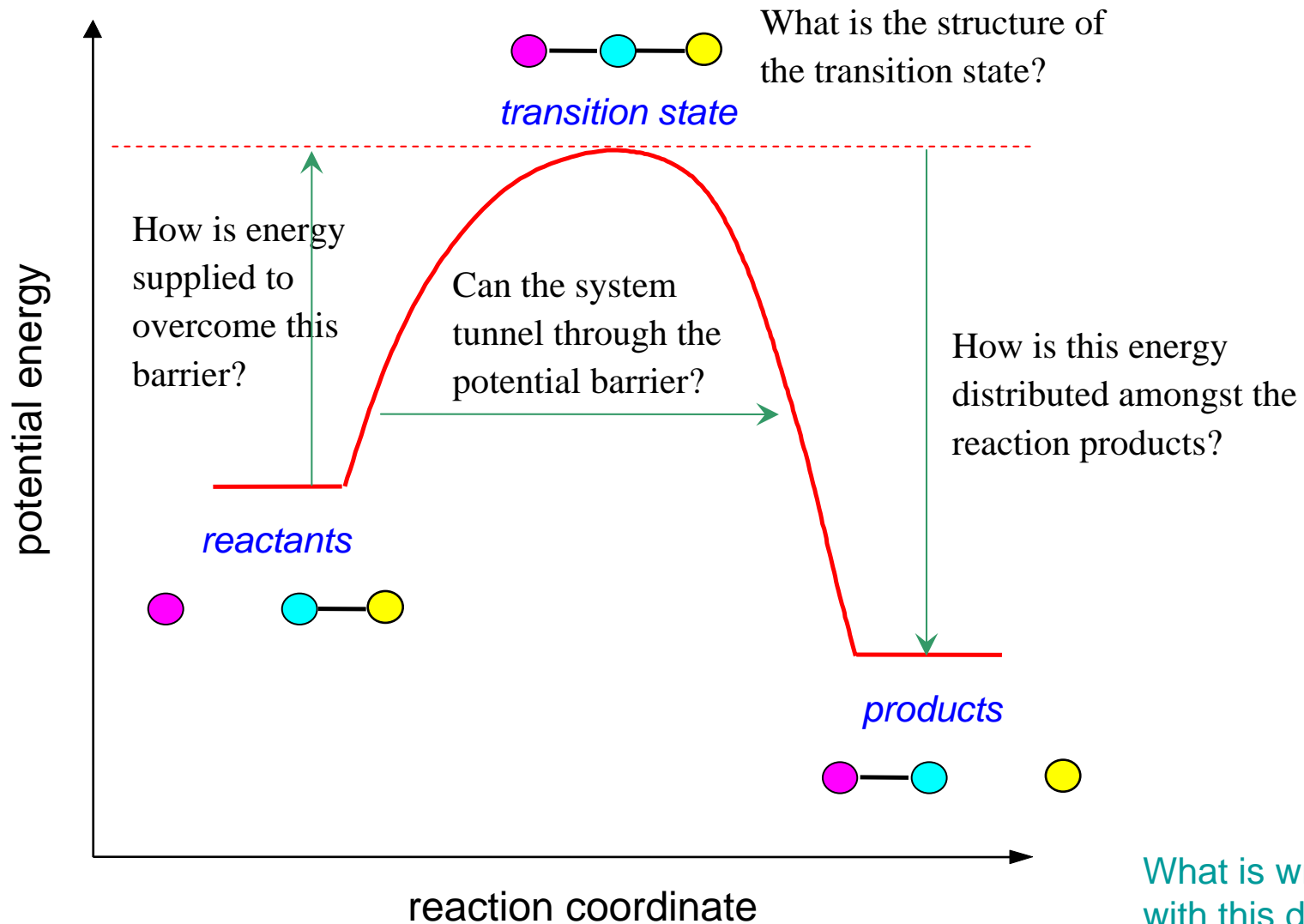


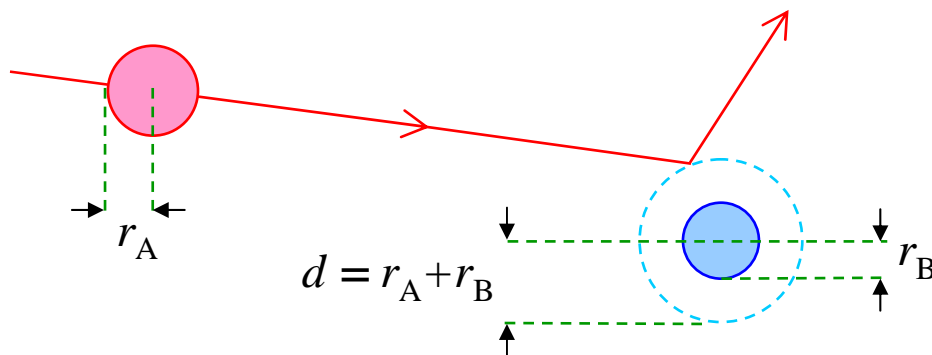
Reaction Dynamics

What is the probability that the system will move from reactants to products?

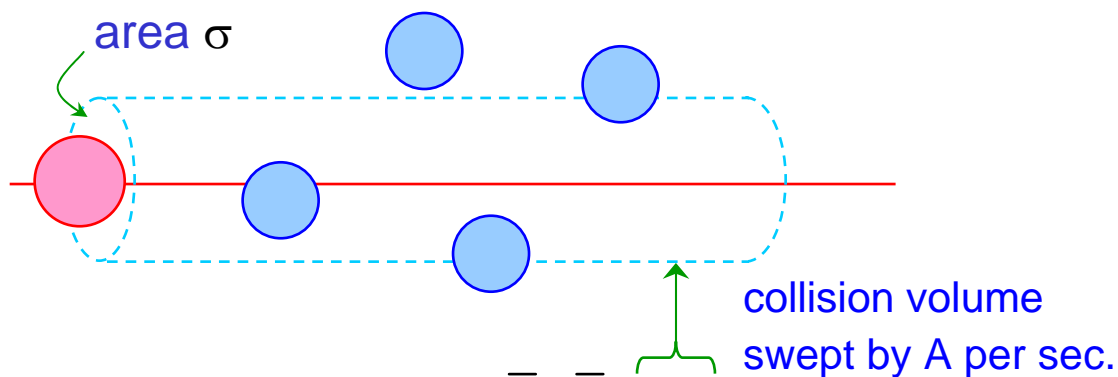


Collision Theory 1

In the simple **hard sphere** model of molecular collisions, the **impact parameter** (distance of closest approach) is the sum of the radii of the collision pair.



Collision cross-section $\sigma = \pi d^2$



Collision frequency

$$Z_{AB} = \bar{N}_A \bar{N}_B \sigma v_{rel}$$

collision frequency per A molecule

number of collisions
per unit time
per unit volume

$$= (\text{m}^{-3}) (\text{m}^{-3}) (\text{m}^2) (\text{m s}^{-1}) \Rightarrow \text{m}^{-3} \text{s}^{-1}$$

Collision Theory 2

Maxwell $\bar{v}_{\text{rel}} = \left[\frac{8RT}{\pi M_A} + \frac{8RT}{\pi M_B} \right]^{1/2} = \left(\frac{8RT}{\pi \mu} \right)^{1/2}$

where $\mu = \frac{M_A M_B}{M_A + M_B}$ is the reduced mass.

Activation Energy: Only a fraction of collisions have sufficient kinetic energy to overcome the activation barrier.

reaction rate = $Z_{AB} e^{-E_a/RT}$ molecules $\text{m}^{-3} \text{s}^{-1}$

Bimolecular Rate Constant

$$-\frac{d[A]}{dt} = \frac{Z_{AB}}{L} e^{-E_a/RT} \quad \text{mol m}^{-3} \text{s}^{-1}$$

$L = \text{Avogadro's no.}$

$$= \frac{N_A N_B}{L} \sigma v_{\text{rel}} e^{-E_a/RT} \quad \text{mol m}^{-3} \text{s}^{-1}$$

$$= 10^6 L[A][B] \sigma v_{\text{rel}} e^{-E_a/RT} \quad \text{mol m}^{-3} \text{s}^{-1}$$

$$= 10^3 L[A][B] \sigma v_{\text{rel}} e^{-E_a/RT} \quad \text{mol dm}^{-3} \text{s}^{-1}$$

$$k_{AB} = 10^3 L \sigma v_{\text{rel}} e^{-E_a/RT} \quad \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$$

$$k_{AB} = 10^3 L d^2 \left(8\pi RT \frac{(M_A + M_B)}{M_A M_B} \right)^{1/2} e^{-E_a/RT} \quad \text{M}^{-1} \text{s}^{-1}$$

Collision Theory 3

Basic collision theory has several deficiencies, which can be partially overcome by making more sophisticated models.

1. Orientation Dependence

The reactions of polyatomic molecules typically depend on their mutual orientation.

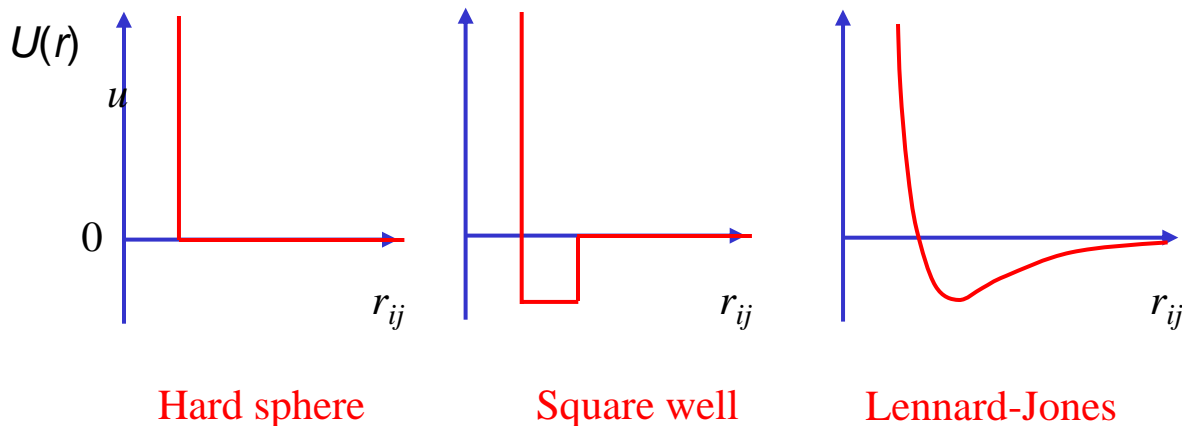
Solution: Replace σ with σ^* , the **reactive cross-section**:

$$\sigma^* = P \sigma$$

↙ **steric factor**

2. Intermolecular Interactions

Molecules are not incompressible hard spheres!



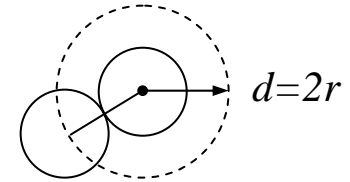
3. The collision energy depends on the impact parameter, which is angular dependent.

4. There is no way to predict the activation energy.

Collisions in Gases

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

Divide by 2 to get the excluded volume $= \frac{1}{2} N \cdot \frac{4}{3} \pi d^3 = N \cdot \frac{16}{3} \pi r^3$



d can be estimated from the van der Waals coefficient :

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

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: $\pi d^2 \lambda = V / N$

\Rightarrow 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 $\sqrt{2}$.

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

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

$$\tau_{coll} = \lambda / \langle v \rangle$$

The collision rate

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

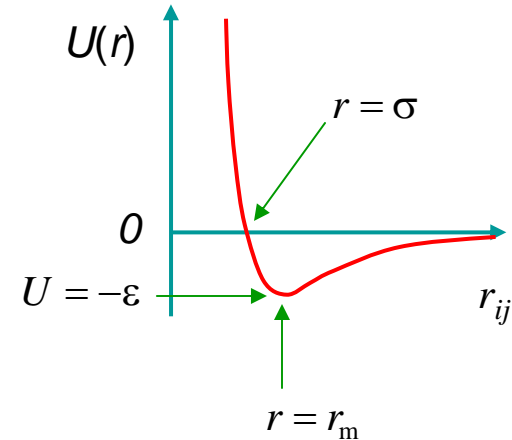
Total collision rate between particles 1 and 2

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

Intermolecular Potentials

Lennard-Jones

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Buckingham

$$U(r) = \left[A e^{-Br} - \left(\frac{C}{r} \right)^6 \right]$$

$$U(r) = \varepsilon \left[\frac{6}{\alpha - 6} e^{-\alpha \left(1 - \frac{r}{r_m} \right)} - \frac{\alpha}{\alpha - 6} \left(\frac{r_m}{r} \right)^6 \right]$$

Stockmayer

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - \frac{\mu^2}{4\pi\varepsilon_0 r^3} (2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \phi)$$

extra term for interaction of two dipoles

Internal Coordinates and Reduced Mass

If the potential energy of a system depends only on the internal coordinates of the system, then the motion of the centre of mass can always be separated from the internal motion.

Consider two point masses m_1 and m_2 , both in motion and interacting with each other.

$$E = \frac{1}{2}m_1(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) + \frac{1}{2}m_2(\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + V(x_1, y_1, z_1, x_2, y_2, z_2)$$

Define centre of mass coordinates: $X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}$ $Y = \frac{m_1y_1 + m_2y_2}{m_1 + m_2}$ $Z = \frac{m_1z_1 + m_2z_2}{m_1 + m_2}$

and internal coordinates: $x = x_1 - x_2$ $y = y_1 - y_2$ $z = z_1 - z_2$

then
$$E = \underbrace{\frac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2)}_{\text{translational energy}} + \underbrace{\frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)}_{\text{internal energy}} + V(x, y, z)$$

where reduced mass $\mu = \frac{m_1m_2}{m_1 + m_2}$

For bimolecular collisions the kinetic energy in internal coordinates is $\frac{1}{2}\mu v_{\text{rel}}^2$

where the relative velocity $v_{\text{rel}} = v_1 - v_2$ vector quantities

Distribution of Molecular Speeds

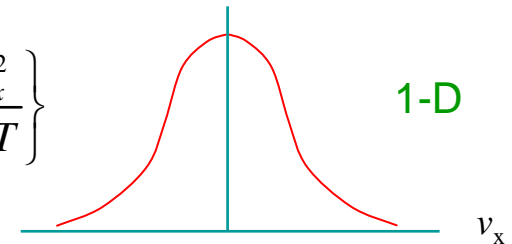
Boltzmann Distribution of Energies:

$$\frac{N(v_x)}{N(v_x=0)} = \exp\left\{-\frac{\varepsilon(v)}{k_B T}\right\} = \exp\left\{-\frac{mv_x^2}{2k_B T}\right\}$$

For a normalized distribution

$$\int P(v_x) dv_x = 1$$

$$P(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left\{-\frac{mv_x^2}{2k_B T}\right\}$$



i.e a **Gaussian** distribution distribution

of speeds with standard deviation $\sigma = (k_B T / m)^{1/2}$

Mean squared speed in 3-D

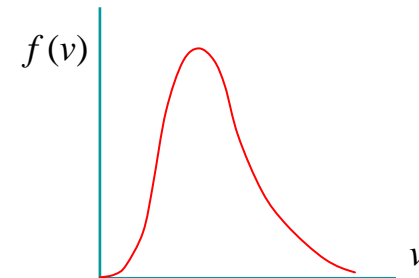
$$v^2 = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3k_B T / m$$

Kinetic energy = $\sum_{i=1}^N \frac{1}{2} m v_i^2 = \frac{1}{2} N m \langle v^2 \rangle = \frac{3}{2} N k_B T = \frac{3}{2} R T$

Equipartition Principle

Probability density for molecular speeds

$$f(v) = 4\pi v^2 P(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left\{-\frac{mv^2}{2k_B T}\right\}$$



by integrating over the angles of spherical polar coordinates

Most probably speed: $v_p = (2k_B T / m)^{1/2}$

for maximum of $f(v)$

Mean speed: $\int_0^{\infty} v f(v) dv = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$

Structure in Liquids

Liquid densities are similar to those of solids. Intermolecular distances are typically a few times molecular diameters.

Crystals have 'regular' and extended structures.

Liquids may have local structure – 'shells' of neighbours.

The number of next nearest neighbours can be estimated.

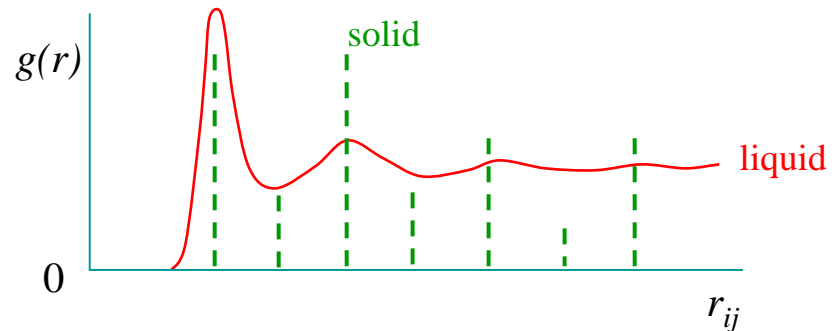
$$\frac{\text{N.N.}(\text{liquid})}{\text{N.N.}(\text{solid})} \approx \frac{\text{density}(\text{liquid})}{\text{density}(\text{solid})} \Rightarrow \frac{\sim 10}{12}$$

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.

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:

- ❖ 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 $u(r) = T = \frac{1}{2} m \langle v \rangle^2$

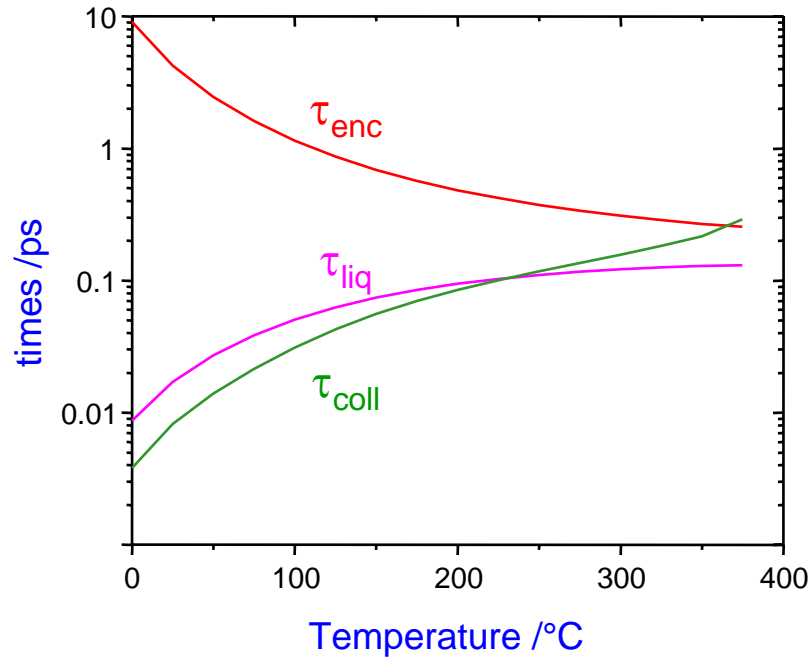
- ❖ from molecular properties, e.g. $\tau_{\text{liq}} = \frac{\rho d^2}{6\eta}$ $\rho = \text{density, } \eta \text{ viscosity}$

- ❖ 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 100-1000 times longer than the time between collisions for a liquid of “normal” density.

Collisions per Encounter

calculated for Mu + hydroquinone



$$\tau_{enc} = \frac{8k_D^{-1}}{[H_2O]} \quad \tau_{liq} = \frac{\rho d^2}{6\eta} \quad \tau_{coll} = \frac{D_{liq}}{D_{gas}} Z_{gas}^{-1}$$

