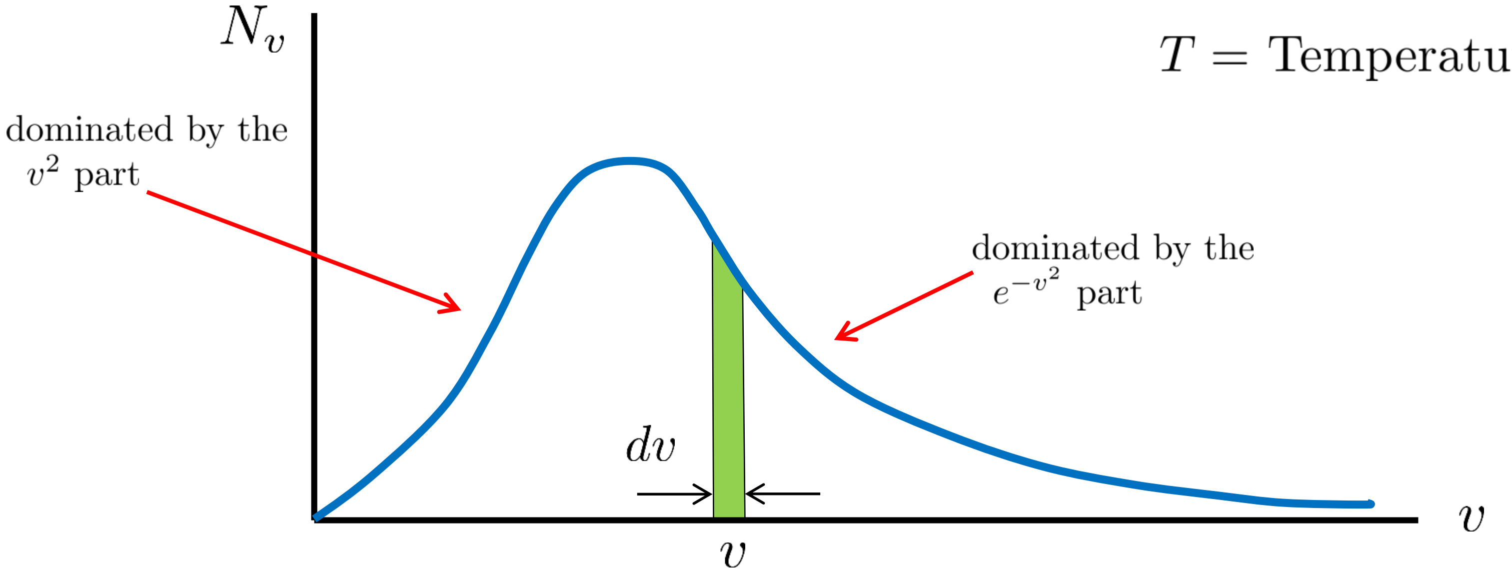
$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}$$

$m =$ particle mass

$k_B =$ Boltzmann's Constant

$= 1.38 \times 10^{-23}\ J/K$

$T =$ Temperature in K



Interpretation: $N_v dv =$ the number of particles with speed between v and $v + dv$

How do the molecules in a gas achieve this **equilibrium** distribution? **Collisions**

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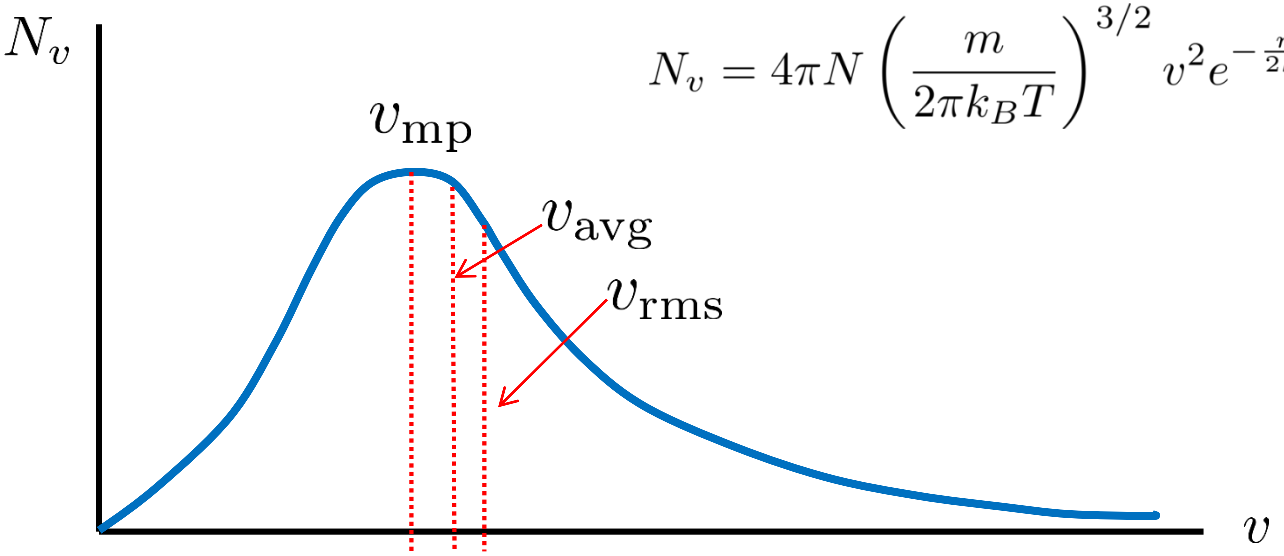
Important Speeds for the Maxwell-Boltzmann Distribution



$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}}$$

Most probable speed: Set $\frac{dN_v}{dv} = 0$ and solve for v $\xrightarrow[\text{(some math)}]{}$ $v_{\rm mp} = \sqrt{\frac{2k_BT}{m}}$

(speed for N_v maximum)

Average Speed: $v_{\rm avg} = \frac{1}{N}\int_0^\infty vN_v dv$ $\xrightarrow[\text{(some math)}]{}$ $v_{\rm avg} = \sqrt{\frac{8k_BT}{\pi m}}$

Root Mean Square Speed: $v_{\rm rms} = \left[\frac{1}{N}\int_0^\infty v^2 N_v dv\right]^{1/2}$ $\xrightarrow[\text{(some math)}]{}$ $\boxed{v_{\rm rms} = \sqrt{\frac{3k_BT}{m}}}$

Of these average speeds, the rms speed is the most important - - why?

It's the one that will give us the average kinetic energy.

Whiteboard Problem 20-2: How fast are the molecules of air in this room moving?

The air in this room is mostly diatomic Nitrogen, N_2, at about 20°C and has a Maxwellian distribution of speeds.

a) **Calculate the rms speed of the Nitrogen molecules in this room. (LC)** (For N_2: A = 28)

b) **Calculate the rms speed for any Hydrogen molecules in this room. (LC)** (For H_2: A=2)

Hint: use what you have from part a and think in terms of ratios.

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Here are the equations for the statistically important speeds. If you're done calculating v_{rms}, go ahead and calculate v_{mp} and v_{avg} and see what you get.

$$v_{\mathrm{mp}} = \sqrt{\frac{2k_BT}{m}} \qquad v_{\mathrm{avg}} = \sqrt{\frac{8k_BT}{\pi m}} \qquad v_{\mathrm{rms}} = \sqrt{\frac{3k_BT}{m}}$$

Mean Free Path

Consider a gas particle moving randomly in a gas:

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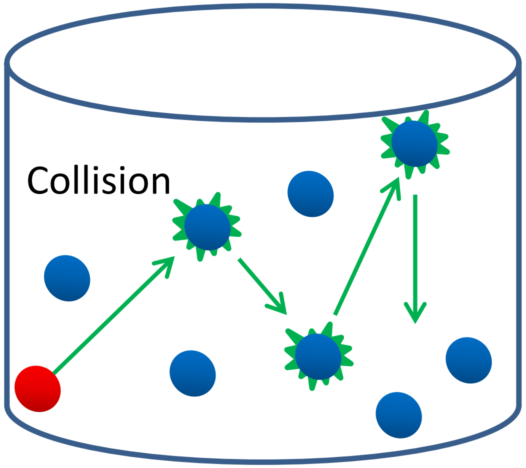

How far does a given particle travel between collisions with other molecules?

Sometimes a short distance, sometimes a much longer distance. So we define an average:

$$\textbf{Mean Free Path}, \ \lambda = \text{average distance travelled between collisions}$$

Your author derives a simple expression for the **Mean Free Path**:

$$\boxed{\lambda = \frac{1}{4\sqrt{2}\pi\left(\frac{N}{V}\right)r^2}}$$

Where: $(\frac{N}{V}) = \text{number density}$

$$r = \text{particle radius}$$
$$\approx 0.5 \times 10^{-10}\ m \text{ monatomic gas}$$
$$\approx 1.0 \times 10^{-10}\ m \text{ diatomic gas}$$

Does this equation make sense? Consider: $\lambda \propto \frac{1}{r^2}$ or $\lambda \propto \frac{1}{(N/V)}$

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Whiteboard Problem 20-3

The air in this room is mostly N_2 at T = 20°C and p = 1 atm.

a) **What are the number density and mean free path (LC) of N_2 molecules in this room at p = 1 atm?**

b) Integrated circuits are manufactured in vacuum chambers with a pressure of 10^{-10} mm of Mercury which is 1.32 X 10^{-13} atm = 1.33 X 10^{-8} Pascals. **What are the number density and mean free path (LC) for N_2 molecules in the chamber? (use T = 20°C)**

How do we find the number density (N/V)? We want to use the Ideal Gas Law, PV = nRT. But, how do find the number of moles, n?

What form of the IGL should we use? ***What else is there besides PV = nRT ?***

We have been using the "**Chemists' form of the IGL**": **PV = nRT**

There's also the "**Physicists' form of the IGL**": **$PV = Nk_BT$**

Using this, we can get the number density easily:

$$\left(\frac{N}{V}\right) = \frac{P}{k_B T}$$

Kinetic Theory Definition of Pressure

On the microscopic level, the particles in a gas move randomly and make perfectly elastic collisions with the walls of the container.

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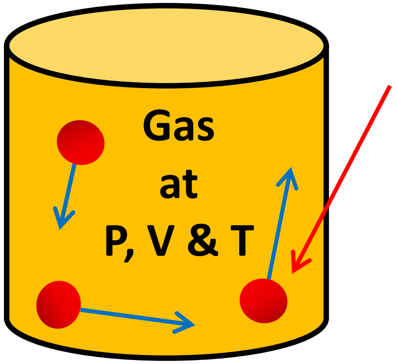
Each collision exerts a very tiny force on the wall; **when these are added up over the billions of collisions every second, this is macroscopic pressure**.

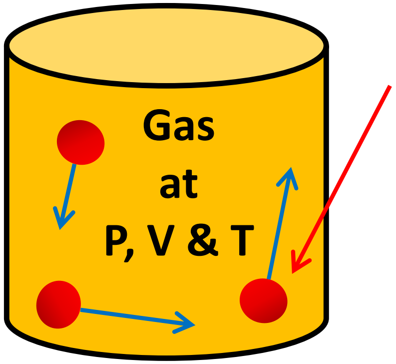
In your text, your author presents a lengthy derivation that relates the macroscopic pressure to some of the averaged microscopic properties:



N Particles of mass m

$$\text{Pressure:}\ \ P = \frac{1}{3}\left(\frac{N}{V}\right) m v_{\text{rms}}^2$$

Kinetic Theory Definition of Temperature



N Particles
of mass m

For one particle, the translational* kinetic energy is:

$$\epsilon = \tfrac{1}{2} m v^2$$

The average of this over all of the particles is:

$$\epsilon_{\rm avg} = \tfrac{1}{2} m (v^2)_{\rm avg} = \tfrac{1}{2} m v_{\rm rms}^2$$

So, we can write the pressure as:

$$P = \frac{1}{3}\left(\frac{N}{V}\right) m v_{\rm rms}^2 = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2} m v_{\rm rms}^2\right) = \frac{2}{3}\left(\frac{N}{V}\right)\epsilon_{\rm avg}$$

So: $PV = \dfrac{2}{3} N \epsilon_{\rm avg}$ **Now, compare this to the IGL:** $PV = N k_B T$

Thus: $\boxed{\epsilon_{\rm avg} = \tfrac{3}{2} k_B T}$

Now, we can answer the question: ***"what does temperature measure?"***

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"Temperature measures the average translational kinetic energy of the gas particles"

Note: combining: $\epsilon_{\rm avg} = \tfrac{1}{2} m v_{\rm rms}^2 = \tfrac{3}{2} k_B T \Rightarrow v_{\rm rms} = \sqrt{\dfrac{3 k_B T}{m}}$

(which we already had from the MB distribution)

*translational here refers to the motion of the particle through 3D space, as opposed to any rotational or vibrational motion.

Whiteboard Problem: 20-4

By what factor does the **rms speed (v_{rms})** of a molecule change if the gas temperature is increased from 10°C to 1000°C? **(LC)**

Thermal Energy and Specific Heats

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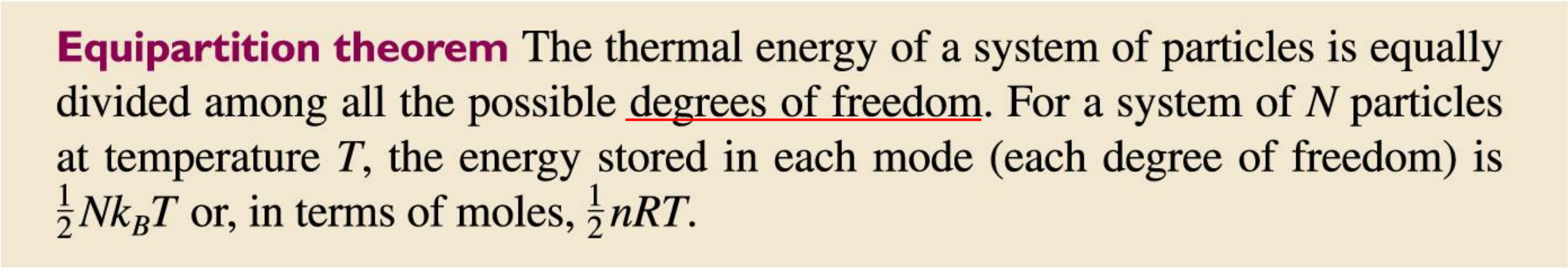
Consider the random motion of particles of a **monatomic gas, solid, and a diatomic gas,** and remember that the energy contained in this random motion is the **thermal energy**.



Equipartition theorem The thermal energy of a system of particles is equally divided among all the possible degrees of freedom. For a system of N particles at temperature T, the energy stored in each mode (each degree of freedom) is $\frac{1}{2}Nk_BT$ or, in terms of moles, $\frac{1}{2}nRT$.

Degree of freedom = a distinct independent way to move (mode) where the energy is stored

As shown in section 20.5 of your text, this allows us to arrive at approximate expressions to calculate the thermal energy and the specific heats of some substances.

Monatomic Gas*:
(3 degrees of freedom)

$$E_{\text{th}} = \tfrac{3}{2}Nk_BT = \tfrac{3}{2}nRT$$

$$C_V = \tfrac{3}{2}R \qquad C_P = C_V + R = \tfrac{5}{2}R \qquad \gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

Solid*:
(6 degrees of freedom)

$$E_{\text{th}} = 3Nk_BT = 3nRT \ \text{ and } C = 3R$$

Diatomic Gas*:
(8 degrees of freedom, but only 5 are important because of quantum effects)

$$E_{\text{th}} = \tfrac{5}{2}Nk_BT = \tfrac{5}{2}nRT \ \text{ and } C_V = \tfrac{5}{2}R \qquad C_P = \tfrac{7}{2}R \qquad \gamma = \tfrac{7}{5}$$

*As explained in your text, this model a good approximation for monatomic gases, fair for elemental solids, but for diatomic gases, is only good for temperatures between about 100 K to 1000 K.

Whiteboard Problem: 20-5

The thermal energy of 1.0 mole of a substance is increased by 1.0 J.

- **a) What is the temperature change if the substance is a monatomic gas?**
- **b) What is the temperature change if the substance is a diatomic gas?**
- **c) What is the temperature change if the substance is a solid?**

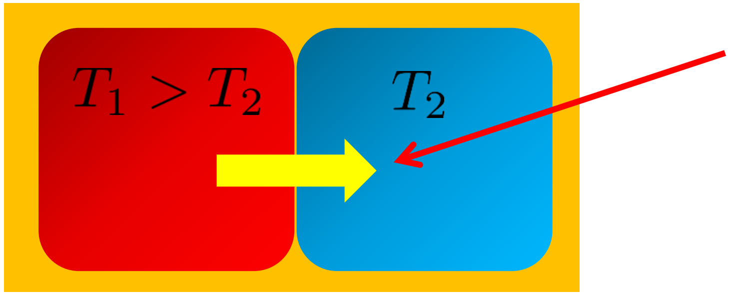
(LC, Rank the temperature changes)

d) Why is there a difference?

For monatomic, all of the thermal energy is in translation, while for the diatomic and the solid, some of the thermal energy is in other modes or degrees of freedom – but temperature is a measure of the random translational kinetic energy.

Thermal Interactions and Heat

Until now, we've been using the "pseudo-definition" of heat:



Heat, Q, is energy transferred due to a temperature difference.

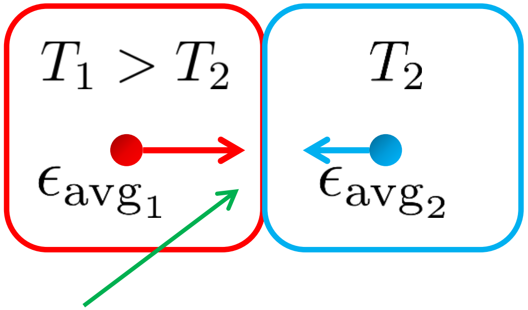
Q = 0 when the temperatures are equal

If the entire system is insulated, we know macroscopically:

$$E_{\text{th}_1} \text{ decreases and } E_{\text{th}_2} \text{ increases}$$

$$\text{But } E_{\text{th}_{\text{total}}} = E_{\text{th}_1} + E_{\text{th}_2} = \text{constant}$$

But, what is going on physically at the microscopic level to transfer this energy?



Perfectly elastic collision

Remember from PHY181, for a perfectly elastic collision:

$$\text{If } \epsilon_1 > \epsilon_2 \Rightarrow \text{energy is transferred from 1 to 2}$$

So, <u>for most collisions</u>, energy flows from gas 1 to gas 2.

This net flow of energy through collisions is Heat.

The flow continues until:

$$\epsilon_{\text{avg}_1} = \epsilon_{\text{avg}_2} \text{ or } T_1 = T_2$$
$$(\text{remember: } \epsilon_{\text{avg}} \propto T)$$

Whiteboard Problem: 20-6

2.0 g of monatomic Helium (A = 4) at an initial temperature of 300 K is mixed in an insulated container with 8.0 g of diatomic Oxygen (O_2, A = 32) at 600 K. The two gases interact thermally and come to a common final temperature, $\mathbf{T_f}$.

a) **Make an "educated guess" at their common final final temperature in Kelvin. (LC)**
(no calculations permitted – just make a reasonable guess!)

b) **Calculate their common final temperature in Kelvin. (LC)**
(Hint: use the fact that the total thermal energy is constant.)

PhET Gas Properties Simulation

- **If you like the PhET Gas Properties Simulation, feel to play with it and the other simulations at:**
  https://phet.colorado.edu/