More Kinetic Theory of Gases

Physics 1425 Lecture 32

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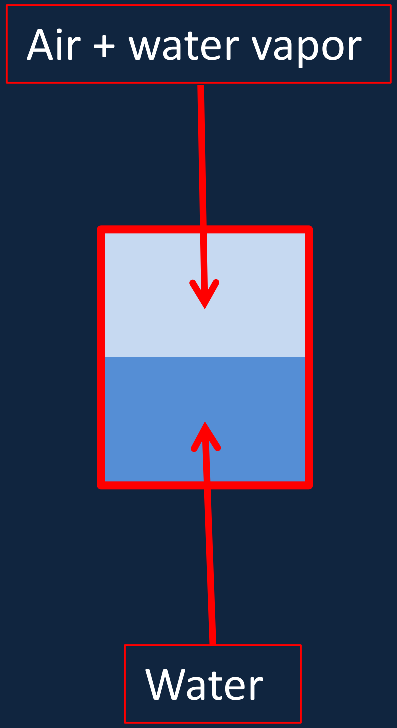
Vapor Pressure and Humidity

- The H_2O molecules in liquid water strongly attract each other, holding the liquid together. But these molecules are still jiggling around, with a Maxwell speed distribution. This means a fraction of them near the surface are moving fast enough to escape, forming a vapor above the surface.
- In a closed container, with enough water present, an equilibrium situation is reached between escaping and returning molecules.

Water and Vapor in Equilibrium

- In equilibrium in a closed container, the molecules in the vapor have the same average kinetic energy as the air molecules, so exert pressure on the walls of the container proportionate to their numbers.
- This is the saturated vapor pressure. It varies with temperature like $e^{-a/T}$, not surprising since its origin is molecules fast enough to escape.



Water Vapor Pressure

- At room temperature, saturated vapor pressure is about 2.5% of atmospheric pressure.
- At 100°C, it equals atmospheric pressure: this means small bubbles formed in the liquid by fast moving molecules coming together are no longer crushed by the surrounding atmospheric pressure, the water boils.
- In mountain resorts like Aspen, water boils at a lower temperature, producing inferior tea.

Relative Humidity and Dew Point

- If water is constantly boiled off in a closed room, there's a limit to how much water vapor the air can hold: it becomes saturated. That limit depends on the temperature. Attempts to add more water result in condensation on the walls, fog formation, etc. At this point, relative humidity = 100%.
- Relative humidity =

  vapor pressure/saturated vapor pressure

Dew point: temperature at which dew forms—that is, water condenses out as the air cools. (For given vapor pressure, dew point is found from tables.)

Pressure Cooking

- A pressure cooker works at a gauge pressure of about one atmosphere: that is, inside the cooker, pressure is about 2 x 10^5 Pascals.
- The vapor pressure of water rises from 1 atm to 2 atm on heating from 100°C to 120°C.
- This means that inside the cooker, the boiling water is at 120°C, cooking times are faster.

Clicker Question

- It’s freezing rain outside, 0°C and 100% humidity (meaning a vapor pressure of about 600 Pa), the only source of humidity in your drafty house is the outside air (no humidifier or boiling water), the house is at 20°C (svp about 2400 Pa).
- What is the relative humidity in the house?

A. 100%

B. 50%

C. 25%

Clicker Question

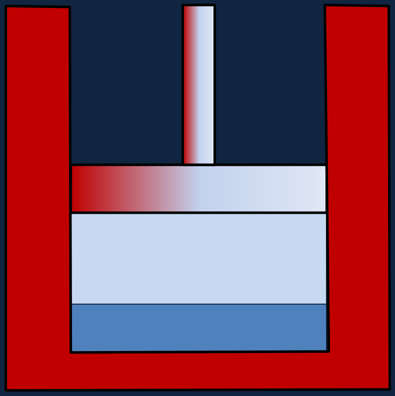
- A closed cylinder contains water and water vapor in equilibrium at 20°C and atmospheric pressure.
- The piston is slowly pushed down until the pressure inside is doubled, all at 20°C.
- What happened to the water vapor pressure?

A. It doubled

B. It increased, but less than doubling.

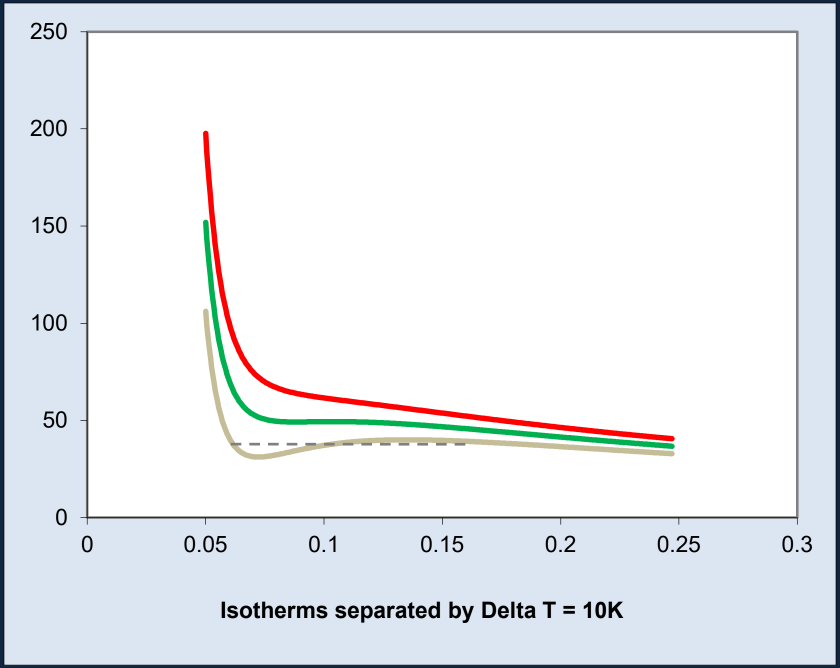
C. It stayed the same.

D. It went down.



Van der Waals Equation

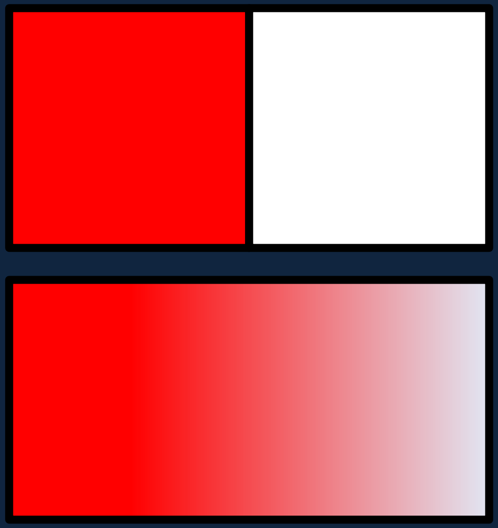
- The ideal gas law assumes molecules take up no room and don’t interact.
- Van der Waals equation replaces V by $V - b$, b representing room taken up by molecules (taking $n = 1$ mole).
- It replaces P with $P - a/V^2$, the molecules’ mutual attaction lessens P at the walls.
- Below the critical point, part of the curve is unstable, is replaced by a straight line separating gas and liquid.



These curves are the best fit Van der Waals for oxygen at its critical $T = 153$K and 143K, 163K.

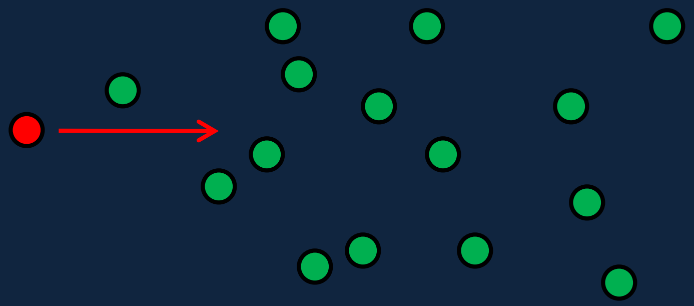
Diffusion

- Suppose we have two boxes, one containing red gas, one air, at room temperature, separated by a partition which we gently (but quickly!) remove.
- Some time later, the gases can be observed to have diffused into each other to some extent.
- But the molecules are moving at about 500 meters per second!
- What's taking so long? Watch it happen here!



Pinball Scenario

- Gases take a long time to mix because an O_2 molecule, say, moving into N_2 will bounce around like a ball in a pinball machine—a zigzaggy path.
- Just how much room is there between those molecules?



Clicker Question

- Guesstimate what fraction of the air space air molecules actually occupy in this room.

A. 1/100

B. 1/1,000

C. 1/10,000

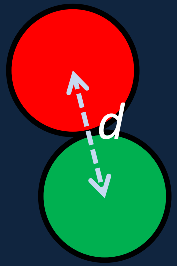
D. 1/100,000

Hint: think about relative densities!

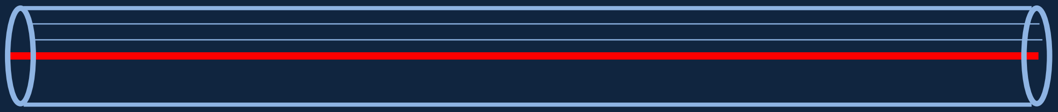
Clicker Answer

- The density of air is of order 1 kg/m^3, the density of water—and liquid air—is of order 10^3 kg/m^3.
- Since liquids are almost incompressible, it's reasonable to assume that *their* molecules are filling most of the space—pressing against each other.
- We conclude that the same molecules in gas have about 1,000 times more room each, so are separated on average by around 10 diameters.

Mean Free Path

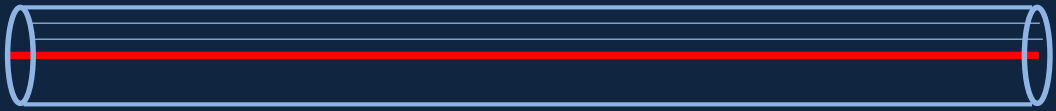


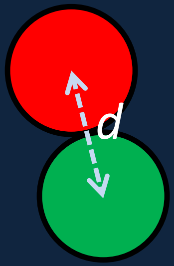
- The mean free path is defined as the average distance a molecule travels between collisions with other molecules.
- Imagine the molecule's straight line path—a collision occurs when another molecule's center is inside a cylinder of radius d centered on that path.
- In traveling a distance ℓ, the molecule "sweeps out" a volume $\pi d^2 \ell$.



Mean Free Path Continued…

- In traveling a distance ℓ, the molecule "sweeps out" a volume $\pi d^2 \ell$.





- Remember the average volume per molecule in air is around $1{,}000d^3$.
- Therefore, the molecule will hit another one on average after traveling ℓ where $\pi d^2 \ell = 1{,}000d^3$.
- Bottom line: the mean free path ℓ in air is around $300d$, where d is the molecular diameter.
- Important! We've found this without knowing what the molecular diameter is!

A Random Walk

- To get some idea how far a molecule can progress with a pinball type zigzag path, we begin with the simpest example; a one-dimensional random walk, defined as follows:
- I have a fair coin, on average it comes up heads exactly 50% of the time.
- I take a walk, tossing the coin to determine each step: one step forwards for heads, one backwards for tails.
- How far did I get, most likely, after 100 steps?

1-D Random Walk Distance

- How far did I get, most likely, after 100 steps?
- Equally likely forwards or backwards, of course, but if you did this many times, what would be your most likely ending distance from the starting point?
- Let's do the math: the first step is displacement x_1, = +1 for forwards, -1 for backwards. The other steps are similarly variables x_2, x_3, … x_{10} all +1 or -1 with equal probability.

1-D Random Walk Distance

- Let's do the math: the first step is displacement x_1, =+1 for forwards, -1 for backwards. The other steps are similarly variables x_2, x_3, … x_{10} all +1 or -1 with equal probability.
- We're trying to find how far away we get, we don't care which way, so let's find the average squared distance:
- $(x_1 + x_2 + \ldots + x_{10})^2 = x_1^2 + x_2^2 + \ldots + x_{10}^2 + 2x_1x_2$ + lots of such cross terms.
- On the right hand side, the square terms all equal one, and the cross terms are equally likely positive or negative, so average to zero.

1-D Random Walk Distance

- Average squared distance:
- $(x_1 + x_2 + \ldots + x_{10})^2 = x_1^2 + x_2^2 + \ldots + x_{10}^2 + 2x_1x_2 + \ldots.$
- On the right hand side, the square terms all equal one, and the cross terms are equally likely positive or negative, so average to zero.
- Bottom line: if this random walk is repeated many times over, the average squared distance from beginning to end

$$\overline{(x_1 + x_2 + \ldots + x_{10})^2} = 10$$

The root mean square distance is therefore √10.

Clicker Question

- After many ten-step random walks, confirming the argument given above, I decide to do a new set of random walks that will on average get me twice as far from the start.
- How many steps long are these new walks?

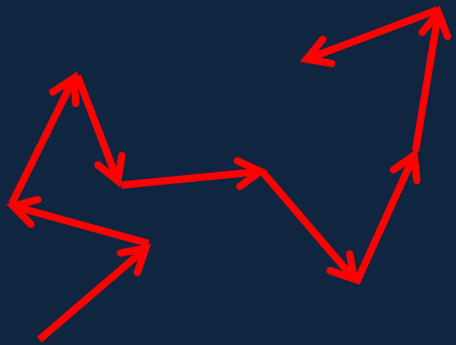
A. 20 steps

B. 40 steps

C. 80 steps

D. 100 steps

Real Diffusion



- Is more complicated than our 1-D random walk, but not that much!
- The path is made up of a sequence of randomly oriented vectors, let’s say all of length ℓ.
- The rms distance *r* from start to finish is given by

$$r=\sqrt{\overline{\left(\overrightarrow{\ell_1}+\overrightarrow{\ell_2}+\ldots\overrightarrow{\ell_N}\right)^2}}=\sqrt{N}\ell.$$

- Just as in 1 D, the cross terms $\overrightarrow{\ell_i}\cdot\overrightarrow{\ell_j}$ average to zero over many paths.

Finding the Size of Molecules

- When real gases diffuse into each other, the molecules follow many different paths, so our averaging over paths gives a good picture of how far they get: a distance $\sqrt{N}\ell$ in N steps of length ℓ.
- We know from the pressure discussion that O_2 molecules travel at about 500 m/sec in air in this room.
- This means that in time t, they will have moved vt in random steps of length ℓ, that's N steps, $N = vt/\ell$.
- So the actual distance diffused in time t is

$$r = \sqrt{N}\ell = \sqrt{\frac{vt}{\ell}}\ell = \sqrt{vt\ell}.$$

Finding the Size of Molecules

- So the actual distance diffused in time *t* is

$$r = \sqrt{N}\ell = \sqrt{\frac{vt}{\ell}}\ell = \sqrt{vt\ell}.$$

- This can be measured experimentally! It's found that O_2 gas under room conditions diffuses around 0.5cm in one second. This gives a mean free path ℓ about 50nm, and a molecular size 1/300 of that, from our earlier work. (Not very accurate, but pretty good.)
- This is the way the size of atoms, and Avogadro's number, were first found, by Loschmidt in the 1860's.
- (Avogadro had no idea what his number was!)

Clicker Question

- For still air at atmospheric pressure and 20°C, an O_2 molecule on average moves a net distance of 0.5 cm in one second. Assuming no air currents, how far does it get on average in one hour?

A. 18 m.

B. 2.2 m.

C. 1.8m.

D. 0.3m.

Clicker Answer

- 0.3 m: it goes as $\sqrt{t}$.
- Note on homework problem: the book gives an example of ammonia diffusing in air, finds for 10 cm time of 125 secs, makes clear this is order-of-magnitude only.
- BUT in the homework they want a "precise" answer! Just take 125 secs for 10 cm, and use that it goes as $\sqrt{t}$.