Kinetic Theory of Gases: Pressure, Effusion, Collisions

The Kinetic Theory of Gases uses $\overline{c}$ and $f(c)$ to find:

- Pressure
- Transport properties
- Collision frequency
- Mean free path

Begin with pressure, $p = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$

Take point of view introduced by Bernoulli in 1738:

1. rectilinear container, side area $A*B$, depth $D$
2. gas molecules have velocity $c=(u,v,w)$
3. no collisions between gas molecules (ideal gas)

Pressure = (force/unit area) exerted by gas molecules hitting wall $= F/(A*B)$

For a single molecule,

$$F = \frac{\text{momentum transfer at wall}}{\text{interval between gas-wall collisions}} = \frac{\Delta(mc)}{\Delta t} = \frac{mv - (-mv)}{2D/v} = \frac{mv^2}{D}$$

$$p = \frac{mv^2}{D} \cdot \frac{1}{AB} = \frac{mv^2}{ABD} = \frac{mv^2}{(volume)}$$

Then for $N$ molecules,

$$P_{total} = \sum_{i=1}^{N} p_i = \frac{m}{V} \sum_{i=1}^{N} v_{i}^2$$

but, $\overline{v^2} = v_{rms}^2 = \sum_{i=1}^{N} v_{i}^2$ and $\overline{c^2} = \int c^2 f(c) dc = \overline{u^2} + \overline{v^2} + \overline{w^2}$
and also, $\overline{u^2 + v^2 + w^2}$ because space is isotropic.

So, $\overline{u^2 + v^2 + w^2} = \frac{1}{3}c^2$

Thus $p = \frac{m}{V} \sum_{i=1}^{N} v_i^2 = \frac{m}{V} n v^2 = \frac{m}{V} \frac{1}{3} N c^2$

But $\overline{c^2} = \frac{3kT}{m}$ so $p = \frac{\rho}{V} \frac{N}{\beta} \frac{kT}{\rho} = \frac{NkT}{V}$

Or $pV = NkT$ for $N$ molecules or $pV = nRT$ for $n$ moles

In Lecture 28, we get the same result by explicit angle averaging with $f(\vec{c})$

We can also use this approach to estimate the rate of gas collisions with the wall. We will just state the result here.

The number of molecules striking area $dA$ on wall per unit time is:

$$\frac{\# \text{ of molecules}}{\text{unit area} \, dA \, \text{on wall}} \, \text{per unit time} = \left( \frac{N}{V} \right) \frac{\sin \theta d\theta d\phi}{4\pi} f(\vec{c}) d\vec{c}$$

$$f(\vec{c}) = \left( \frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)}$$

$$\text{Flux} = \frac{\# \text{ of molecules}}{\text{unit area} \, \text{unit time}} = \frac{1}{4} \left( \frac{N}{V} \right) \overline{c}; \overline{c} = \left( \frac{8kT}{\pi m} \right)^{1/2}$$

So for example, how many "air" molecules strike the average 5.62 student sitting here in class?
Let us use a theoretical chemist's model of a 5.62 student to find the effective area:

- A cube 0.5m on each side
- \( \text{Area} = 6 \cdot (0.5m)^2 = 1.5m^2 = 1.5 \times 10^4 \text{cm}^2 \)

We previously found \( \overline{c} = 4.6 \times 10^4 \text{cm/s} \) (air, 300K)

Density (N/V) = \( N_A \frac{n}{V} = N_A \frac{p}{RT} \approx 2.4 \times 10^{19} \text{cm}^{-3} \) at P=1 atm, T=300K

So \( \frac{1}{4} (1.5 \times 10^4 \text{cm}^2)(4.6 \times 10^4 \text{cm/s})(2.4 \times 10^{19} \text{cm}^{-3}) = 4 \times 10^{27} \text{ air molecules hitting you each second!!} \)

We can also calculate gas effusion in this way. Let \( dA \) be a small hole of area \( \delta A \).

Effusion rate = -flux \( \cdot \delta A \)

\[
= -\frac{1}{4} \left( \frac{N}{V} \right) \overline{c} \delta A \\
= -\frac{1}{4} \delta A \left( \frac{pN_A}{RT} \right) \left( \frac{8RT}{\pi M} \right)^{1/2} \\
= -\frac{pN_A \delta A}{\left(2\pi MRT\right)^{1/2}}
\]

Applications:
1. Experimental measurement of \( \overline{c} \) (or, practically, of \( p \))
2. Produce a molecular beam of species in the container
3. Vapor pressure measurements

This treatment is still incomplete, however. It takes no account of collisions between gas molecules.
Interactions between molecules (review notes for lecture #18):

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Trajectories</th>
<th>Equation of State</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Ideal Gas)</td>
<td>pV=nRT</td>
<td></td>
</tr>
<tr>
<td>U(R)=0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hard Sphere ("Billiard Ball")

\[
pV = nRT + B(T)\left(n^2 \frac{RT}{V}\right)
\]

\[
B(T) = \frac{2\pi}{3} N_A \sigma^3
\]
Lennard-Jones

\[ pV = nRT + B(T)(n^2 \frac{RT}{V}) \]

\[ B(T) = \frac{2\pi}{3} N_A \sigma^3 [1 - f_c(\varepsilon, T)] \]

\[ U(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right] \]

**Basic Questions in Kinetic Theory:**

1. What is the frequency of collisions in a gas?
2. How far do molecules move between collisions?

Do this for the **hard-sphere** model (in simplified fashion):

Define a collision as follows:
"collision diameter"
\[ d_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \]

"collision cross section"
\[ \sigma = \pi d_{AB}^2 \]

collision frequency (in the gas)
\[ Z_{AB} = \pi d_{AB}^2 u N_A N_B \text{ (cm}^{-3}\text{s}^{-1}) \]

Average of distances between collisions is mean free path \( \lambda \).
To calculate $Z_A$ or $Z_{AB}$, we must know average relative speed, $u$, which is average of the magnitude of the relative velocity, $c$.

This is done in the attached supplement. The result is delightfully simple:

$$\overline{c} = \left(\frac{8kT}{\pi \mu} \right)^{1/2}$$

where $\mu = \text{reduced mass} = \frac{m_1m_2}{m_1 + m_2}$

So for "A" in "B", $Z_A = \pi d_{AB}^2 \left(\frac{8kT}{\pi \mu_{AB}}\right)^{1/2} N_B$

For a one-component gas, $\mu = \frac{m_A^2}{2m_A} = \frac{m_A}{2}$

$$Z_A = \pi d_{AB}^2 N_A \left(\frac{8kT}{\pi m_A/2}\right)^{1/2} = \sqrt{2}\pi d_A^2 \overline{c}_A N_A$$

So collision rate,

$$Z_{AA} = \frac{\sqrt{2}}{2} \pi d_A^2 \overline{c}_A N_A^2$$

Mean free path is just

(average particle velocity)$\times$(average time between collisions)

$$\lambda = \frac{\overline{c}_A}{Z_A} = \frac{\overline{c}_A}{\sqrt{2}\pi d_A^2 \overline{c}_A N_A}$$

$$\lambda = \frac{1}{\sqrt{2}\pi d_A^2 N_A}$$

This was all derived for a hard-sphere gas. For a Lennard-Jones gas, things get more complicated! The result can be found on p. 260 on the first
edition of Steinfeld, Francisco, Hase, “Chemical Kinetics and Dynamics.” In the notation we have been using here:

\[
\frac{Z_A}{N_A} = \Omega_{AB}^{(2,2)} \pi d_{AB}^2
\]

Values of the “Omega-integral” are tabulated in Hirschfelder, Curtiss, & Bird.

Let us make some numerical estimates. Again, take air at \( p = 1 \text{ bar}, \ T = 300 \text{ K} \)

“nominal” molecular weight = 29 g/mol

\[
\frac{N}{V} \text{ (1 bar, 300K)} = \frac{N_A p}{RT} = \frac{6.022 \times 10^{23}}{(82.06 \text{ cm}^3 \cdot \text{bar/mol} \cdot K)(300K)}
\]

\[
= 2.4 \times 10^{19} \text{ mol/cm}^3
\]

\[
\frac{c_A}{\pi m_A} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi m}\right)^{1/2} = \frac{4.59}{M(\text{kg/mol})^{1/2}}
\]

\[
= 4.67 \times 10^4 \text{ cm/s}
\]

Now we need “collision diameter” \( d_A \). This can be determined experimentally from the second virial coefficient, transport properties (coming up next week), or molecular beam scattering.

For \( N_2 \) or \( O_2 \sigma_{LJ} \) is about 3.6 Å or 3.6 \( \times 10^{-8} \text{cm} \)

So \( \pi d_A^2 \) is \( 3.8 \times 10^{-15} \text{cm}^2 \)
### Rules of Thumb:

**Collision frequency** ~$6 \times 10^9$, at 1 atm, ~$10^7$, at 1 Torr (1/760 atm)

**Mean free path** ~ $10^{-5}$ cm (0.1 μm), at 1 atm, ~$10^{-2}$ cm (0.1mm), at 1 Torr

### Calculation of Average Relative Speed

$$f(\vec{c}_1) = \left( \frac{m_1}{2\pi kT} \right)^{3/2} e^{-m_1\vec{c}_1^2 / 2kT}$$

$$f(\vec{c}_2) = \left( \frac{m_2}{2\pi kT} \right)^{3/2} e^{-m_2\vec{c}_2^2 / 2kT}$$

$$\vec{c} = \left( \frac{m_1^{1/2} m_2^{1/2}}{2\pi kT} \right)^{3/2} \int_0^\infty \int_0^\infty \vec{c}_1 e^{-(m_1\vec{c}_1^2 + m_2\vec{c}_2^2) / 2kT} d\vec{c}_1 d\vec{c}_2$$

- Need to change variables, need to change to relative velocity, so define center-of-mass velocity, $\vec{V}$

$$(m_1 + m_2)\vec{V} = m_1 \vec{c}_1 + m_2 \vec{c}_2$$

$$\vec{c} = \vec{c}_2 - \vec{c}_1$$

$$\vec{c}_1 = \vec{V} - \frac{m_2}{m_1 + m_2} \vec{c}$$

$$\vec{c}_2 = \vec{V} + \frac{m_1}{m_1 + m_2} \vec{c}$$
Now, \( m_1c_1^2 + m_2 + c_2^2 = (m_1 + m_2)V^2 + \frac{m_1m_2}{m_1 + m_2}c^2 \)

Jacobian for 2 variables:

\[
d\vec{c}_1 d\vec{c}_2 = J\left(\frac{\vec{c}_1, \vec{c}_2}{\vec{c}, \vec{V}}\right) d\vec{V}d\vec{c}
\]

\[
J\left(\frac{\vec{c}_1, \vec{c}_2}{\vec{c}, \vec{V}}\right) = \left(\frac{\partial \vec{c}_1}{\partial \vec{V}}\right)\left(\frac{\partial \vec{c}_2}{\partial \vec{c}}\right) - \left(\frac{\partial \vec{c}_1}{\partial \vec{c}}\right)\left(\frac{\partial \vec{c}_2}{\partial \vec{V}}\right) = 1
\]

\[
\ddot{c} = \left(\frac{m_1^{1/2}m_2^{1/2}}{2\pi kT}\right)^3 \int \int_{\acute{c}} ce^{-\left[(m_1+m_2)v^2+\mu c^2\right]/2kT} d\vec{c}d\vec{V}
\]

\[
\left(\frac{m_1^{1/2}m_2^{1/2}}{2\pi kT}\right)^3 = \left(\frac{\mu}{2\pi kT}\right)^{3/2} \left(\frac{m_1 + m_2}{2\pi kT}\right)^{3/2}
\]

\[
\ddot{c} = \int \left[ \int_{\acute{c}} \left(\frac{m_1 + m_2}{2\pi kT}\right)^{3/2} e^{-\left[(m_1+m_2)v^2/2kT\right]} d\vec{V} \right] \cdot \left(\frac{\mu}{2\pi kT}\right)^{3/2} ce^{-\mu c^2/2kT} d\vec{c}
\]

\[
\ddot{c} = \left(\frac{\mu}{2\pi kT}\right)^{3/2} \int_{\acute{c}} ce^{-\mu c^2/2kT} d\vec{c} = \left(\frac{\mu}{2\pi kT}\right)^{3/2} \int_{\acute{c}=0}^{\pi} \int_{\acute{\theta}=0}^{2\pi} \int_{\acute{\phi}=0}^{2\pi} c^3 e^{-\mu c^2/2kT} \sin \acute{\theta} d\acute{\theta} d\acute{\phi} dc
\]

\[
\ddot{c} = \left(\frac{8kT}{\pi \mu}\right)^{1/2}, \mu = \frac{m_1m_2}{m_1 + m_2}
\]
There is a relation between the distribution of arrival times \( q(t) \) and the distribution of speeds \( h(v) \):

\[
q(t)dt = h(v)dv
\]

Dynamics determines the exact relation between distance, speed, and time \( L = vt \). Using the Dirac delta function to set this relation gives:

\[
\int_0^\infty dv h(v) \delta \left( v - \frac{L}{t} \right) = h\left( \frac{L}{t} \right).
\]

Thus, measurement of \( q(t) \) allows us to infer the functional form of \( h \) according to:

\[
h\left( \frac{L}{t} \right) = q(t) \left. \frac{dt}{dv} \right| = q(t) \frac{t^2}{L}
\]

The flux is obtained by multiplying the amplitude in the arrival time distribution at the corresponding time \( t \) with a factor \( t^2/L \). The flux of molecules with large \( v \) arrive at the detector early and have not spread out in arrival times as the later arriving ones.
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