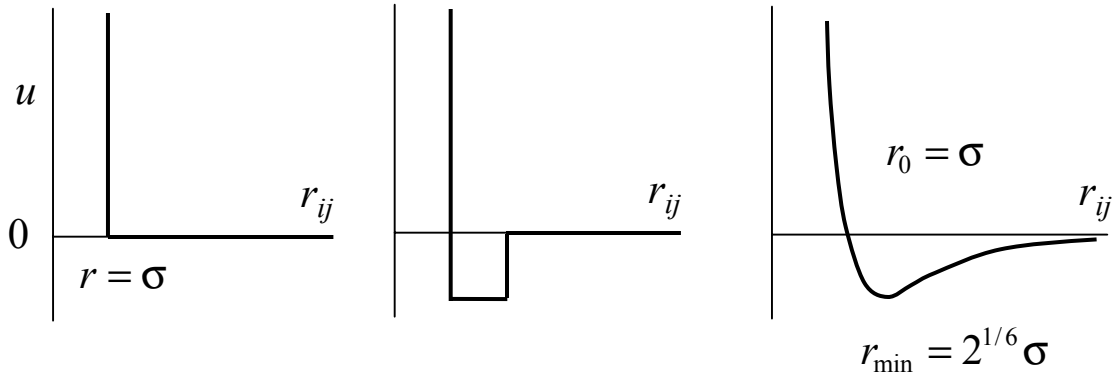


Intermolecular Interactions in Liquids

The average properties of a gas mostly depend on *kinetic* energy. The structure and properties of a liquid also depend on potential energy, usually *approximated* by a two-body model:

$$V = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij})$$

The *pair* potential u describes the intermolecular interactions.



Hard sphere

Square well

$$\text{Lennard-Jones: } u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

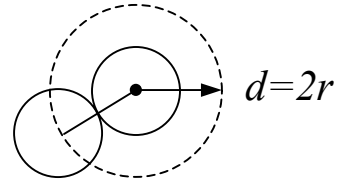
$$\text{Buckingham: } u(r) = Ae^{-Br} - \frac{C}{r^6}$$

Taking argon as an example, $\sigma = 3.40 \text{ \AA}$; $r_{\min}(\text{LJ}) = 3.82 \text{ \AA}$.
In the solid, the atom-atom separation is 3.72 \AA .

Collisions in Gases

The effective volume of a hard sphere is 4 x the sphere volume!

$$\text{Excluded volume} = \frac{1}{2} N \cdot \frac{4}{3} \pi d^3$$



For a simple gas

$$P = \frac{RT}{\bar{V} - b} \quad b = \frac{2}{3} \pi d^2 N_{\text{Av}}$$

The pressure is greater in a hard-sphere gas than an ideal gas.

Without attractive forces there is no gas-liquid condensation.

The ‘space’ occupied by each molecule is: $\pi d^2 \lambda = V / N$

i.e. the mean free path $\lambda = \frac{1}{\pi d^2 \bar{N}}$ (approx. only)

This treatment ignores collisions between particles moving in different directions. The “average” collision is at right angles, so the mean free path is reduced by $\sqrt{2}$.

$$\langle v_{\text{rel}} \rangle = \langle v_{12} \rangle = \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2} = \left[\frac{8k_B T}{\pi m_1} + \frac{8k_B T}{\pi m_2} \right]^{1/2} = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2}$$

Then for molecule 1 moving among 2,

$$\lambda_{1(2)} = \frac{\langle v_1 \rangle}{\langle v_{12} \rangle} \frac{1}{\pi d_{12}^2 \bar{N}}$$

The mean time between collisions $\tau_{\text{coll}} = \lambda / \langle v \rangle$

The collision rate $Z_{1(2)} = \tau_{1(2)}^{-1} = \lambda / \langle v \rangle = \langle v_{12} \rangle \pi d_{12}^2 \bar{N}$

and $Z_{12} = Z_{1(2)} \bar{N}_1 = Z_{2(1)} \bar{N}_2 = \langle v_{12} \rangle \pi d_{12}^2 \bar{N}_1 \bar{N}_2$

Collisions in Liquids

“Intermolecular forces do not depend on velocities, so the velocity distribution is valid for a liquid as well as a gas.”

$$\langle v \rangle = \left(\frac{8k_B T}{\pi m} \right)^{1/2}$$

However, there is ambiguity in the definition of a collision in a liquid – there is no unique instant of contact
– there is no mean free path.

The collision rate (inverse collision time) can be estimated:

a) from a ‘known’ potential.

$\tau = 2 \times$ the time to travel from the minimum of the L-J potential to a value of r such that $u(r) = T = \frac{1}{2} m \langle v \rangle^2$

For liquid argon at 85 K, this gives $\tau = 0.5$ ps.

b) from molecular properties, e.g. $\tau_{\text{liq}} = \rho d^2 / 6\eta$

c) by scaling the gas collision frequency with the diffusion constant

$$\tau_{\text{liq}} = Z^{-1}(\rho) = Z_{\text{gas}}^{-1} \frac{D(\rho)}{D(\rho_{\text{gas}})}$$

The ‘residence time’ for a molecule in a solvent cage is typically 100-100 times longer for a liquid of “normal” density.

“Structure” in Liquids

Liquid densities are similar to those of solids.

Crystals have ‘regular’ and extended structures.

Liquids may have local structure – ‘shells’ of neighbours.

The number of next nearest neighbours can be estimated:

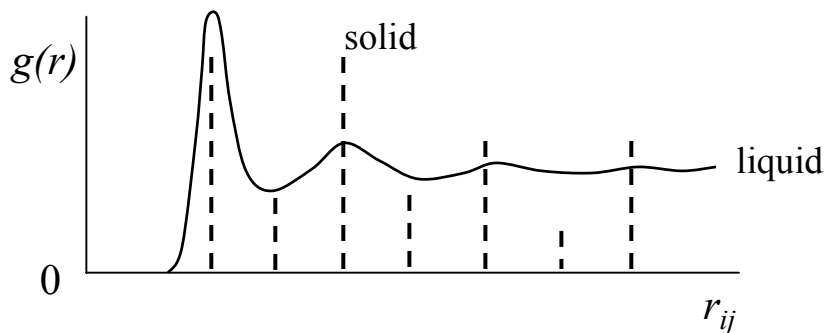
$$\frac{\text{N.N.}(liquid)}{\text{N.N.}(solid)} \approx \frac{\text{density}(liquid)}{\text{density}(solid)} \Rightarrow \frac{\sim 10}{12}$$

There are voids because of disorder in the shells.

A statistical representation is given by the

radial distribution function = pair correlation function

$$= \frac{\text{probability of finding molecule 2 at } r \text{ from 1}}{\text{probability of finding molecule 2 far from 1}}$$



$g(r)$ is determined experimentally by neutron (l) or X-ray (s) scattering; and simulated numerically by:

Monte Carlo method: 10^2 - 10^4 molecules in random positions; average properties calculated for many configurations.

Molecular Dynamics: molecules initially random but new positions calculated every fs from classical equations of motion.

Both methods use periodic boundary conditions.

Diffusion *versus* Activation

encounter pair



Apply the steady-state approximation to $\{AB\}$:

$$\frac{d}{dt}[\{AB\}] = k_D[A][B] - (k_{-D} + k_R)[\{AB\}] = 0$$

$$\text{rate} = k_R[\{AB\}] = \frac{k_D k_R}{k_{-D} + k_R}[A][B]$$

The effective rate constant has two limits:

$$\text{Slow diffusion: } k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} \rightarrow k_D \quad \text{if } k_R \gg k_{-D}$$

$$\text{Fast diffusion: } k_{\text{eff}} \rightarrow \frac{k_D k_R}{k_{-D}} = K_{\{AB\}} k_R = k_{\text{act}} \quad \text{if } k_{-D} \gg k_R$$

Intermediate situations can be described by:

$$k_{\text{eff}} = \frac{k_D k_R}{k_{-D} + k_R} = \frac{k_D (k_D k_R / k_{-D})}{k_D + (k_D k_R / k_{-D})} = \frac{k_D k_{\text{act}}}{k_D + k_{\text{act}}}$$

Or even better:

$$\frac{1}{k_{\text{eff}}} = \frac{1}{k_D} + \frac{1}{k_{\text{act}}}$$

Diffusion-limited Rate Constants

If the encounter pair has an equilibrium concentration,

Smoluchowski: $k_D = 4\pi r_{AB} D_{AB}$ ($\text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$4000\pi r_{AB} D_{AB} N_{Av} \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$$

where encounter distance: $r_{AB} = r_A + r_B$

coefficient of relative diffusion: $D_{AB} = D_A + D_B$ ($\text{m}^2 \text{ s}^{-1}$)

D_A, D_B are often (poorly) estimated by the

Stokes-Einstein equation: $D = \frac{k_B T}{\pi \beta \eta r_s}$

η is the viscosity of the solvent, r_s is the hydrodynamic radius

$\beta = 6$ for ideal Stokes diffusion (continuous medium)

$\beta = 4$ for the opposite limit (solute radius \approx solvent radius)

Assuming the hydrodynamic radius \approx reaction radius,

$$k_D = \frac{4k_B T}{\beta \eta} \left[\frac{1}{r_A} + \frac{1}{r_B} \right] (r_A + r_B) = \frac{4k_B T}{\beta \eta} \left[2 + \frac{r_B}{r_A} + \frac{r_A}{r_B} \right]$$

which does not vary much with r_A/r_B .

Thus $k_D \approx \frac{16k_B T}{\beta \eta_s} \approx 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in water at 300 K

It is determined by solvent properties!

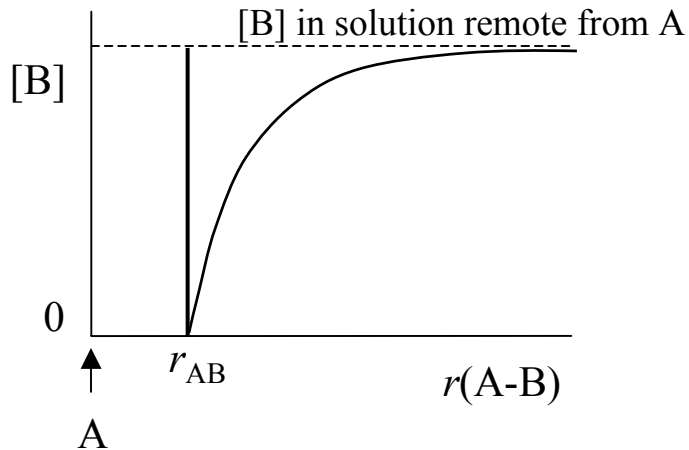
The viscosity dominates the temperature dependence.

What if the Diffusion is not at Equilibrium?

This can happen when a reactant suddenly ‘appears’ in a homogeneous solution of its reaction partner.

e.g. photogeneration of a transient species,

or stopping a particle (muon, positron, ...) from a beam.



At short times the reaction rate is enhanced by ‘contact’ pairs.

In general, the rate “constant” is time dependent:

$$k_{AB}(t) = k_{\infty} \left(1 + \frac{r_{AB}}{\sqrt{\pi D_{AB} t}} \right)$$