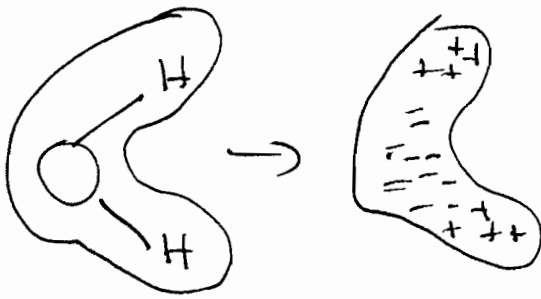


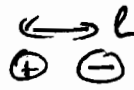
For neutral molecules, need to describe charge distribution



H₂O

Electric multipoles

Simplest one is dipole moment (vector)

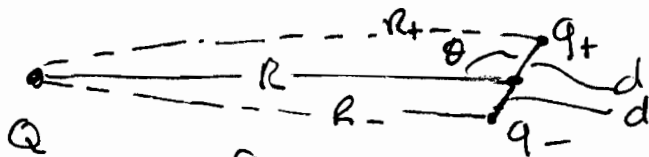


+q, -q

$$p = q \cdot l$$

$$\vec{p} = \sum_i q_i \vec{r}_i$$

Charge-dipole interaction



$$u = \frac{1}{4\pi\epsilon_0} q \left(\frac{q}{R_+} - \frac{q}{R_-} \right) =$$

$$= \frac{1}{4\pi\epsilon_0} q \left[\frac{q}{\sqrt{R^2 + d^2 + 2dR \cos\theta}} - \frac{q}{\sqrt{R^2 + d^2 - 2dR \cos\theta}} \right]$$

Taking limit of $d/R \ll 1$ (ignoring d^2/R^2)

$$u \approx \frac{1}{4\pi\epsilon_0} q \left[\frac{q}{R} \left[1 + \frac{2d}{R} \cos\theta \right]^{-1/2} - \frac{q}{R} \left[1 - \frac{2d}{R} \cos\theta \right]^{-1/2} \right]$$

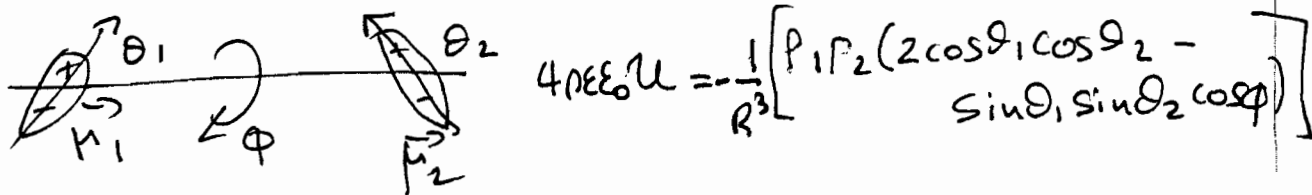
$$\approx \frac{q}{4\pi\epsilon_0} \left[\frac{q_+ + q_-}{R} - \frac{d \cos\theta}{R^2} \cdot (q_+ + q_-) \cdot d \right] \Rightarrow$$

$$u \approx - \frac{Q \cdot P \cos\theta}{R^2}$$

$2dq = P$ (dipole moment)

Dipole-Dipole interaction

In a similar way, two dipoles \vec{p}_1 and \vec{p}_2



when the two dipoles are parallel, $\phi = 0$, $\theta_1 = \theta_2 = 0$, most favorable energy,

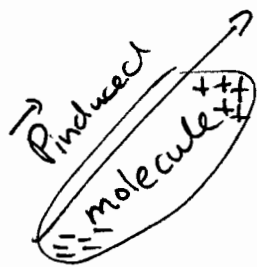
$$U = - \frac{2p_1p_2}{4\pi\epsilon_0 R^3}$$

perpendicular, $\theta_1 = 0$ $\theta_2 = \frac{\pi}{2}$ $U = 0$

The next important term in a multipole expansion for a distribution with no net charge or dipole moment is the quadrupole



However, for any molecule, even uncharged, symmetric ones such as CH_4 or Ar , there are important contributions to the intermolecular interactions coming from the polarizability of the electron clouds.



$$\vec{p}_{\text{induced}} = \underline{\alpha} \cdot \vec{E}$$

+ \longrightarrow -
 electric field
 \vec{E}

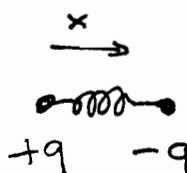
$\underline{\alpha}$ is a symmetric matrix, so polarizability is a tensor, usually given in diagonal form

$$\underline{\alpha} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix} \begin{matrix} x, y, z \\ \text{are molecular} \\ \text{axes} \end{matrix}$$

Van der Waals (dispersion) Interactions

Present for all atoms, even those with spherical symmetry such as Ar. (London, 1930)

Simple model (Drude oscillator), 1D

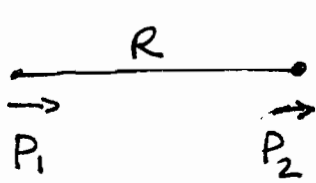

 electrons performing harmonic 1-D motion:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} k x^2 \psi = E \psi$$
 ↑ wavefunction

$k = \text{force constant}$ frequency $\omega = \sqrt{k/m}$

eigenvalues for E : $E_v = (v + \frac{1}{2}) \hbar \omega$ $v = 0, 1, 2, \dots$

Now consider two such molecules at distance R_j
 Instantaneous dipole - induced dipole interaction:



$$U(P_1, P_2) = \frac{-2 P_1 P_2}{4 \pi \epsilon_0 R^3} = -\frac{2 \delta x_1 \delta x_2 q^2}{4 \pi \epsilon_0 R^3}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x_2^2} + \left[\frac{1}{2} k (\delta x_1)^2 + \frac{1}{2} k (\delta x_2)^2 - \frac{2 \delta x_1 \delta x_2 q^2}{4 \pi \epsilon_0 R^3} \right] \psi = E \psi$$

Substitute $a_1 = \frac{\delta x_1 + \delta x_2}{2}$ $a_2 = \frac{\delta x_1 - \delta x_2}{2}$

$k_1 = k - \frac{2q^2}{4 \pi \epsilon_0 R^3}$ $k_2 = k + \frac{2q^2}{4 \pi \epsilon_0 R^3}$

to obtain:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial a_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial a_2^2} + \left[\frac{1}{2} k_1 a_1^2 + \frac{1}{2} k_2 a_2^2 \right] \psi = E \psi$$

Two independent oscillators with frequencies

$$\omega_1 = \omega \sqrt{1 - \frac{2q^2}{4 \pi \epsilon_0 R^3 k}}$$
 ,
$$\omega_2 = \omega \sqrt{1 + \frac{2q^2}{4 \pi \epsilon_0 R^3 k}}$$

$E_0 = \frac{1}{2} h \omega$ Substitute ω_1, ω_2 + Taylor expand:

$$E_0(R) = h\omega - \frac{q^4 h \omega}{2(4\pi\epsilon_0)^2 R^6 k^2} + \dots \quad (1)$$

dispersion interaction $U(R)$

k is related to polarizability α

$\leftarrow E$ field $\quad P = \alpha \cdot E = q \cdot l$ definition of p
 $\leftarrow \text{dipole}$ $\quad k \cdot l = q \cdot E$ force balance
 $\Rightarrow k \cdot l = \frac{q^2 l}{\alpha} \Rightarrow \alpha = \frac{q^2}{k} \quad (2)$

Substitute (2) in (1) above: $U(R) = - \frac{\alpha^4 h \omega}{2(4\pi\epsilon_0)^2 R^6}$

Generalize to 3D: $U(R) = - \frac{3\alpha^4 h \omega}{4(4\pi\epsilon_0)^2 R^6}$

$h\omega$ is the first excitation energy

Repulsive Interactions + Combined Potentials

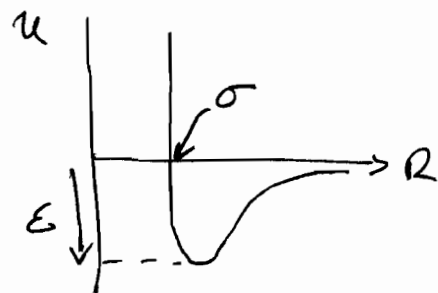
Short range "exchange" forces (electron cloud overlap)

$\sim \exp(-2R/a_0)$ a_0 : Bohr radius

Exponential form was considered "inconvenient" in early days of computers (slow to compute), so the most common combined repulsive + attractive potential is the Lennard-Jones expression

$$U_{LJ}(R) = 4E \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$$

E : energy parameter
 σ : size parameter



Reduced (dimensionless) form

$$R^* = R/\sigma \quad U^* = U/E$$

$$U^* = 4 \left(\frac{1}{(R^*)^{12}} - \frac{1}{(R^*)^6} \right)$$

More general form ("Mie potential")

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

Advantages of using LJ potentials: extensive literature equations of state known
12 = 2 x 6

Disadvantage: functional form of repulsion incorrect

Sometimes used: Buckingham exp-6 potential:

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

($r_m \neq \sigma$). At very short r , exp-6 energy becomes negative - need to correct in Monte Carlo

Unlike-pair Interactions

For different atom types, need "combining rules"

$$U_A = 4\epsilon_A \left[\left(\frac{\sigma_A}{r} \right)^{12} - \left(\frac{\sigma_A}{r} \right)^6 \right] \quad U_B = 4\epsilon_B \left[\left(\frac{\sigma_B}{r} \right)^{12} - \left(\frac{\sigma_B}{r} \right)^6 \right]$$

For U_{AB} (same functional form), need $\epsilon_{AB}, \sigma_{AB}$

Common empirical rules are called Lorentz-Bethelot:

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B) \quad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

Other combining rules may provide better agreement to experiments for mixture properties.

e.g. Lorig (JCP 59, 2464 (1973))

$$\epsilon_{AB} \sigma_{AB}^6 = \sqrt{\epsilon_A \sigma_A^6 \epsilon_B \sigma_B^6} \quad \epsilon_{AB} \sigma_{AB}^{12} = \left[\frac{(\epsilon_A \sigma_A^{12})^{1/3} + (\epsilon_B \sigma_B^{12})^{1/3}}{2} \right]^3$$

e.g. $\left. \begin{array}{l} \epsilon_A = 100 \quad \sigma_A = 4 \\ \epsilon_B = 50 \quad \sigma_B = 4 \end{array} \right\} \begin{array}{l} \epsilon_{LB} = 70.7 \quad \sigma_{LB} = 4 \\ \epsilon_K = 70.4 \quad \sigma_K = 4 \end{array} \right\} \begin{array}{l} \text{Lorig} \\ \text{different} \\ \text{for unlike-} \\ \text{site atoms} \end{array}$

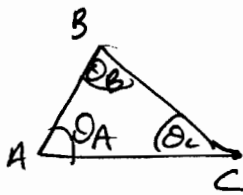
$\left. \begin{array}{l} \epsilon_A = 100 \quad \sigma_A = 4 \\ \epsilon_B = 50 \quad \sigma_B = 3 \end{array} \right\} \begin{array}{l} \epsilon_{LB} = 70.7 \quad \sigma_{LB} = 3.5 \\ \epsilon_K = 60 \quad \sigma_K = 3.56 \end{array}$

Many-body effects

In general, $U(A,B,C) \neq U(A,B) + U(A,C) + U(B,C)$

- e.g., ^{for} polarizable molecules this is particularly severe
 But also for udw (induced dipole), electron overlap, ...

Leading 3-body correction is Axilrod-Teller



$$U^{AT}(r_{AB}, r_{AC}, r_{BC}) = V_{ABC} \cdot \frac{3 \cos \theta_A \cos \theta_B \cos \theta_C}{(r_{AB} r_{AC} r_{BC})^3}$$

where $V_{ABC} = -\frac{3 \alpha^3 C_6}{4(4\pi\epsilon_0)^3}$ ← LJ coeff.

On average, U^{AT} is repulsive, ~10% of energy of liquid Ar at triple point

because of high computational cost ($O(N^3)$ vs $O(N^2)$] usually non-additive interactions are approximated by effective

2-body potentials

