Kinetic Theory

Maxwell Velocity Distribution

For one molecule $\qquad P(q,p)\, d^3q\, d^3p \propto e^{-\beta p^2/2m}\, d^3q\, d^3p$

let $f(q,v)$ denote the probability of a particle to have position between q & $q+dq$ & velocity between v & $v+dv$

$$f(q,v)\, d^3q\, d^3v \propto e^{-\beta \frac{v^2 m}{2m}}\, d^3q\, d^3v$$

How do we calculate the constants of proportionality?

$$\int_{all\ q\ \&\ v} f(q,v)\, d^3q\, d^3v = 1 \qquad normalization$$

for N particles

$$f(q,v)\, d^3q\, d^3v = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta m \frac{v^2}{2}}\, d^3q\, d^3v$$

$\Big|$ $f(q,v)\, d^3q\, d^3v$ is the mean # of particle w/ position between q & $q+dq$ velocity between v & $v+dv$
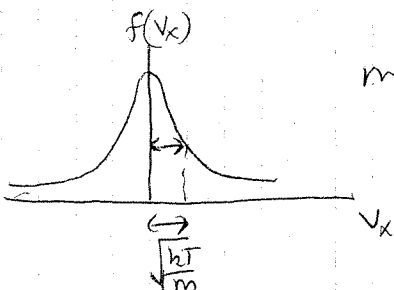
Speed distribution

$f(\vec{v}) = ?$
$F(|v|) = ?$ $\Big\}$ how are these related to $f(q,v)$?

$$f(\vec{v})\, d^3v = \int_q f(q,v)\, d^3v\, d^3q = N\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta \frac{m}{2} v^2}\, d^3v$$

mean # of molecules with velocity between v & $v+dv$

$$f(v_x)\, dv_x = \int_q \int_{v_y} \int_{v_z} f(q,v)\, d^3q\, d^3v = N\left(\frac{m\beta}{2\pi}\right)^{1/2} e^{-\beta \frac{m}{2} v_x^2}\, dv_x$$
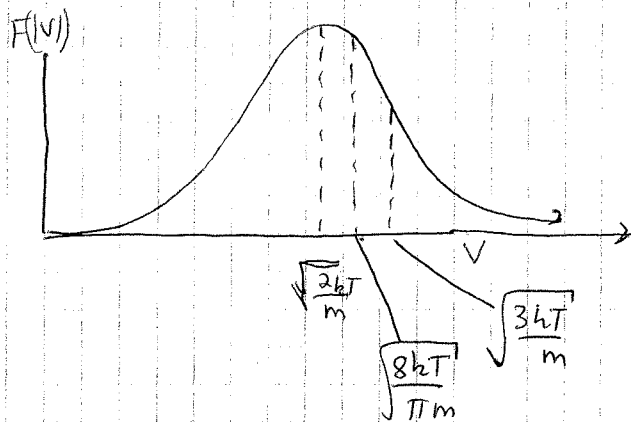
mean # of molecules w/ v_x between v_x & v_x+dx

$F(|v|)\, dv = $ the mean # of molecules with a speed $v = |\vec{v}|$ in the range between v & $v+dv$

$$F(|v|)\, dv = \int f(q,v)\, d^3v = f(\vec{v})\, 4\pi v^2\, dv$$

spherical shell of radius v & thickness dv

$$F(|v|)\,dv = 4\pi N \left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-\beta m v^2/2}\,dv$$

$$\overline{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$$

$$\overline{v}^2 = \frac{3kT}{m} \quad \left(\begin{array}{l}\text{can get this from}\\ \text{equipartition Thm as well}\end{array}\right)$$
$$\tfrac{1}{2}mv^2 = \tfrac{3}{2}kT$$
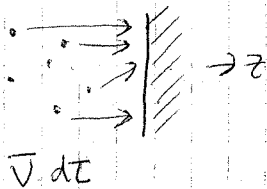
most probable speed at $F(|v|)$ max

$$V_{prob} = \sqrt{\frac{2kT}{m}}$$

V_{rms} of N_2 gas is $\sim 500\,m/sec \sim$ speed of sound

Flux of Particles at a wall

Estimate

$\overline{v}\,dt$

$\tfrac{1}{3}$ of molecules have velocity in z direction

$\tfrac{1}{2}$ of these are in the $+z$ direction

if mean speed of molecules is $\overline{v}$

$n =$ molecules/unit volume

$$\frac{\text{\# of particles}}{\text{hitting the wall}} = \frac{n}{6} A \overline{v}\, dt$$

$\Phi_o =$ \# of molecules that strike a unit area/unit time
$$\simeq \tfrac{1}{6} n \overline{v}$$

Pressure of a gas estimate

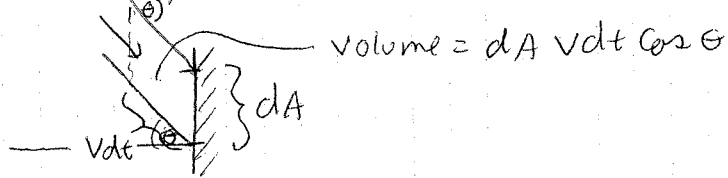$$F = \frac{dp}{dt} \qquad dP = 2mv \text{ for elastic collisions}$$

$$P = \Phi_o \cdot 2m\overline{v} = \tfrac{1}{3} n m \overline{v}^2 \qquad \tfrac{1}{2}m\overline{v}^2 = \tfrac{3}{2}kT \text{ by equipartition}$$

$$\boxed{P = nkT}$$

Exact Calculation:

Need to worry about accounting for directions in collisions. For pressure both estimates for Φ & $\frac{df}{dt}$ have errors that cancel out.

volume $= dA \, V \, dt \cos\theta$

dA

$V \, dt$

$\Phi(\vec{v}) d^3v \equiv$ the # of particles w/ velocity between V & $V+dV$ which strike a unit area of the wall per unit time

$\Phi(\vec{v}) d^3v = d^3v \, f(\vec{q}, \vec{v}) \, V \cos\theta$

$\Phi_0 \equiv$ total # of particles that strike a unit area of the wall per unit time

$$\Phi_0 = \int_{V_z>0} d^3v \, f(q,v) \, V \cos\theta \qquad \begin{matrix} 0 < \phi < 2\pi \\ \frac{\pi}{2} < \theta < \pi \end{matrix} \Big\} \frac{1}{4}\Omega = \pi \quad 0 < V < \infty \Big\} V_z > 0$$

$$d^3v = V^2 \, dV \, \underbrace{\sin\theta \, d\theta \, d\phi}_{\pi \text{ for integral}}$$

$$\Phi_0 = \frac{N}{V} \left(\frac{m\beta}{2\pi}\right)^{3/2} \int dV \, V^2 \, V \underbrace{\cos\theta \sin\theta \, d\theta \, d\phi}_{\pi} \, e^{-\beta \frac{mv^2}{2}}$$

One of the techniques proposed for seperation of isotopes for making A-Bom

$$= \frac{N}{V} \sqrt{\frac{kT}{2\pi m}} \qquad \text{for ideal gas} \quad \Phi_0 = \frac{P}{\sqrt{2\pi mkT}}$$

Effusion — seperation of isotope of different mass   hole $<< \ell$ (mean free path)

So if we have two containers connected by a tiny hole

$$\frac{P_1}{\sqrt{T_1}} = \frac{P_2}{\sqrt{T_2}} \quad \text{in steady state}$$

if diameter $>> \ell$ pressure equilibrates

Polyatomic Molecules

Ideal gas in the classical limit

$$Z = \frac{\xi^N}{N!} \qquad \xi = \sum_s e^{-\beta \epsilon_s}$$

For a polyatomic molecule we need to figure out what goes into ϵ_s

$$\mathcal{H} = \mathcal{H}_t + \mathcal{H}_e + \mathcal{H}_r + \mathcal{H}_v$$

$$\epsilon_s = \epsilon_t + \epsilon_e + \epsilon_r + \epsilon_v$$

$\mathcal{H}_t$ — translational motion of cm

$\mathcal{H}_e$ — electronic state

$\mathcal{H}_r$ — rotational motion

$\mathcal{H}_v$ — vibrational motion

Since these are additive $\qquad \xi = \xi_t \xi_e \xi_v \xi_v$

Ex: diatomic
$$\mathcal{H}_t = \frac{p^2}{2(m_1 + m_2)} \qquad \xi_t = \frac{V}{h^3}\left[2\pi(m_1 + m_2) kT \right]^{3/2} \text{ just like before}$$

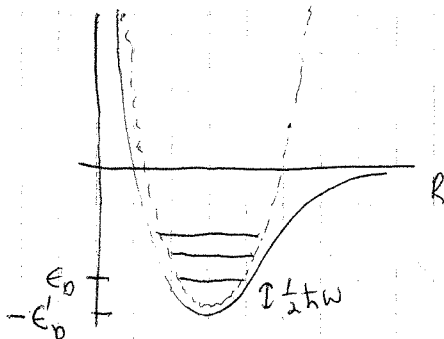$\mathcal{H}_e$ typically only lowest energy state matters & molecules are in ground state
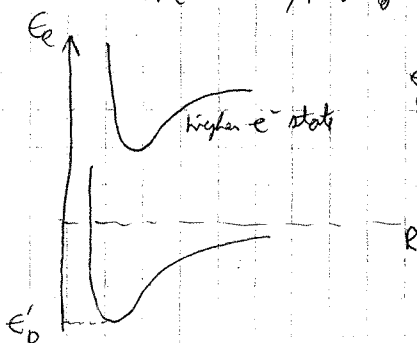
$$\xi_e = \underbrace{\Omega_0}_{\substack{\text{degree of} \\ \text{degeneracy}}} e^{\beta \epsilon_0'}$$

$\Omega_0 = 1$ for no degenerate state

$\mathcal{H}_v$ bottom of well looks like a harmonic oscillator

near minimum
$$\epsilon_e(R) = -\epsilon_0' + \frac{1}{2} b \xi^2$$

where $\xi \equiv R - R_0$

$$b = \frac{\partial^2 \epsilon_e(R_0)}{\partial R^2}$$

$$K = \frac{1}{2}\mu \dot{R}^2 = \frac{1}{2}\mu \dot{\xi}^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$
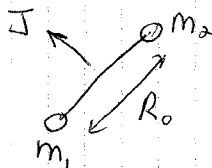
$$\omega = \sqrt{\frac{b}{\mu}}$$

From QM $\quad \varepsilon_V = \hbar\omega(n + \frac{1}{2}) \quad$ where $n = 0, 1, 2, 3$

$$\zeta_V = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

typically $\beta\hbar\omega \gg 1$ so this reduces to

$$\zeta_V = e^{-\frac{1}{2}\beta\hbar\omega} \qquad \text{Cannot use equipartition}$$

For Rotation

moment of Inertia

$$A = \frac{1}{2}\mu R^2$$

So if $m_1 = m_2 \quad A = \frac{1}{4}R^2 m \quad$ or $\quad m\left(\frac{R}{2}\right)^2 \checkmark$

If $\hbar J$ is the ₰ momentum its classical energy is given by

$$\frac{(\hbar J)^2}{2A} \qquad \text{for QM } J^2 \text{ can assume the values } J(J+1)$$
$$\text{w/ } J = 0, 1, 2 \dots$$

$$\varepsilon_r = \frac{\hbar^2}{2A} J(J+1) \qquad \text{for each value of } J \text{ there are } 2J+1 \text{ possible}$$
$$\text{quantum states of the same energy}$$

$$\zeta_r = \sum_{J=0}^{\infty}(2J+1) e^{-\beta\frac{\hbar^2}{2A} J(J+1)} \qquad m_j = -J, -J+1, \dots J-1, J$$

if $\frac{\hbar^2}{2AkT} \gg 1$ almost all molecules in lowest rotational state

if $\frac{\hbar^2 J(J+1)}{2AkT} \ll 1$ then spacing of rotational levels is small
& we can use a classical or Continuum calc.

$$U = J(J+1)$$
$$\zeta_r \cong \int_0^{\infty} du\, e^{-\beta\frac{\hbar^2}{2A} U} = \frac{2A}{\beta\hbar^2}$$

If two nuclei are identical then $180°$ rotation is the same as a $0°$
rotation $\zeta_r = \frac{AkT}{\hbar^2}$ if two nuclei are different $\zeta_r = \frac{2AkT}{\hbar^2}$

From Equipartition each rotational axis is quadratic in J so we get $\frac{1}{2}kT$ for each direction

excitation along axis is harder since next energy level $\epsilon \propto \frac{1}{A}$ if A is small next level is very high

$$\xi = \xi_t \, \xi_e \, \xi_r \, \xi_v = \frac{V}{h^3}\left[2\pi(m_1+m_2)kT\right]^{3/2} \Omega_0 \, e^{\beta\epsilon_0'} \, e^{-\frac{1}{2}\beta\hbar\omega} \frac{2A}{\beta\hbar^2}$$

$$Z = \frac{\xi^N}{N!} \qquad \text{etc.}$$

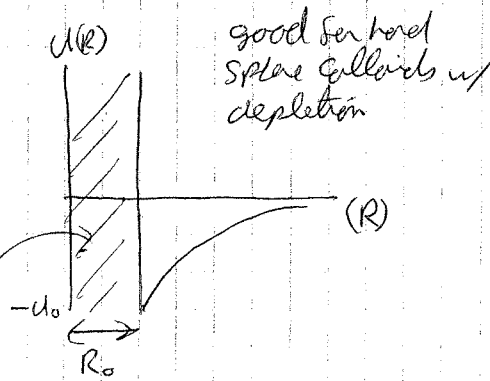
Deriving the Van der Waals Eq of state

$$Z = \frac{1}{N!}\left[\iint e^{-\beta\left(\frac{P^2}{2m} + U_e\right)} \frac{d^3r \, d^3p}{h^3}\right]^N$$

(we've already done before)

(effective potential due to all other particles)

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}N}\left[\int e^{-\beta U_e(v)} d^3r\right]^N$$

integrate over volume

good for hard sphere colloids w/ depletion

excluded volume

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}N}\left[(V-V_x)\, e^{-\beta\overline{U}_e}\right]^N$$

excluded volume per particle

total mean potential energy is $N\overline{U}_e$

there are $\frac{1}{2}\left(N(N-1)\right)$ pairs of molecules

$\sim N^2$

$$N\overline{U}_e = \frac{1}{2}N^2\overline{U}$$

$$\overline{U}_e = \frac{1}{2}N\overline{U}$$

to get $\overline{U}$ integrate over all possible distances

$$\overline{U} = \frac{1}{V}\int_{R_0}^{R} U(R)\,4\pi R^2 \, dR = -\frac{4\pi U_0}{V}\int_{R_0}^{R}\left(\frac{R_0}{R}\right)^{S} R^2 \, dR \qquad \text{you need } S>3 \text{ for integral to converge}$$

$$\overline{U}_e = \frac{1}{2}N\overline{U} = -a'\frac{N}{V} \qquad a' \equiv \frac{2\pi}{3}R_0^3\left(\frac{3}{S-3}\right)U_0$$

excluded volume is $\quad \frac{1}{2} N^2 \left(\frac{4}{3} \pi R_0^3 \right)$

$\underbrace{}_{\substack{\# \text{ of} \\ \text{pairs}}} \quad \underbrace{}_{\text{excluded volume/pair}}$

$$V_x = b'N \qquad b' = \frac{2\pi}{3} R_0^3 = 4\left[\frac{4\pi}{3} \left(\frac{R_0}{2} \right)^3 \right]$$

Now we're done

$$Z = \frac{1}{N!} \left[\left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}N} \right] \left[(V - b'N) \, e^{-\beta a' \frac{N}{V}} \right]^N$$

$$\bar{P} = \frac{1}{\beta} \frac{d \ln Z}{dV} = \frac{1}{\beta} \frac{d}{dV} \left[N \ln (V - b'N) - N\beta \, U_e \right]$$

$$\bar{P} = \frac{NkT}{V - b'N} - a' \frac{N^2}{V^2}$$

$$\boxed{ \left(\bar{P} + a' \frac{N^2}{V^2} \right) \left(\frac{V}{N} - b' \right) = kT }$$

Chemical Equilibrium

Single phase $\quad$ m different molecules $B_1, \dots B_m$

need Conservation of atoms of each kind

ex: $2H_2 + O_2 = 2H_2O \qquad$ 4 H's & 2 O's on each side

or $2H_2 + O_2 - 2H_2O = 0$

Constraint $\quad \sum\limits_{i=1}^{m} b_i B_i = 0$

Change in Number of B_i molecules N_i is always proportional to the # of molecules appears in the balanced chemical Eq.
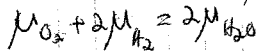
$$dN_i = \lambda b_i$$

Consider an isolated (fixed E) system in chemical Equilibrium enclosed in a fixed volume V

$$S = S(E, V, N_1 \dots N_m) = max$$

$$dS = 0 \qquad \text{Since E \& V are fixed}$$

$$\sum \mu_i \, dN_i = 0 \qquad \text{or} \qquad \sum \mu_i b_i = 0$$

$$\mu_{O_2} + 2\mu_{H_2} = 2\mu_{H_2O}$$

what about rxn rates?

Where does K come from?

$$\frac{N_{H_2O}^2}{N_{H_2}^2 N_{O_2}} = K_N \quad \text{or}$$

$$\frac{[H_2O]^2}{[H_2]^2 [O_2]} = K$$

save info about N_a

Chemical equilibrium between ideal gases:

Suppose we knew the free energy of a mixture of gases

$$F = F(T, V, N_1, \dots N_m)$$

for a specified $T \& V$

$$\Delta F = \sum_i \frac{\partial F}{\partial N_i}\Big)_{T,V,N} b_i = \sum_i \mu_i b_i$$

in equil $\Delta F = 0$ so $\sum b_i \mu_i = 0$

So if we knew F we can calculate μ_i & we would be done!

For each molecule

$$\varsigma \equiv \sum_r e^{-\beta E_r} \qquad \text{for } N \text{ molecules } \quad Z = \frac{\varsigma^N}{N!}$$

For mixtures of gasses that don't interact

$$Z = \frac{\varsigma^{N_1} \varsigma^{N_2} \dots \varsigma^{N_m}}{N_1! \, N_2! \dots N_m!} = Z_1 Z_2 \dots Z_m$$

$$\ln Z = \sum_i \ln Z_i$$

$$\bar{E} = \sum_i \bar{E}_i \qquad \text{since } \bar{E} = \frac{-\partial \ln Z}{\partial \beta}$$

$$\bar{P} = \sum_i \bar{P}_i \qquad \text{since } \bar{P} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

$$F(T,V) = \sum_i F_i(T,V) \qquad \text{since } F = -kT \ln Z$$

$$\text{etc.}$$

$$F = -kT \sum_i N_i \left(\ln \varsigma_i - \ln N_i + 1 \right) \qquad \begin{array}{l} \text{used sterlings formula} \\ N! = N \ln N - N \end{array}$$

$$\mu_i = \frac{\partial F}{\partial N_i}\Big)_{T,V,N_{j \neq i}} = -kT \left(\ln \varsigma_i - \frac{N \frac{1}{N}}{N} - \ln N + 1 \right) = -kT \ln \frac{\varsigma_i}{N_i}$$

Law of Mass action

In a reaction, The free energy change is:

$$\Delta F = -kT \sum b_i \left(\ln q_i - \ln N_i \right) = \Delta F_0 + kT \sum_i b_i \ln N_i$$

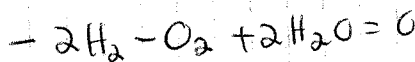where $\Delta F_0 \equiv -kT \sum_i b_i \ln q_i$

Standard free energy change of the reaction depends only on T & V not on N_i

$$\Delta F = \Delta F_0 + kT \sum_i b_i \ln N_i = 0 \text{ in chemical equil.}$$

$$\sum_i \ln N_i^{b_i} = \ln \left(N_1^{b_1} N_2^{b_2} N_3^{b_3} \cdots N_m^{b_m} \right) = -\frac{\Delta F_0}{kT}$$

$$N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m} = \underbrace{K_N(T,V)}_{\substack{\text{equilibrium} \\ \text{constant}}} \equiv e^{-\Delta F_0/kT} = q_1^{b_1} q_2^{b_2} \cdots q_m^{b_m}$$

· back to our example:

$$-2H_2 - O_2 + 2H_2O = 0$$

$$N_{H_2}^{-2} N_{O_2}^{-1} N_{H_2O}^{2} = K_N$$

$$\frac{N_{H_2O}^2}{N_{H_2}^2 N_{O_2}^2} = K_N \quad \text{or equivalently} \quad \frac{[H_2O]^2}{[H_2]^2 [O_2]} = K$$

do we know how to calculate K for this reaction? need q for liquids use Vander waals z

Simpler <u>Gas reaction</u>
Case
$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$
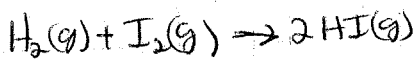
$$K(T) = \frac{q_{HI}^2}{q_{H_2}^2 q_{I_2}^2} \qquad \text{each of these is a diatomic molecule}$$

$$q = q_t q_e q_v q_r = \frac{V}{h^3} \left[2\pi (m_1 + m_2) kT \right]^{3/2} \Omega_0 \, e^{\beta \varepsilon_0} \, e^{-\frac{1}{2}\beta\hbar\omega} \frac{2A}{\beta \hbar^2}$$

etc.