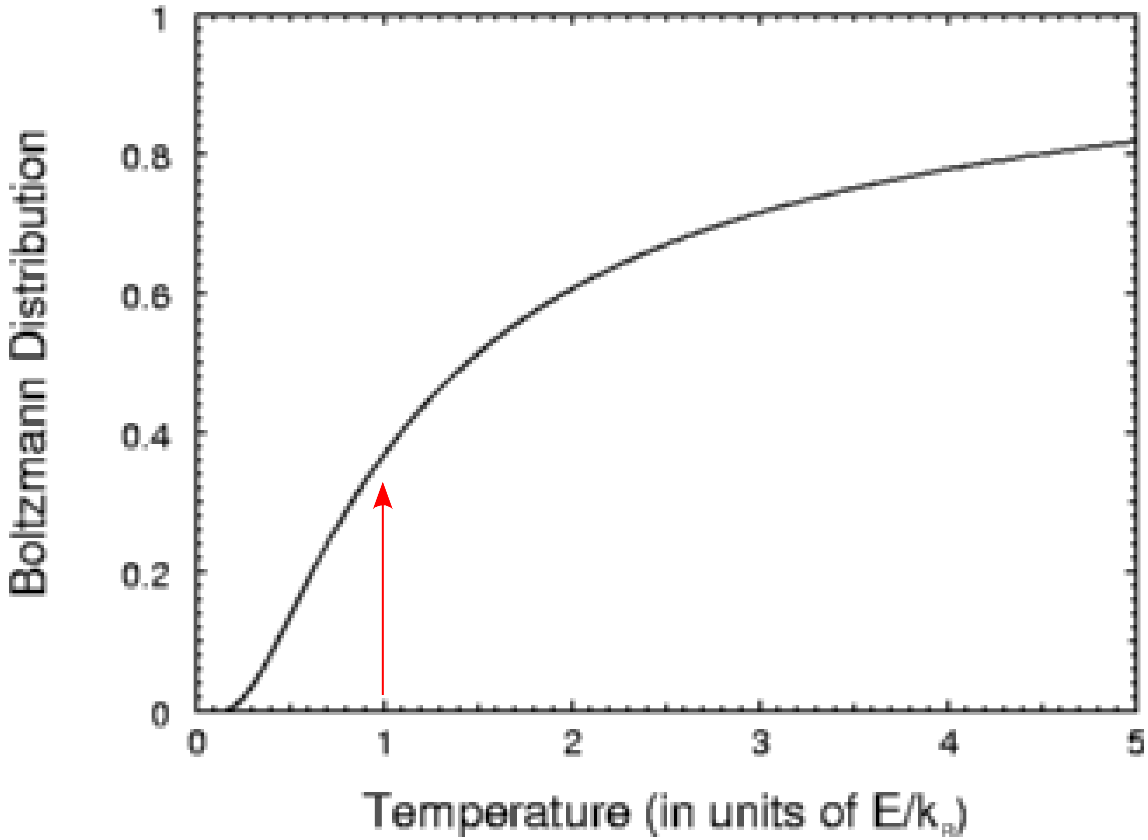
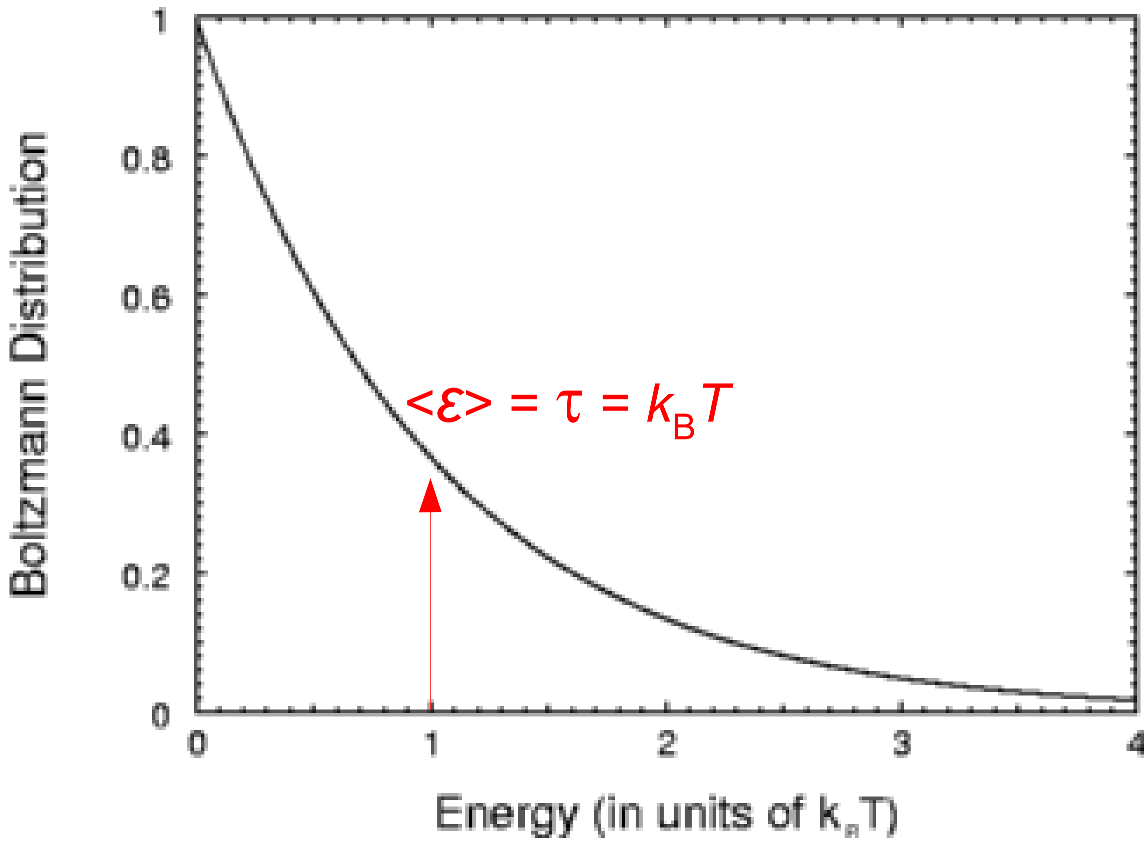
Boltzmann Distribution Revisited



Looked at as a the probability of a state with a given **energy** being occupied at different **temperatures**,
the Boltzmann distribution only starts to "get big" when

$$\boxed{T > \varepsilon/k_B.}$$

Averaging over the Boltzmann Distribution



Looked at as a probability distribution over **energy** at a **fixed temperature**, the Boltzmann distribution is just an exponential decay. When we normalize this and use it to find the **mean** energy $<\varepsilon>$, the result is just $\boxed{<\varepsilon> = \tau = k_B T.}$

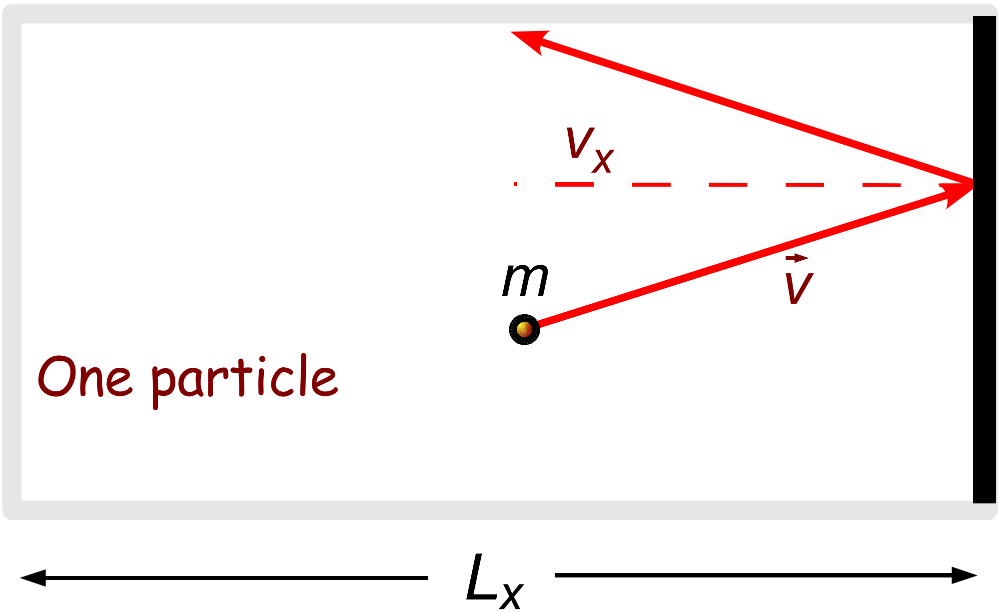
Equipartition Theorem

Although the average potential energy of a gas molecule in the atmosphere (for instance) is, by the preceding analysis, just τ, the **Equipartition Theorem** states that the average energy associated with each **degree of freedom** of a system is $\frac{1}{2}\tau$. The discrepancy arises because most "degrees of freedom" (like the x, y and z components of the velocity of a gas atom) have a range from $-\infty$ to $+\infty$ (rather than from 0 to $+\infty$ like for the height of a gas molecule in the atmosphere) and also appear **squared** in the energy. This adds a factor of ½. Proving this is nontrivial, so I will spare you the details.

It follows immediately that the mean energy U of an ideal gas of N particles in thermal equilibrium at temperature τ is just

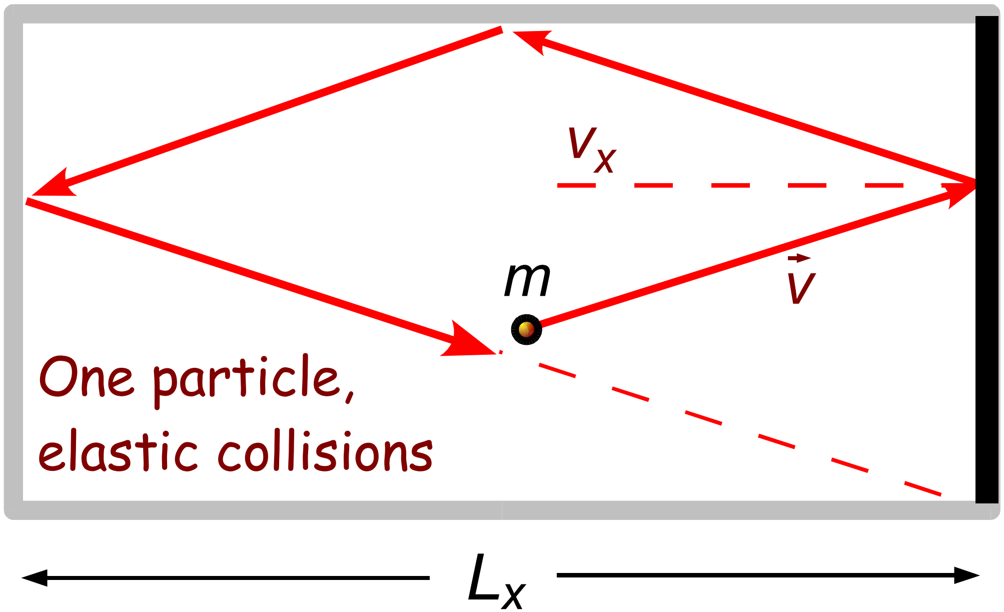
$$\boxed{U = 3/2\, N\, \tau}$$

PRESSURE



Assume specular, elastic collisions with the walls (like on a perfect pool table).

PRESSURE



Momentum transferred to wall on right at each collision is $\Delta p_x = 2\, m\, v_x$.

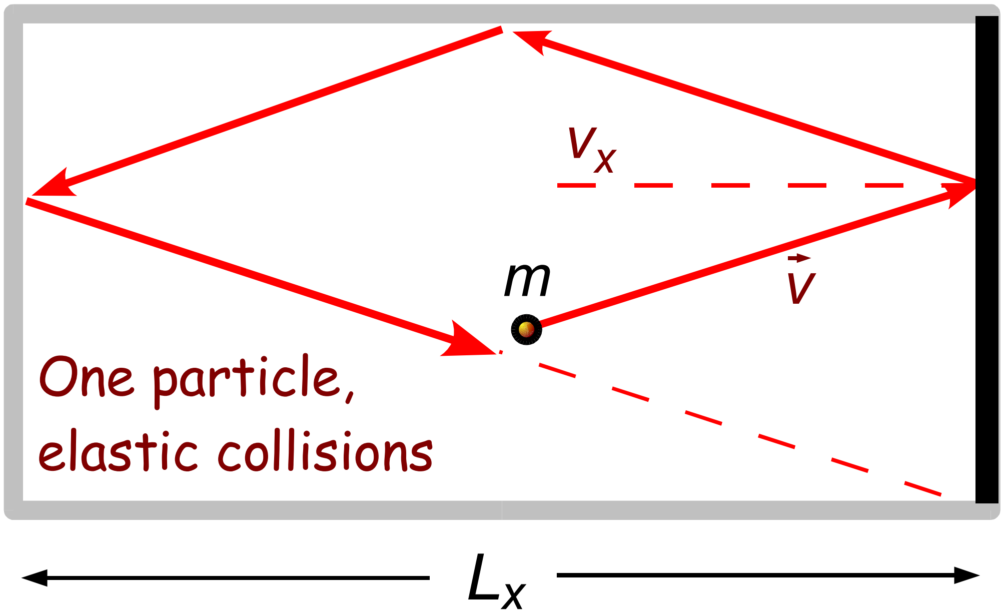
Time between collisions with that wall (2 transits of L_x) is

$$\Delta t = 2\, L_x / v_x$$

Average **force** (momentum transfer per unit time) due to **1** particle $F_x{}^1 = \Delta p_x / \Delta t = m\, v_x^2 / L_x$. This force is spread over the area A of the wall on the right for a **pressure** (force per unit area) $P_1 = F_x{}^1/A$ or $P_1 = m\, v_x^2 / AL_x$. But $AL_x = V$, the **volume** of the box. Thus

$$\boxed{P_1 = m\, v_x^2 / V}$$

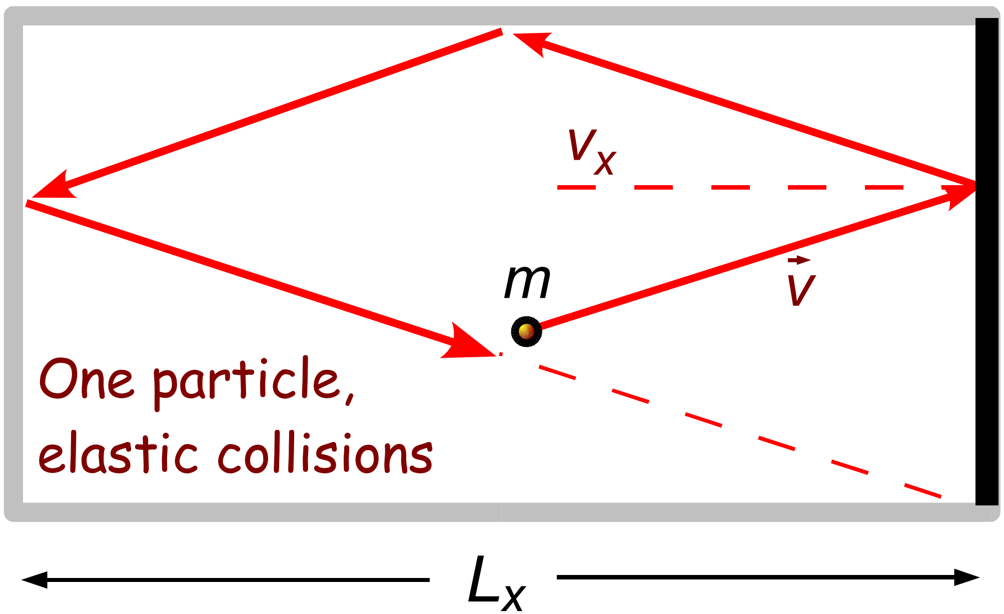
PRESSURE



We have a time-averaged pressure $P_1 = m\, v_x^2 / V$ due to one particle bouncing back and forth at v_x. Now let's calculate the average value of v_x^2 at a given temperature τ.

The average values of $\langle v_x^2 \rangle$, $\langle v_y^2 \rangle$ and $\langle v_z^2 \rangle$ are surely the same by symmetry, and the sum of all three is just $\langle v^2 \rangle$, so we can take $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$, giving $\langle P_1 \rangle = \frac{1}{3}\, m \langle v^2 \rangle / V = \frac{2}{3} \langle \frac{1}{2}\, m\, v^2 \rangle / V$ or $\langle P_1 \rangle V = \frac{2}{3} \langle \varepsilon \rangle$. This is the pressure due to **one** such particle.

PRESSURE



The pressure due to **one** such particle is $\langle P_1 \rangle V = \frac{2}{3} \langle \varepsilon \rangle$.

If there are N such particles bouncing around, each one contributes the same $\langle P_1 \rangle$, giving a net pressure P obeying $PV = \frac{2}{3} N \langle \varepsilon \rangle$.

But $N\langle \varepsilon \rangle$ is just (on average) the total kinetic energy of the ideal gas, $U = 3/2\, N\, \tau$, giving

$$\boxed{PV = N\,\tau}$$

the Ideal Gas Law!