

# Giancoli Ch18: Kinetic Theory of Gases

**Kinetic theory:** the analysis of matter in terms of atoms in continuous random motion.  $\therefore$  computational limit  $\rightarrow$  can not apply Newton's law to each individual particle;  $\therefore$  statistical approach (average of quantities = macroscopic variables)

## 1 Molecular Interpretation of Temperature

Postulates of an ideal gas:

1. large N
  2. Separation between molecules  $\gg$  diameter of molecules
  3. Particle interact only classically (i.e. no EM repulsion attraction(?), also quantum mechanics is not considered)
  4. Perfectly elastic collision with walls (assume  $t \rightarrow 0$  for collision  $\therefore$  in collision  $E_p \xrightarrow{\text{completely}} E_k$  vice versa (?))
- Such assumption coincide with Boyle's law; relation between collision probability (surface area), pressure, and volume (think of a mathematical geometrical proof for this)

### 1.1 Mechanics applied to gas molecules

We are trying to find the pressure of gas exert on container:

$$\text{Newton's 3rd law : } F_{\text{mcl on wall}} = -F_{\text{wall on mcl}} = \frac{dp}{dt} \quad \text{pressure due to collision; assume elastic}$$
$$\Delta p = 2mV_x \text{ for each collision each collision separated by time } \Delta t$$

this is also the time required for one molecules to travel across the container and back again

$$\therefore x = 2l \rightarrow \Delta t = \frac{2l}{V_x}$$

$$F = \frac{\Delta p}{\Delta t} = \frac{2mV_x}{\frac{2l}{V_x}} = \frac{m(V_x)^2}{l}$$

We do not take into account:

1. V lost by collision with other mcl  $\therefore$  statistically if we  $\Sigma$  up,  $V \approx$  same
2. Collision with top and bottom  $\therefore$  will not alter  $V_x$  component
3. force from collision at intervals  $\therefore$  large N undergo collision  $\rightarrow F_{\text{avg}} \approx$  constant

$$\begin{aligned}
F_{\text{due to all molecules}} &= \Sigma F_{\text{one molecule}} = \frac{m}{l}(V_{x1}^2 + V_{x2}^2 + \dots + V_{xN}^2) \\
\overline{V_x^2} &= \frac{(V_{x1}^2 + V_{x2}^2 + \dots + V_{xN}^2)}{N} \\
N\overline{V_x^2} &= (V_{x1}^2 + V_{x2}^2 + \dots + V_{xN}^2) \\
F &= \frac{m}{l}N\overline{V_x^2} \because \text{velocity random, we assume } \overline{V_x} = \overline{V_y} = \overline{V_z} \\
\therefore \overline{V} &= \overline{V_x^2} + \overline{V_y^2} + \overline{V_z^2} = 3\overline{V_x} \\
F &= \frac{m}{l}N\frac{\overline{V_x}}{3} \\
P &= \frac{F}{A} = \frac{\frac{m}{l}N\frac{\overline{V}}{3}}{A} \\
\therefore V &= \text{volume} = Al \qquad PV = \frac{2}{3}N(\frac{1}{2}m\overline{V^2}) \quad \text{and} \quad PV = NkT \\
kT &= \frac{2}{3}(\frac{1}{2}m\overline{V^2}) = \frac{2}{3}\tau \quad \text{where } \tau \text{ is kinetic energy} \\
\therefore \tau &= \frac{3}{2}kT \tag{1}
\end{aligned}$$

This is also a reasonably accurate prediction for how fast molecules move on average in liquids and solids.

$$\tau = \frac{1}{2}m\overline{V^2} = \frac{3}{2}kT$$

$$\therefore \text{Root mean square velocity} = V_{rms} = \sqrt{\overline{V^2}} = \sqrt{\frac{3kT}{m}} \tag{2}$$

Kinetic Energy near absolute zero: The  $V_{rms}$  formula implies that as  $T \rightarrow 0$  then  $V_{rms} \rightarrow 0$

Quantum Mech: as  $T \rightarrow 0$  then  $V_{rms} \rightarrow$  small nonzero minimum value. Even at abs zero, molecular motion doesn't cease (even though macroscopically the substance has probably transformed into a solid or liquid)

## 2 Distribution of Molecular Speeds

### 2.1 Maxwell Distribution

Probable distribution of speeds in a gas containing N molecules

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} \tag{3}$$

- v: Relative number of molecules
- m: mass of a single molecule

### 2.2 Temperature dependent

- not symmetrical distribution skewed to the right
- Temperature  $\uparrow$  then distribution shift to the right
- $\therefore$  this way larger portion exceeds  $E_a$  threshold

## 2.3 Calculations

- Finding  $\bar{v}$  :

$f(v)dv \rightarrow$  number of mol that have speed between  $v$  and  $v+dv$

Taking  $\lim dv \rightarrow 0$ , we see that  $f(v)dv =$  number of molecules that has a specific speed<sup>1</sup>

$$\bar{v} = \frac{\sum \text{probability of speed}_i \times \text{number of molecules that has speed}_i}{N}$$

Again taking the limit for integration, we get a formula for average speed

$$\bar{v} = \frac{\int_0^\infty v f(v) dv}{N}$$

Through tedious integration (which I haven't attempted),

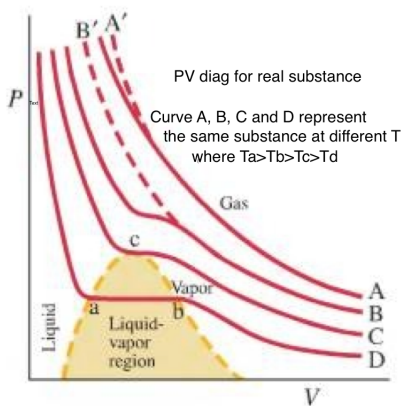
$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \approx 1.60 \sqrt{\frac{kT}{m}}$$

- Finding most probable speed ( $V_p$ ):

By observing the Maxwell distribution (which resembles a Gaussian curve), intuitively the most probable speed is at the maximum. Simple optimization  $\frac{df(v)}{dt} = 0$  yields our value for  $V_p$ <sup>2</sup>

$$V_p = \sqrt{\frac{2kT}{m}} \approx 1.41 \sqrt{\frac{kT}{m}} \quad 3$$

## 3 Real Gases and Change of Phase



- The dotted line is the ideal gas prediction. At lower temperature (A) real gas  $\rightarrow$  ideal
- Our ideal gas postulate 4 breaks down,  $\therefore E_p$ <sup>4</sup> no longer negligible
- Critical temperature( $T_c$ ) occur @ critical point
- Critical point is where curve on graph is horizontal
- If  $T < T_c$ , (g) $\rightarrow$  (l) if you apply sufficient pressure
- But if  $T > T_c$ , even  $\infty$  pressure can not cause (g) $\rightarrow$  (l)
- Vapor**: substance in a gaseous state when  $T < T_c$  (artificially made so it's like that)
- Gas**: substance in a gaseous state when  $T > T_c$  (naturally like that)

<sup>1</sup>  $\therefore$  total number of molecules in gas( $N$ )= $\int_0^\infty f(v)$

<sup>2</sup> There are two solutions, find the one that yields the maximum

<sup>3</sup> Recall  $V_{rms} = \sqrt{\frac{3kT}{m}} \approx 1.73 \sqrt{\frac{kT}{m}}$ , we again confirm that all speeds are smaller than  $V_{rms}$

<sup>4</sup> 1) lower temperature ( $\approx$  liquefaction) higher pressure, molecules closer,  $\therefore E_p$  of attractive force  $\uparrow$

2) as temperature lowers (s.t.  $T \rightarrow$  b.p.),  $E_k \downarrow$ , so  $E_k$  no longer  $\gg E_p$   $\therefore$  must take  $E_p$  into consideration

3) V-nb volume consideration (gas compressible  $\rightarrow$  liquid  $\approx$  incompressible)

### 3.1 PT diagram (a.k.a Phase diagram)

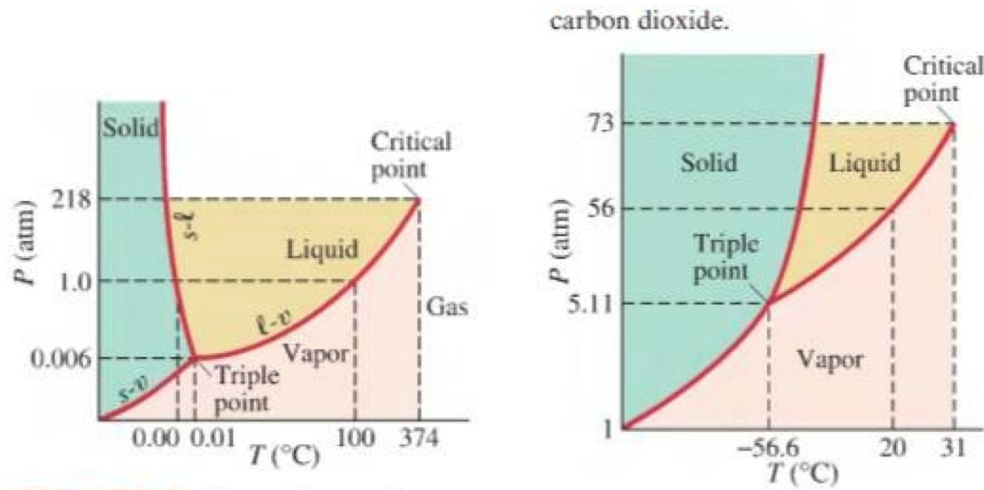


Figure 1: Right: Water; Left: CO2

- Curve: values of  $P$  and  $T$  for which the two indicated phases coexist in equilibrium
- Triple Point: three phases coexist in equilibrium<sup>5</sup>
- s-l curve: slope up-leftward if substance expands while freezing  $\therefore$  given a higher pressure, it will require lower pressure to freeze<sup>6</sup>
- Most substance contract while freezing  $\therefore$  slope right-leftward<sup>7</sup>
- Phase transition can also occur in the same phase. (e.g. Helium has two forms in liquid phase, Helium II :superfluid ( 0 viscosity, wall climbing)
- LCD (liquid crystal) are in a phase between solid and liquid (Is this talking about plasma??)

## 4 Vapor Pressure and Humidity

### 4.1 $P_{vap}$ and Evaporation

- Evaporation occurs when high-speed surface atoms<sup>8</sup> in a liquid escape into air
- Evaporation is a cooling process  $\therefore$  high  $T \rightarrow$  high  $V$ , all high  $V$  escape,  $\therefore$  average  $V$  is lower  $\rightarrow$  average temperature lower
- Equal rates of condensation and evaporation  $\rightarrow$  equilibrium
- If  $\leftrightarrow$  then space above liquid surface: **saturated**
- **(Saturated) vapor pressure**: pressure of vapor when it is saturated
- Vapor pressure independent of volume  $\therefore$  if  $V \downarrow$  then  $\rho_{molecule} \uparrow$ .  $\frac{d}{dt}(Condensation) \gg \frac{d}{dt}(Evaporation)$  so that vapor pressure is maintained
- Vapor pressure depend on Temp  $\therefore$  high  $T \rightarrow$  large  $E_k \rightarrow$  surface mcl escape  $\rightarrow P_{vap} \uparrow$  then reach equilibrium (@ the new higher  $P_{vap}$ )

<sup>5</sup>Sublimation : @ low pressure, (s)  $\rightarrow$  (g)

<sup>6</sup>Think of this as stuff being further apart so they are harder to freeze

<sup>7</sup>The same reasoning applies, given a higher pressure, it will require less lower pressure to freeze since it contracted relative to the initial point where it began freezing (at that initial point: normal-sized)

<sup>8</sup>Speed of particles  $\approx$  follow Maxwell distribution

## 4.2 Boiling

- $P_{vap} \uparrow$  as  $T \uparrow$  until  $P_{vap} = P_{external} \rightarrow$  boiling
- Bubble at surface: Initially collapse  $\because P_{inside} < P_{external}$
- Once  $P_{inside} \geq P_{external}$ , bubble rise up : (l)  $\rightarrow$  (g)  $\therefore$  boiling occurs <sup>9</sup>
- Ex) Pressure cooking v.s. high-altitude cooking

## 4.3 Partial Pressure and Humidity

<sup>10</sup> <sup>11</sup> Partial pressure: the pressure each gas would exert if it alone were present ( $0 \leq P_{partial} \leq P_{vap}$ )  
Total pressure of gas mixture =  $\Sigma$  partial pressure of each gas

$$\text{Relative humidity at a given temperature} = \frac{\text{partial pressure of } H_2O}{\text{saturated vapor pressure of } H_2O} \times 100\%$$

# 5 Van der Waals Equation of State

## 5.1 Van der Waals gas

Ideal gas but take into account:

1. molecule has finite non-zero size compared to  $V_{container}$  unavailable volume is what the molecule takes up, it is dependent of the size and number of the molecules.(nb)

$$\therefore V_{actual} = V - nb \quad (4)$$

Using this in ideal gas law and dividing by n, we get **Clausius equation of state**:

$$P\left(\frac{V}{n} - b\right) = RT \quad (5)$$

This tells us that  $P_{real} > P_{ideal}$ , which makes intuitive sense because as  $V \downarrow \rightarrow$  more collision  $\rightarrow P \uparrow$

2. the intermolecular force may be greater than size if molecule assume to be hard spheres colliding

- Intermolecular force is:
  - small range
  - hold molecules in (l) and (s) @ low T
  - Electrical in nature
- Inward attractive force oppose the pressure on walls
- the magnitude of this force decrease with each shell (?)
- proportional to shell density in each shell layer  $\propto \left(\frac{n}{V}\right)^2$
- 

$$P_{actual} = P + \frac{a}{\left(\frac{V}{n}\right)^2}$$

- Fig 18-11 (?)

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<sup>9</sup> 1atm = 760 torr

<sup>10</sup> Supersaturate:  $P_{H_2O \text{ partial}} > P_{vap}$

<sup>11</sup> **Dew point**: temperature at which  $P_{H_2O \text{ partial}} = P_{vap}$

## 5.2 Equation of state

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$$\therefore (P + \frac{a}{(\frac{V}{n})^2})(\frac{V}{n} - b) = RT$$

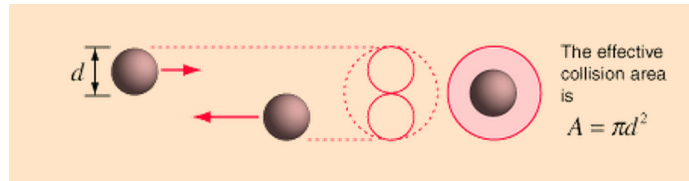
$$\text{Van der Waals equation of state} \quad P = \frac{RT}{(\frac{V}{n} - b)} - \frac{a}{(\frac{V}{n})^2} \quad (6)$$

- This is a closer approximation of real gas but only with the improvement of removal of 2 assumption. No proposed equation of state is accurate for all gas under all condition.
- Van der Waal happens to be useful under many conditions.
- @ low  $\rho$  :  $\frac{a}{(\frac{V}{n})^2} \ll P$  and  $\frac{V}{n} \gg b$  so the equation reduces back to ideal gas law  $PV=nRT$

## 6 Mean Free Path

- particular molecule follow zigzag path  $\therefore$  multiple collision with other molecules
- **Mean-free path**: average distance travelled between each collision.
- Assumptions:
  1. ignore intermolecular force
  2. ideal gas
  3. assume other particles are stationary<sup>12</sup>

Figure 2: height of cylinder= $v\Delta t$   
 volume of cylinder= $\pi(2r)^2(v\Delta t)$   
 $\#$  of collision per sec =  $\frac{N}{V_{molecule}} V_{cylinder} = \frac{N}{V_{molecule}} \pi(2r)^2(v\Delta t)$



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$$l_m = \frac{\text{distance travelled in time } \Delta t}{\text{number of collision in time } \Delta t} = \frac{\bar{v}\Delta t}{\frac{N}{V}\pi(2r)^2(v_{relative}\Delta t)}$$

From Maxwell's distribution, we find that:

$$v_{relative} = \sqrt{2}\bar{v}$$

$$\therefore l_m = \frac{1}{4r^2\sqrt{2}\pi\frac{N}{V}} \quad (7)$$

- $l_m$  loses meaning at low  $\rho$   $\therefore$  collision frequency with wall > collision frequency with other molecules (ex. when  $l_m$  > length of box)

## 7 Diffusion

- $C$  : concentration
- $J$  : rate of diffusion =  $\frac{\# \text{ of molecules diffusing across the area}}{\Delta t} = \frac{N}{\Delta t}$
- $J \propto$  concentration gradient =  $\frac{\Delta C}{\Delta x}$

<sup>12</sup>Our use of  $V_{relative}$  later in the derivation accounts for this

- Fick's Law(Diffusion equation)<sup>13</sup> :

$$J = DA \frac{\Delta C}{\Delta x} = DA \frac{dC}{dx} \quad (8)$$

- can use definitions, and various trivial things to solve for t:  $t \approx \frac{\Delta x^2}{D}$

## 8 Question

- pg 477 “molecules exert weak attractive force on each other between collisions”, if molecules are of the same charge ,which they should be? Shouldn't the force be repulsive?
- How does this work?  $t \rightarrow 0$  for collision  $\therefore$  in collision  $E_p \xrightarrow{\text{completely}} E_k$
- LCD (liquid crystal) are in a phase between solid and liquid (Is this talking about plasma??)
- During pg 477 derivation, why do we need to consider back and forth across container (2l) instead of simply using l?
- pg486 Exercise E : Why is answer b)decrease?
- for Van der Waals equation why is proportional to shell density in each shell layer  $\propto (\frac{n}{V})^2$ ? (surface area of shell?volume of shell?)

**Last Update:January 11, 2014**

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<sup>13</sup>make sure the units for J, C correspond to each other