

# More Kinetic Theory of Gases

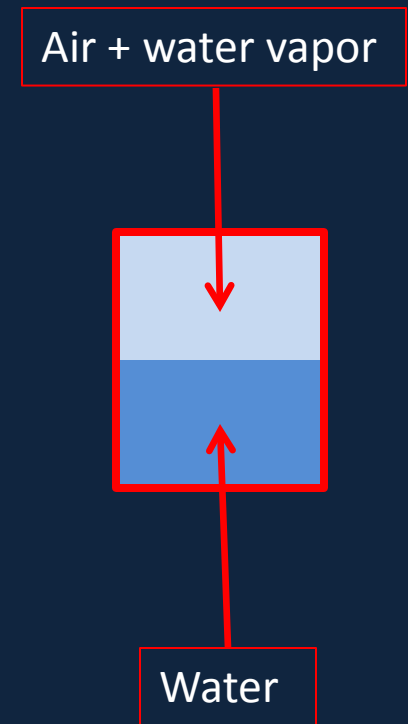
## Physics 1425 Lecture 32

# Vapor Pressure and Humidity

- The  $\text{H}_2\text{O}$  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  $2 \times 10^5$  Pascals.
- The vapor pressure of water rises from 1 atm to 2 atm on heating from  $100^\circ\text{C}$  to  $120^\circ\text{C}$ .
- This means that inside the cooker, the boiling water is at  $120^\circ\text{C}$ , cooking times are faster.

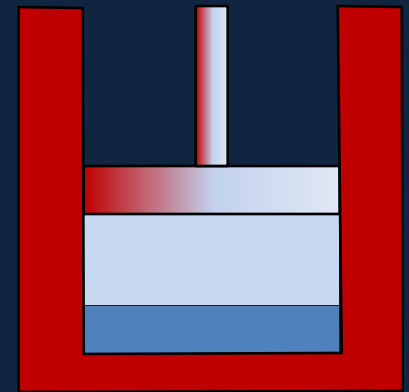


# Clicker Question

- It's freezing rain outside,  $0^{\circ}\text{C}$  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  $20^{\circ}\text{C}$  (svp about 2400 Pa).
- What is the relative humidity in the house?
  - A. 100%
  - B. 50%
  - C. 25%

# Clicker Question

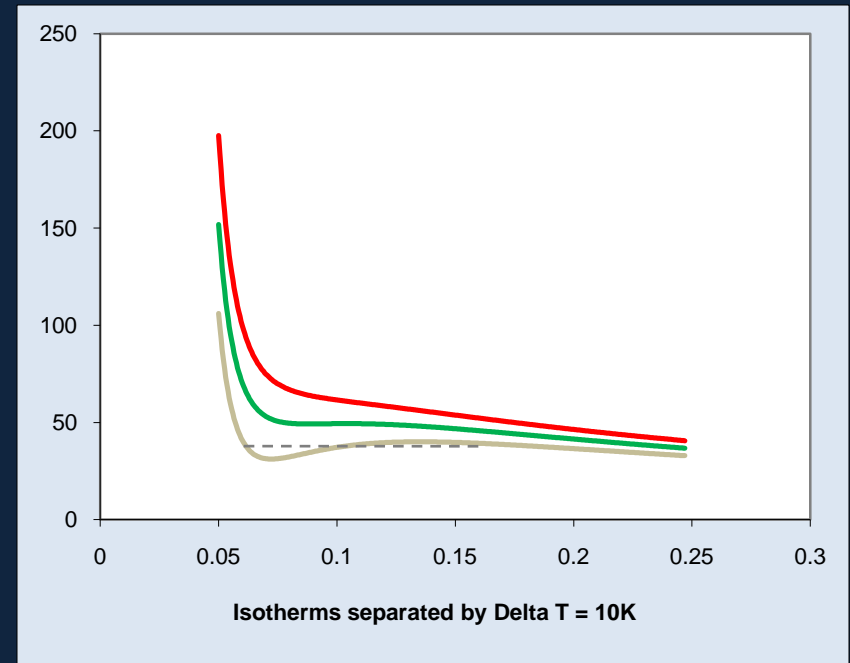
- A closed cylinder contains water and water vapor in equilibrium at  $20^{\circ}\text{C}$  and atmospheric pressure.
- The piston is **slowly** pushed down until the pressure inside is **doubled, all at  $20^{\circ}\text{C}$ .**
- **What happened to the water vapor pressure?**
  - A. It doubled
  - B. It increased, but less than doubling.
  - C. It stayed the same.
  - D. It went down.





# Van der Waals Equation

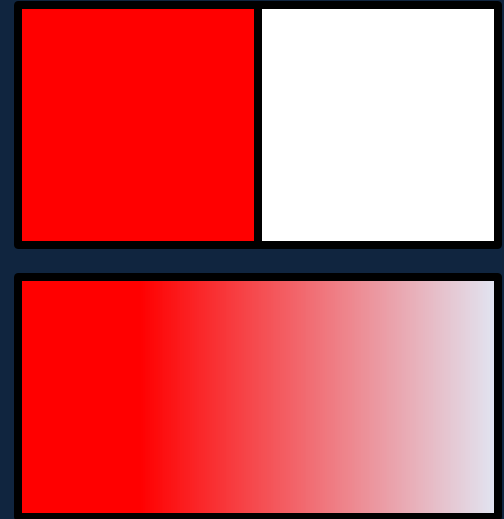
- The ideal gas law assumes molecules take up no room and don't interact.
- Van der Waals equation replaces  $V$  by  $V - b$ ,  $b$  representing room taken up by molecules (taking  $n = 1$  mole).
- It replaces  $P$  with  $P - a/V^2$ , the molecules' mutual attraction lessens  $P$  at the walls.
- 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  $T = 153\text{K}$  and  $143\text{K}, 163\text{K}$ .

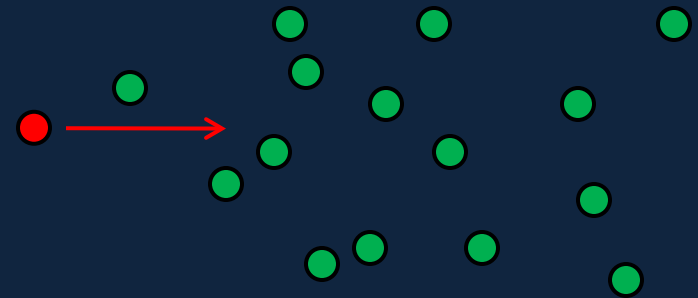
# Diffusion

- 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?**



# 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?



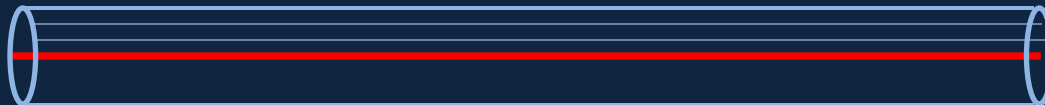
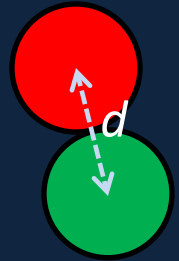
# Clicker Question

- 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!

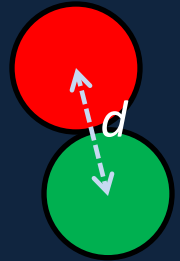
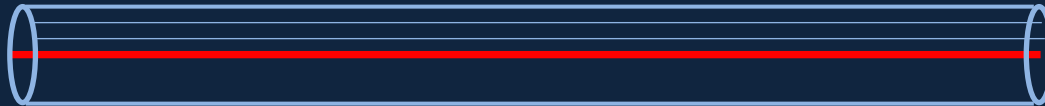
# Mean Free Path

- 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  $\ell$ , the molecule “sweeps out” a volume  $\pi d^2 \ell$ .



# Mean Free Path Continued...

- In traveling a distance  $\ell$ , 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  $\ell$  where  $\pi d^2 \ell = 1,000d^3$ .
- Bottom line: the mean free path  $\ell$  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 simplest 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  $x_2, x_3, \dots, x_{10}$  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  $x_2, x_3, \dots x_{10}$  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**:
- $(x_1 + x_2 + \dots + x_{10})^2 = x_1^2 + x_2^2 + \dots + x_{10}^2 + 2x_1x_2 + \text{lots of such cross terms.}$
- 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:
- $(x_1 + x_2 + \dots + x_{10})^2 = x_1^2 + x_2^2 + \dots + x_{10}^2 + 2x_1x_2 + \dots$
- 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

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

The root mean square distance is therefore  $\sqrt{10}$ .

# Clicker Question

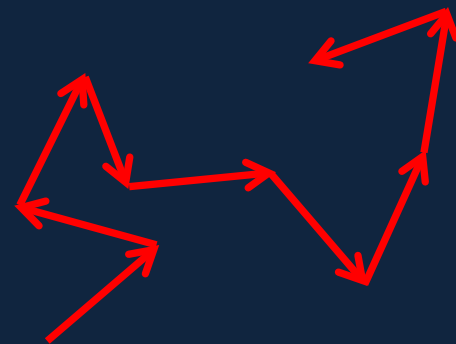
- After many ten-step random walks, confirming the argument given above, I decide to do a **new set** of random walks that will on average get me **twice as far from the start**.
- How many steps long are these new walks?
  - A. 20 steps
  - B. 40 steps
  - C. 80 steps
  - D. 100 steps

# 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  $\ell$ .
- The rms distance  $r$  from start to finish is given by

$$r = \sqrt{\left(\vec{\ell}_1 + \vec{\ell}_2 + \dots + \vec{\ell}_N\right)^2} = \sqrt{N} \ell.$$

- Just as in 1 D, the cross terms  $\vec{\ell}_i \cdot \vec{\ell}_j$  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  $\ell$ .
- We know from the pressure discussion that  $\text{O}_2$  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  $\ell$ , that's  $N$  steps,  $N = vt/\ell$ .
- So the actual distance diffused in time  $t$  is

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

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

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- **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  $\ell$  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<sub>2</sub> 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.