General Physics I

Lect16. Temperature and Distribution

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Office Hours

- Tuesday 12:30-13:30 E5-226
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- Thursday 13:00-14:00 TA office hour

Kinetic Energy: Two Gases in a Box with Piston

- In container (1) the atoms have mass m_1, velocity v_1, and there are n_1 per unit volume. Same for (2). What are the conditions for equilibrium?
- Recall $P=(2/3)n\langle mv^2/2\rangle$, so
$$n_1\langle m_1 v^2_1/2\rangle=n_2\langle m_2 v^2_2/2\rangle$$
- The energy of the two boxes will come to an equilibrium temperature eventually, as the piston wiggles and keeps P_1 and P_2 equal----**heat conduction**!
- The system comes to an equilibrium where it picks up energy from the atoms at about the same rate as it puts energy back into them, for both sides.

(1)   (2)
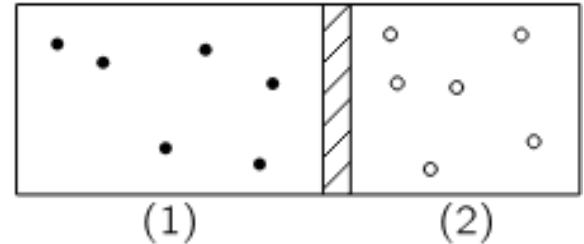
Kinetic Energy: Two Gases

- We have two molecules of different mass colliding and the collision is viewed in the center-of-mass (CM) system.

$$\vec{v}_{CM}=(m_1\vec{v}_1+m_2\vec{v}_2)/(m_1+m_2)$$

- From conservation, we know the relative velocity $\vec{w}=\vec{v}_1-\vec{v}_2$ is changed, s.t. $|\vec{w}|=|\vec{w'}|$ but in different directions

- We know at equilibrium, $\vec{w}$ will not have a preference direction as the collisions are totally randomized, hence

$$<\vec{v}_{CM}\cdot\vec{w}>=0$$

Expand $\vec{v}_{CM}\cdot\vec{w}=(\vec{v}_1-\vec{v}_2)(m_1\vec{v}_1+m_2\vec{v}_2)/(m_1+m_2)$
$=[(m_1\vec{v}_1{}^2-m_2\vec{v}_2{}^2+(m_2-m_1)(\vec{v}_1\cdot\vec{v}_2)]/(m_1+m_2)$
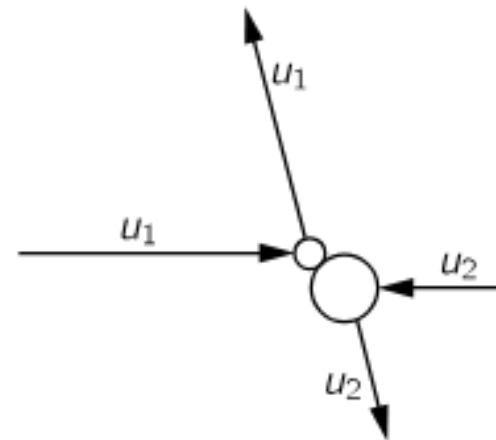
Fig. 39–3. A collision between unequal atoms, viewed in the CM system. $u_1=|\mathbf{v}_1-\mathbf{v}_{CM}|, u_2=|\mathbf{v}_2-\mathbf{v}_{CM}|$.

$<\vec{v}_1\cdot\vec{v}_2>=0$ since the two particles are different, hence
$$<m_1\vec{v}_1{}^2>=<m_2\vec{v}_2{}^2>$$
Same kinetic energy!

Temperature

$$<m_1\vec{v}_1^2>=<m_2\vec{v}_2^2>$$

Theorem 1: the mean value of the kinetic energy is kT/2 for each independent motion (d.o.f.)

- For two different gases, their average kinetic energy is the same in equilibrium----the heavy ones will move slower than the light ones. We see that, not just for gas, this quantity seems to agree for matter in an equilibrium state.
- We use the word "**temperature**" to denote the mean molecular kinetic energy of gas, but it is rather the property of itself rather than just gas.
- There is a simple linear relation between <u>mean kinetic energy</u> and temperature T, for each d.o.f.

$$\frac{1}{2}k_B T$$

k_B=1.38×10^{-23} joule for every Kelvin, "Boltzmann constant"

Comparison of temperature scales — From Wikipedia
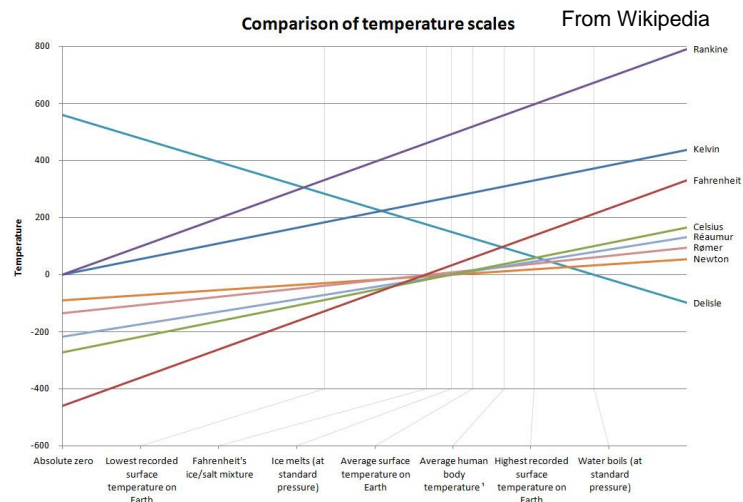
We can establish temperature scales using different reference points – e.g., melting/boiling points of pure water at atmospheric pressure. But Kelvin is probably the most natural one in physics.

- Recall from the last class, we have

$$PV = 2/3 \cdot N \langle \tfrac{1}{2}mv^2 \rangle$$

- Let's now plug in the definition of temperature,

$$PV = Nk_B T$$

- Beware, chemists count atoms in *mole*s, one mole has $N_0 = 6.02 \times 10^{23}$ objects, and they define a number $R = N_0 k_B = 8.31$ J·mole^{-1}K^{-1}

- So in chemistry (or high school textbooks), while they also call it N, it's actually in the unit of moles and the idea gas law writes

$$PV = NRT$$

- "Equation of state" is an equation that relates **state variables**, if we know the rest of the variables (e.g.,V, N,T) we know the last variable (e.g., P)

"At the same temperature, pressure and volume, the *number of atoms* is determined; it too is a universal constant! So equal volumes of different gases, at the same pressure and temperature, have the same number of molecules, because of Newton's laws. That is an amazing conclusion!"

Opposed to the path-dependent variables like mechanical work done or heat transfer as a system moves from one state to another depends on the path taken between states (later)
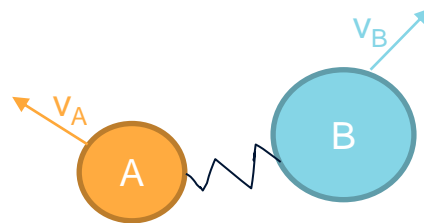
Diatomic Gas

- What happens if there are forces present? Assume the gas molecule is composed of two different atoms, A and B, held by a force (chemical bond, spring). So the center of mass velocity

$$\vec{v}_{CM} = (m_A \vec{v}_A + m_B \vec{v}_B)/(m_A + m_B) = (m_A \vec{v}_A + m_B \vec{v}_B)/M$$

$$\vec{v}_{CM}{}^2 = [m_A \vec{v}_A{}^2 + m_B \vec{v}_B{}^2 + (2m_A m_B)(\vec{v}_A \cdot \vec{v}_B)]/M^2$$

$$<\frac{1}{2} M \vec{v}_{CM}{}^2> = (m_A \frac{3}{2}kT + m_B \frac{3}{2}kT + m_A m_B <\vec{v}_A \cdot \vec{v}_B>)/M$$

$$= \frac{3}{2}kT + m_A m_B <\vec{v}_A \cdot \vec{v}_B>/M$$

We will prove that $<\vec{v}_A \cdot \vec{v}_B>$ is indeed zero in the next slide..

- To prove that $<\vec{v}_A \cdot \vec{v}_B>$ is zero, we do the same trick again with $\langle \boldsymbol{w} \cdot \boldsymbol{v}_{\mathrm{CM}} \rangle = 0$

$$\boldsymbol{w} \cdot \boldsymbol{v}_{\mathrm{CM}} = \frac{(\boldsymbol{v}_A - \boldsymbol{v}_B) \cdot (m_A \boldsymbol{v}_A + m_B \boldsymbol{v}_B)}{M}$$

$$= \frac{m_A v_A^2 + (m_B - m_A)(\boldsymbol{v}_A \cdot \boldsymbol{v}_B) - m_B v_B^2}{M}$$
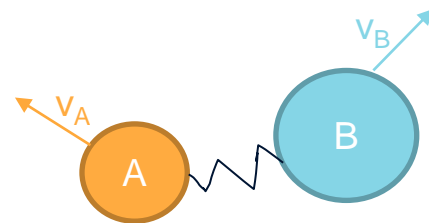
- Now that both A and B are in the equilibrium, $\langle m_A v_A^2 \rangle = \langle m_B v_B^2 \rangle$

$$(m_B - m_A)\langle \boldsymbol{v}_A \cdot \boldsymbol{v}_B \rangle = 0$$

- If the masses of A and B are different, we have $\langle \boldsymbol{v}_A \cdot \boldsymbol{v}_B \rangle = 0$, and the entire molecule can be regarded as a single molecule of mass M, s.t.

$$\left\langle \frac{1}{2} M v_{\mathrm{CM}}^2 \right\rangle = \frac{3}{2} kT \xrightarrow{\begin{array}{c}\text{Total energy 3kT}\\ \frac{1}{2} m_A v_A^2 + \frac{1}{2} m_B v_B^2 \end{array}}$$

The average kinetic energy of the **internal** motions of the diatomic molecule is also 3kT/2!

Statistical Mechanics

- **Statistical Mechanics** is the laws of mechanics that apply just to thermal equilibrium.
- Now try to answer: How are the molecules distributed in space (with a force field)?
- On the top right, we know that molecules at all heights should have the <u>same temperature</u> if we neglect the convection (wind), so what changed?
- Recall P=nkT, we can write the pressure difference of h and h+dh, dP=kTdn, which is equal to the weight $-mgn\,dh$
- So, $\dfrac{dn}{dh} = -\dfrac{mg}{kT}\,n \implies n = n_0 e^{-mgh/kT}$

We find that the density goes down exponentially with height.

- For molecules of different masses, the exponential is different--heavier decrease with altitude faster.
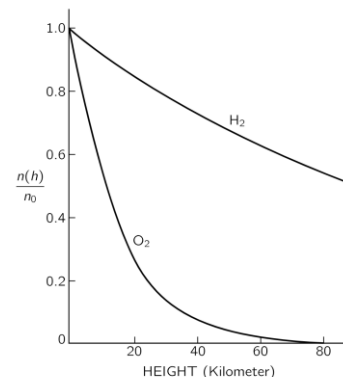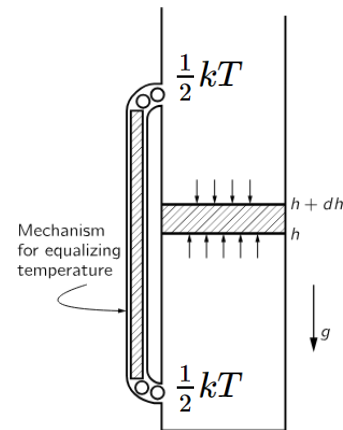

Fig. 40–2. The normalized density as a function of height in the earth's gravitational field for oxygen and for hydrogen, at constant temperature.

O2 decrease by 50% over 10km!

The Boltzmann law

- Note such exponential relation can be applied to any potential. To generalize, assume the gas is subject to a force F in the x-direction, balanced by the pressure change s.t. $Fn\,dx = dP = kT\,dn$, again we find

$$F = kT\,\frac{d}{dx}\left(\ln n\right)$$

- Notice that –Fdx is the work to take a molecule from x to x+dx, i.e., the change in potential energy (P.E.), s.t. $d(\ln n) = -d(\text{P.E.})/kT$

- General spatial distribution (density) of molecule in terms of P.E.:

$$n = (\text{constant})e^{-\text{P.E.}/kT}$$

- **Boltzmann's law**：the probability of finding molecules in a given spatial arrangement varies exponentially with the negative of the potential energy of that arrangement, divided by kT.

- Suppose the potential energy function of each of two molecules (i and j) depends only on their separation, $V(r_{ij})$. The total potential energy would be the sum of all the pairs, in the full set of molecules. The probability of finding molecules in any particular combination is

$$\exp\left[-\sum_{i,j} V(r_{ij})/kT\right]$$

- For $|V(r_0)| \ll kT$, the exponential close to 1, the molecule can be anywhere. The potential does not make much difference for where the particle should be->evaporation
- For $|V(r_0)| \gg kT$, large positive exponent around r_0. So in a given volume, molecules are much more likely to be at the distance of minimum energy than far apart ->condensation
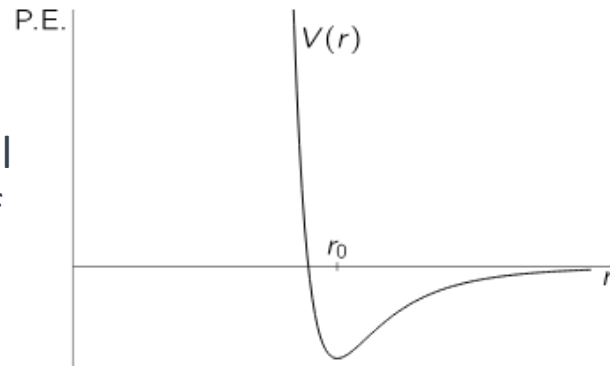
As the temperature falls, the atoms fall together, clump in lumps, and reduce to liquids, solids, and molecules, and as you heat them up they evaporate.

This is a *complicated* problem (due to a tremendous number of variables) sometimes referred to as the "**many-body problem**", or "**condensed matter physics**".

The Distribution of Molecular Speeds

- Now we go on to discuss the distribution of velocities. We start by counting how many molecules are passing from below to above the plane h=0 and h=h.

$$\begin{pmatrix} \text{Number passing } h = 0 \\ \text{with } v_z > u \end{pmatrix} = \begin{pmatrix} \text{number passing } h = h \\ \text{with } v_z > 0 \end{pmatrix}$$
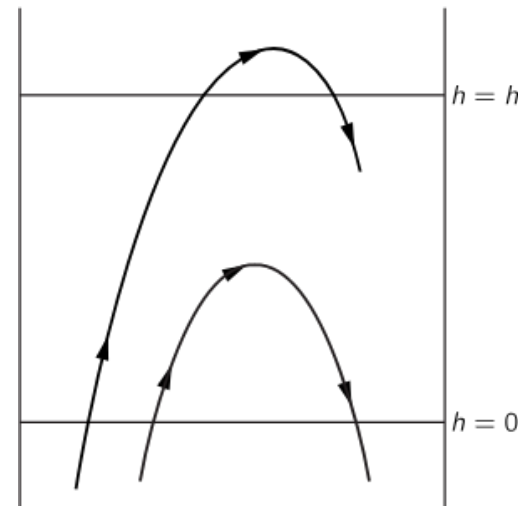
$$mu^2/2 = mgh$$

- From the same temperature we know that the distribution of velocities is the same, we use $n = n_0 e^{-mgh/kT}$ we find before and substitute with u, and find that

$$\frac{n_{>u}(0)}{n_{>0}(0)} = e^{-mgh/kT} = e^{-mu^2/2kT}$$

- Like the previous case, we can generalize the velocity to

$$n_{>u} \propto e^{-\text{kinetic energy}/kT}$$

We shall further simplify the above expression..

$h = h$

$h = 0$

The Distribution of Molecular Speeds

$$\int_{-\infty}^{\infty} f(u)\,du = 1$$

- What is the number of molecules passing through an area per second with a velocity greater than u, expressed in terms of f(u)?

$$\int_{u}^{\infty} uf(u)\,du = \text{const} \cdot e^{-mu^2/2kT}$$

faster molecules pass more frequently

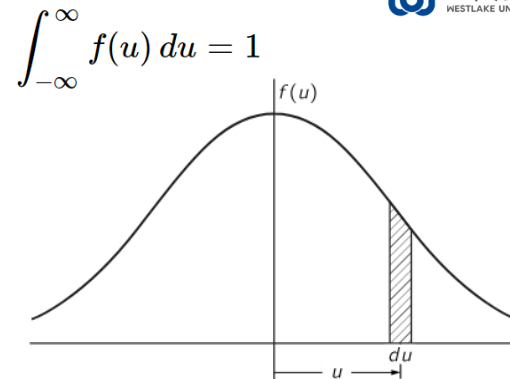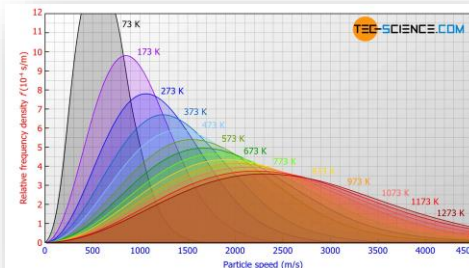Differentiate w.r.t. u, we have:

$$f(u)\,du = Ce^{-mu^2/2kT}\,du$$

f(u)du adds up to unity

$$C = \sqrt{m/2\pi kT}$$

The area denotes the probability of the velocity to be between u and u+du. The full curve area adds up to one.

- Also works in relativity:
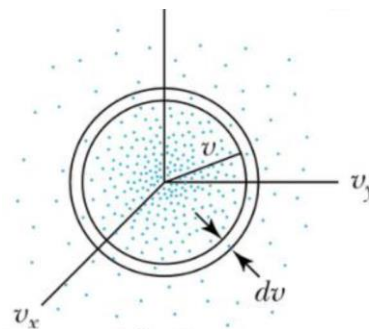
$$f(p)\,dp = Ce^{-\text{K.E.}/kT}\,dp \quad \text{(written in momentum p)}$$

- In 3D,

$$f(v) = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{\left(\frac{3}{2}\right)} v^2 e^{-\frac{mv^2}{kT}}$$

Velocity (momentum) distribution in 3D, v is the speed.

1. To get the value of the integral, let

$$I = \int_{-\infty}^{\infty} e^{-x^2} \, dx.$$

Then

$$I^2 = \int_{-\infty}^{\infty} e^{-x^2} \, dx \cdot \int_{-\infty}^{\infty} e^{-y^2} \, dy$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} \, dy \, dx,$$

which is a double integral over the whole xy-plane. But this can also be written in polar coordinates as

$$I^2 = \int_{0}^{\infty} e^{-r^2} \cdot 2\pi r \, dr$$

$$= \pi \int_{0}^{\infty} e^{-t} \, dt = \pi.$$