Lecture 9c: Kinetic Theory & Brownian Motion

Learning objectives: After this lecture, you will be able to:

1. Explain the origin of random molecular motion in fluids
2. Explain the meaning of Brownian motion and its relevance to fluids in the life sciences
3. Explain how changing the mass and volume of the pollen particles affect Brownian motion
4. Explain the meaning of statistical mechanics and how this model is used to describe the molecular origin of pressure and temperature.
5. Calculate the average kinetic energy of gas molecules along with their average velocities.

12.2 The Atomic Model of an Ideal Gas

Solids and liquids are nearly incompressible because the atomic particles are in close contact with each other. Gases, in contrast, are highly compressible because the atomic particles are far apart. In Chapter 11, we introduced an atomic-level model of an ideal gas, reviewed in Figure 12.3. In this model, we found that heating the gas made its atoms move faster, and that the temperature of an ideal gas is a measure of the average kinetic energy of the atoms that make up the gas. Indeed, it can be shown that the temperature of an ideal gas is directly proportional to the average kinetic energy per atom $K_{\text{avg}}$:

$$ T = \frac{2}{3} K_{\text{avg}} \frac{k_B}{k_B} $$

(12.3)

where $k_B$ is a constant known as Boltzmann's constant. Its value is

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

We can rearrange Equation 12.3 to give the average kinetic energy in terms of the temperature:

$$ K_{\text{avg}} = \frac{3}{2} k_B T $$

(12.4)

The thermal energy of an ideal gas consisting of $N$ atoms is the sum of the kinetic energies of the individual atoms:

$$ E_{\text{th}} = N K_{\text{avg}} = \frac{3}{2} N k_B T $$

(12.5)

Thermal energy of an ideal gas of $N$ atoms

For an ideal gas, thermal energy is directly proportional to temperature. Consequently, a change in the thermal energy of an ideal gas is proportional to a change in temperature:

$$ \Delta E_{\text{th}} = \frac{3}{2} N k_B \Delta T $$

(12.6)
Molecular Speeds and Temperature

The atomic model of an ideal gas is based on random motion, so it’s no surprise that the individual atoms in a gas are moving at different speeds. Figure 12.4 shows data from an experiment to measure the molecular speeds in nitrogen gas at 20°C. The results are presented as a histogram, a bar chart in which the height of the bar indicates what percentage of the molecules have a speed in the range of speeds shown below the bar. For example, 16% of the molecules have speeds in the range from 600 m/s to 700 m/s. The most probable speed, as judged from the tallest bar, is \( \sim 500 \text{ m/s} \). This is quite fast: \( \sim 1200 \text{ mph} \! \).

Because temperature is proportional to the average kinetic energy of the atoms, it will be useful to calculate the average kinetic energy for this distribution. An individual atom of mass \( m \) and velocity \( v \) has kinetic energy \( K = \frac{1}{2}mv^2 \). Recall that the average of a series of measurements is found by adding all the values and then dividing the total by the number of data points. Thus, we can find the average kinetic energy by adding up all the kinetic energies of all the atoms and then dividing the total by the number of atoms:

\[
K_{\text{avg}} = \frac{1}{2} m \frac{\sum v^2}{N} = \frac{1}{2} m \frac{\sum v^2}{N} = \frac{1}{2} m \left( \frac{v^2}{\text{avg}} \right)
\]  

(12.7)

The quantity \( \sum v^2/N \) is the sum of the values of \( v^2 \) for all the atoms divided by the number of atoms. By definition, this is the average of the squares of all the individual speeds, which we’ve written \( (v^2)_{\text{avg}} \).

The square root of this average is about how fast a typical atom in the gas is moving. Because we’ll be taking the square root of the average, or mean, of the square of the speeds, we define the root-mean-square speed as

\[
v_{\text{rms}} = \sqrt{(v^2)_{\text{avg}}} = \text{speed of a typical atom}
\]  

(12.8)

The root-mean-square speed is often referred to as the rms speed. The rms speed isn’t the average speed of atoms in the gas; it’s the speed of an atom with the average kinetic energy. But the average speed and the rms speed are very nearly equal, so we’ll interpret an rms speed as telling us the speed of a typical atom in the gas.

Rewriting Equation 12.7 in terms of \( v_{\text{rms}} \) gives the average kinetic energy per atom:

\[
K_{\text{avg}} = \frac{1}{2} m v_{\text{rms}}^2
\]  

(12.9)

We can now relate the temperature to the speeds of the atoms if we substitute Equation 12.9 into Equation 12.4:

\[
T = \frac{1}{3} \frac{m v_{\text{rms}}^2}{k_B}
\]  

(12.10)

Solving Equation 12.10 for the rms speed of the atoms, we find that

\[
v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}
\]  

(12.11)

rms speed of an atom of mass \( m \) in an ideal gas at temperature \( T \).
Summary: High/Low Reynolds flows

Conservation of mass leads to continuity equation: \( v_1 A_1 = v_2 A_2 \) for incompressible flows
Always applicable!

**High Reynolds Number flow:**

1. **Bernoulli equation** relates \( P, v, \) and \( h \):
   \[
   p_1 + \frac{1}{2} \rho v_1^2 + \rho gh_1 = \text{constant} \rightarrow \text{conservation of energy/Volume}
   \]
   Note: All turbulent flows are High Re but not all High Re number flows are turbulent

2. Bernoulli application: **Venturi effect** \( p_1 - p_2 = \frac{1}{2} \rho (v_2^2 - v_1^2) \)

**Low Reynolds Number flow:**

3. **Newton's law of viscosity** relates shear stress \( \tau \) to fluid velocity \( v \):
   \[
   \tau = \frac{F}{A} = \eta \frac{v}{l}
   \]
   Low Reynolds number flows are **reversible**: small organisms swim differently than we do!

4. The **Stokes equation** \( F_{\text{drag}} = 6\pi \eta v R \) tells us the drag force on a sphere.

5. The **Poiseuille equation** \( Q = \frac{\pi \Delta P}{8 \eta l} R^4 \) describes flow rate in a pipe.

\[
Re = \frac{\rho v l}{\eta} \quad \text{very small}, \text{low Re}
\]
Today: Brownian Motion and Statistical Mechanics

Today's goals with respect to:

Motion of small particles in fluids is random: Robert Brown's experiment (1828)

Brown suspended micron sized pollen grains in water and looked through a microscope and saw Brownian motion

Was this life? He denied them light and air and they continued to dance. He suspended soot and ground sphinx and found the same behavior.

A. Einstein explained Brownian motion in 1905, in the process proving the existence of atoms at last. The mathematics/physics of Brownian motion is now applied to financial markets, biology, chemistry, etc.

Although the famous video "Life in The Cell" seems to omit this!

Randomness is part of physics (and life)

- Fluids (liquids and gases) consist of lots and lots of molecules
- Each molecule obeys the laws of physics (mechanics)
- But they collide with each other and end up moving in random directions with a variety of speeds

Using Newton's 2nd law of motion \( \sum F = m \frac{d^2x}{dt^2} \), could you (in principle) find the position and velocity of every molecule in a gas? Yes. But is it feasible? No.

The rest of the class we will instead use statistical mechanics to understand the behavior of many particles in a fluid/gas.

Lecture 9c: Kinetic theory: Use Newton's laws and some assumptions about molecular motion to understand the relations between temperature, momentum, and energy \((k_B T)\)

Lecture 10a: Thermal energy and the Boltzmann distribution: The Boltzmann distribution tells us how likely a system is to lose or gain energy from its surroundings

Lecture 10b: Random walks and diffusion: Using Einstein's model of microscopic motion to understand the origins of Brownian motion and diffusion

Lecture 10c: Diffusion and Fick's law: Understanding the macroscopic consequences of diffusion, with applications to biology and medical devices.
Molecular Model of Pressure in a gas

Pressure: \( P = \frac{F}{A} \)

The pressure in a gas originates from the collision of gas molecules with the walls of the container.

From Newton's third law the force on the wall (i.e. pressure) is equal and opposite to the force on molecules.

\[ \vec{F}_{\text{on wall}} = -\vec{F}_{\text{on molecule}} \]

When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

Assume: elastic collision

Each collision exerts a tiny force on the wall. The net force due to all the collisions causes the gas to have a pressure.


Physical Sciences 2: Lecture 9c

**Activity 1: How fast is a molecule?**

Let's consider an extremely simple model of an ideal gas: we have a **single molecule** of mass $m$ which is bouncing back and forth in a container. The molecule is moving in one dimension (the $x$-direction) and has repeated collisions with the walls of area $A$. (Ignore gravity here.)

The distance between the walls is $L$. Each time the molecule strikes a wall it changes direction but maintains the same speed, so its velocity is either $+v_x$ or $-v_x$ depending on whether it is moving to the right or left. The volume of the container is $V = AL$.

1. Find an expression for the time $\Delta t$ required for the molecule to go all the way across the container and back.

   $$\Delta t = \frac{\text{dist}}{\text{speed}} = \frac{2L}{v_x}$$

2. The average force exerted on one wall is $\langle F_x \rangle = \frac{\Delta p_x}{\Delta t} = \frac{m(v_i - v_f)}{\Delta t}$. Find an expression for the magnitude of the average **pressure** exerted on one wall, in terms of $m$, $v_x$, and $V$.

   $$\langle P \rangle = \frac{\langle F_x \rangle}{A} = \frac{1}{A} \langle F_x \rangle = \frac{1}{A} \frac{m v_i - v_f}{\Delta t} = \frac{1}{A} \frac{m (-v_x - v_x)}{\frac{2L}{v_x}} = \frac{m v_x^2}{AL}$$

   $$\text{mag.} = \frac{m v_x^2}{V}$$

3. Now imagine that there are a huge number $N$ of molecules, each with different $v_x$. Find an expression for the average pressure exerted by **all of these molecules**. You'll get an expression that includes $\langle v_x^2 \rangle$.

   $$P = \frac{\langle N m v_x^2 \rangle}{V} = \frac{N m \langle v_x^2 \rangle}{V} = m \langle v_x^2 \rangle \Rightarrow m \langle v_x^2 \rangle = \frac{PV}{N}$$

4. In 3 dimensions, the average squared speed $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$. Assuming that each molecule is equally likely to move along any axis, and using the ideal gas law, show that:

   $$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

   $$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

   $$\langle v^2 \rangle = 3 \langle v_x^2 \rangle$$

   $$\frac{1}{2} m \langle v_x^2 \rangle = \frac{3}{2} \frac{PV}{N} = \frac{3}{2} \frac{N k_B T}{N}$$

   $$PV = N k_B T$$
Activity 2: Connecting Microscopic to Macroscopic

1. We see Brownian Motion for small objects, under the microscope, but large objects like us don’t bounce around all day due to Brownian Motion. From the microscopic model introduced in the previous activity, can you guess/explain why Brownian motion only occurs for small objects?

Recall the ideal gas law \( PV = nRT \) or \( PV = Nk_B T \)? Many experiments went into determining the ideal gas law. For each of the following sketch the plot the experimenter may have seen. Then describe the microscopic explanation for this dependence, given the model introduced in the previous activity.

2. Gay-Lussac discovered how pressure \( P \) and temperature \( T \) vary when the volume of a gas is held constant.

\[
P = \left( \frac{Nk_B}{V} \right) T \quad \text{T \uparrow \ V \uparrow \ P \uparrow}
\]

3. Boyle discovered how pressure \( P \) and volume \( V \) vary when the temperature of a gas is held constant.

\[
P = \left( \frac{Nk_B}{V} \right) \text{T \downarrow \ V \uparrow \ P \downarrow}
\]

4. Charles discovered how volume \( V \) and temperature \( T \) vary when the pressure of a gas is held constant.

\[
V = \left( \frac{Nk_B}{P} \right) T \quad \text{T \uparrow \ V \uparrow \ P \uparrow}
\]

**Bonus:** An air bubble of 20cm³ volume is at the bottom of a lake 40 m deep where the temperature is 4°C. The bubble rises to the surface, which is at a temperature of 20°C. Take the temperature of the bubble’s air to be the same as that of the surrounding water. Just as the bubble reaches the surface, what is its volume?

\[
\frac{P_1 V_1}{T_1} = \frac{Nk_B}{\text{const}} \\
\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} \Rightarrow V_2 = \frac{P_1 V_1}{P_2 T_1} T_2
\]

\[
\approx 164.7 \text{ cm}^3
\]
Activity 3: $k_B T$ as the average kinetic energy

In the previous activity, we found: $\langle KE \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$ which, when rearranged, gives the typical speed of a single particle:

$$v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

These expressions are actually more general – it doesn’t require the ideal gas law. The average kinetic energy of anything in any fluid (gas or liquid) is on the order of $k_B T$. The translational kinetic energy in 3-D is $\frac{3}{2} k_B T$.

**Classical Equipartition theorem:** The average kinetic energy for each degree of freedom is $\frac{1}{2} k_B T$.

- For a diatomic molecule like O₂, there are 3 degrees of freedom for translation, 2 more for rotation, and one for vibration, giving an avg. kinetic energy of $\frac{6}{2} k_B T$. Note: Quantum Mechanics restricts it to $\frac{3}{2} k_B T$.

- For methane CH₄, there are 3 degrees of freedom for translation, 3 more for rotation, and 9 more for vibration, giving an average kinetic energy of $\frac{15}{2} k_B T$. Note: Quantum Mechanics restricts it to $\frac{6}{2} k_B T$.

Where is the Moon’s atmosphere? (practice problems)

In order to escape Earth’s gravity, an object near the top of the atmosphere (at an altitude of 100 km) must travel away from Earth at 11 km/s. This speed is called the escape velocity.

1. At what temperature would hydrogen molecules (mass of $3.3 \times 10^{-27}$ kg) have an average velocity $v_{rms}$ equal to Earth’s escape velocity of 11 km/s?

$$v_{rms} = \sqrt{\frac{3 k_B T}{m}} \implies T = \frac{v_{rms}^2 m}{3 k_B} = \frac{(1.1 \times 10^4)^2 \times 3.3 \times 10^{-27}}{3 \times 1.38 \times 10^{-23}} = 10,000 \text{K}$$

2. The escape velocity from the Moon is much smaller than from Earth and is only 2.4 km/s. At what temperature would hydrogen molecules have an average velocity $v_{rms}$ equal to the Moon’s escape velocity?

$$T = \frac{v_{rms}^2 m}{3 k_B} = \frac{(2.4 \times 10^3)^2 \times 3.3 \times 10^{-27}}{3 \times 1.38 \times 10^{-23}} = 460 \text{K}$$

**Bonus:** The average kinetic energy of molecules $\langle KE \rangle = \frac{3}{2} k_B T$ is independent of their mass. Can you argue why heavy and light molecules have the same energy?

- Higher mass means lower speed. These two contributions cancel to give same K.E.
- Also, mixing small & large mass objects, the interactions/bumping will make small objects faster.
Activity 4: Why does Brownian motion look the way it does?

1. Example: how fast does a protein (Lysozyme) move?

(a) The protein lysozyme has a mass of $2.3 \times 10^{-23}$ kg. What is its root-mean-square velocity when it is dissolved in water? Assume $T=20^\circ$C

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \quad 23 \text{ m/s}$$

50 mph

(b) The velocity we obtained for the protein seems really large. If we were to look at it in a microscope, would we see it zipping straight through the fluid at $v_{\text{rms}}$? Explain.

No, bumps around at this speed.

2. Qualitatively, explain how the Brownian motion (specifically $v_{\text{rms}}$) of particles (e.g. pollen) changes if:

(a) the temperature of the fluid is increased

$$v_{\text{rms}} \uparrow$$

(b) the mass of the particle is decreased/increased (keeping the volume constant)

KE stays same so $m \uparrow v_{\text{rms}} \downarrow$

(c) the size of the particles is decreased/increased (keeping the mass constant)

$w_{\text{rms}}$ same

Demo: Small and large ball bearings on a shaker plate. All bearings have the same kinetic energy.

Simulation: a dissolved protein doesn’t get very far before it hits a water molecule.
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One-Minute Paper

Your name: ___________________________ TF: ___________________________

Names of your group members: ___________________________

• Please tell us any questions that came up for you today during lecture. Write “nothing” if no questions(s) came up for you in class.

• What single topic left you most confused after today’s class?

• Any other comments or reflections on today’s class?