CHAPTER 24   INTERMOLECULAR INTERACTIONS

potential energy $u(r)$ between two particles

$$force = f = -\frac{du}{dr}$$

$r = r^* =$ potential energy minimum

long-range coulombic

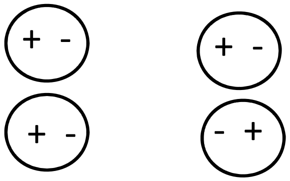
$$u \sim \frac{q_1 q_2}{r}, \quad q_1,\ q_2 =$$ charges on the two species

short-ranged van der Waals

$$u \sim -\frac{C}{r^6}$$

At short distance, *u* must repel one another $\left(Ae^{-Br};\ Ar^{-12}\right)$

dipole-dipole $\sim \frac{1}{r^3}$ – long-range interaction between two H_2O molecules



attractive

repulsive

charge-polarization$\sim -\frac{q\alpha}{2r^4}$ (e.g., Na^+ Ar), α = polarizability of neutral species

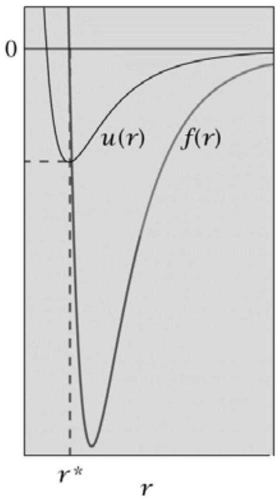


Figure 24.1 Molecular Driving Forces 2/e (© Garland Science 2011)

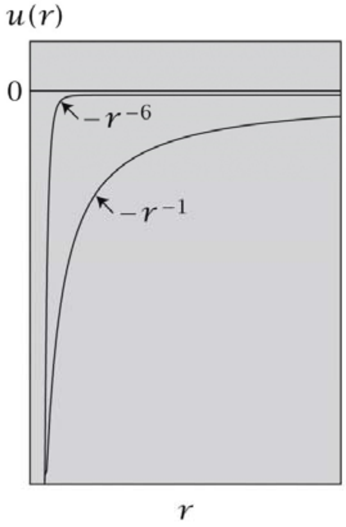


Figure 24.2 Molecular Driving Forces 2/e (© Garland Science 2011)

permanent moments

charge

dipole (e.g., HF) $(\mu = qR)$

quadrupole (e.g., CO_2)

octapole (e.g., CH_4)

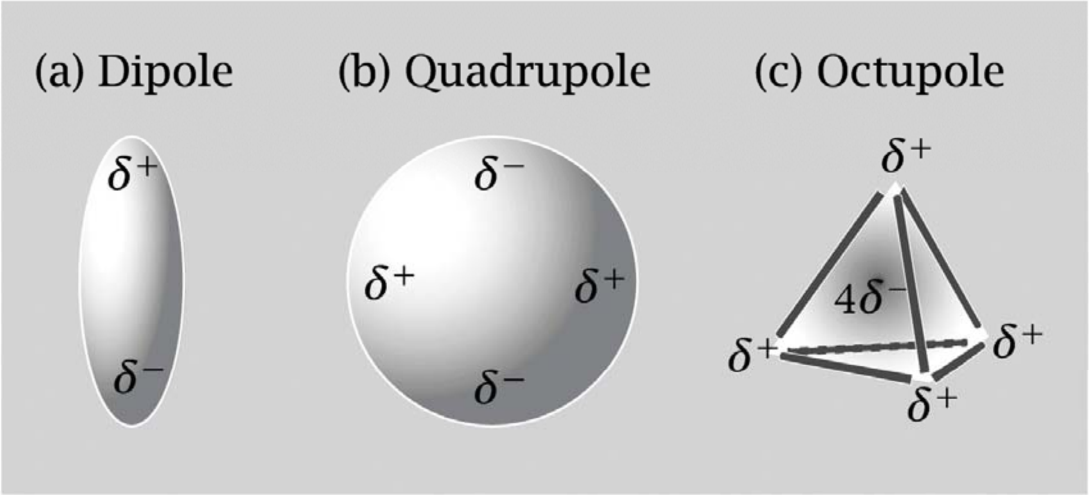


Figure 24.3 Molecular Driving Forces 2/e (© Garland Science 2011)

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charge-dipole $u \sim \dfrac{1}{r^2}$

average over orientations $u \sim \dfrac{1}{3kT}\dfrac{1}{r^4}$

dipole-dipole

average over orientations $u \sim \dfrac{1}{3kT}\dfrac{1}{r^6}$

How do we understand the attraction between two Ar atoms?

London-dispersion

$$u = \frac{C_6}{r^6}: \quad C_6 \propto \alpha_A \alpha_B$$

$\alpha_A, \alpha_B =$ polarizabilities of the two atoms/molecules

Lennard Jones potential

$$u(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

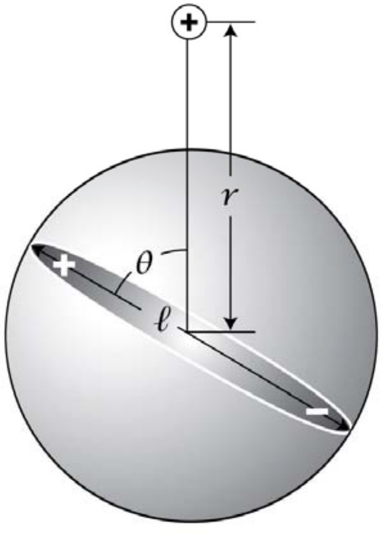
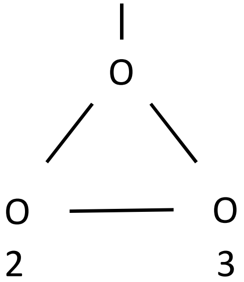


Figure 24.5 Molecular Driving Forces 2/e (© Garland Science 2011)

H-bonds – have electrostatic, dispersion, and polarization contributions



$$u \sim u_{12} + u_{13} + \mu_{23}$$

assume pairwise additive

van der Waals equation of state

$$p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} = \frac{\rho RT}{1 - b\rho} - a\rho^2$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial U}{\partial V}\right)_{T,N} + \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$\downarrow \qquad \downarrow$$

$$\frac{-aN^2}{V^2} \qquad \frac{NkT}{V - Nb} \longleftarrow$$

from lattice model (Ex. 6.1)

↑ from attractions

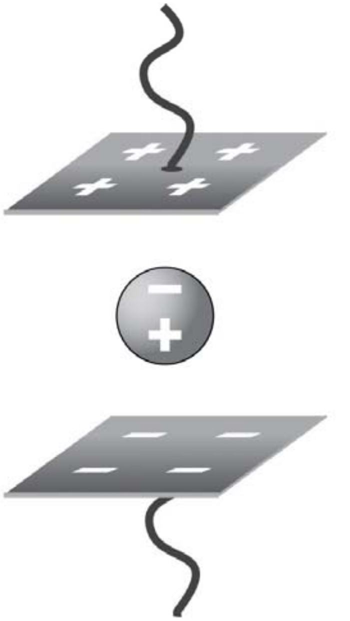


Figure 24.6 Molecular Driving Forces 2/e (© Garland Science 2011)

particles in shell of radius *r* =

(density) x (volume of shell)

ρ x $4\pi r^2 dr$

$$U = \frac{N}{2}\int_0^\infty u(r)\,\rho 4\pi r^2 dr$$

assuming distribution
is uniform

take $u(r) = \begin{Bmatrix} \infty, & r < r^* \\ -u_0\left(\frac{r^*}{r}\right)^6 & r > r^* \end{Bmatrix}$

$\int_0^\infty \rightarrow \int_{r^*}^\infty$ since no particles are between ϕ and *r**

$$U = -\frac{aN^2}{V}, \quad \text{where } a = \frac{2\pi (r^*)^3}{3} u_0$$

$p = -\frac{aN^2}{V^2} - \frac{kT}{b_0}\ell n\left(1 - \frac{Nb_0}{V}\right), \text{ where } b_0 = \frac{V}{M} =$ volume/# lattice sites

$\approx \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}, \;\; b = \frac{b_0}{2} = \frac{1}{2}$ volume of a particle

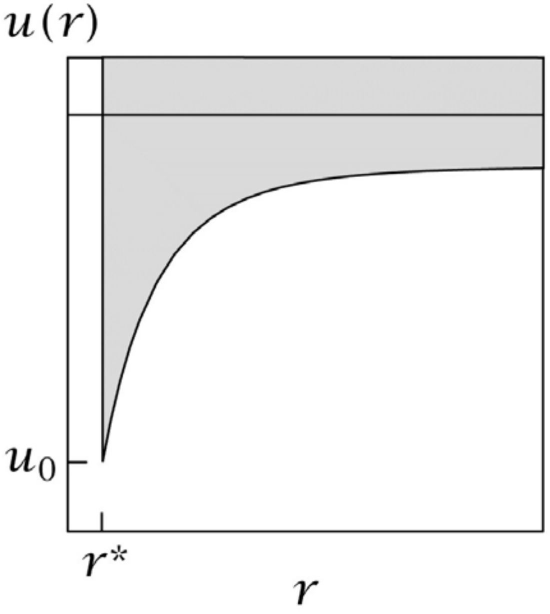


Figure 24.9 Molecular Driving Forces 2/e (© Garland Science 2011)

any potential falling off more rapidly than $\frac{1}{r^3}$
would give this result

Radial distribution functions

true density in shell at *r* from test particle

$$= \rho g(r)$$

$\nwarrow$ radial distribution function

where ρ = average density = *N/V*

$$g(r) = \rho^{true} / \rho^{avg}$$

molecules in 1st solvation shell =

$$\int_0^B \rho q(r) 4\pi r^2 dr$$

$$\int_0^\infty \rho q(r) 4\pi r^2 dr = n - 1 \approx n$$

$$U' = \int_0^B \rho u(r) g(r) 4\pi r^2 dr =$$

energy of interaction between
one particle and all others

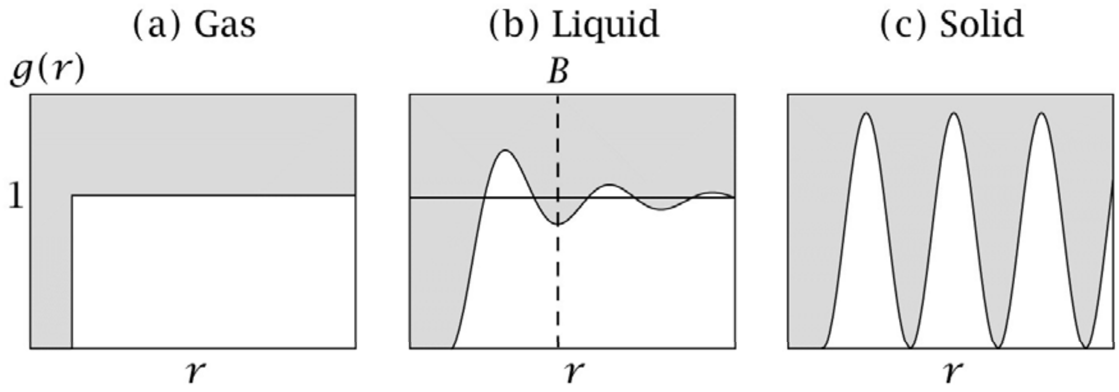


Figure 24.10 Molecular Driving Forces 2/e (© Garland Science 2011)

Lattice model

$$w \text{ (from Chapter 14)} = u\left(r^*\right)$$

$$U = \frac{N}{2}\sum_{r=0}^{\infty} u\left(r\right) g\left(r\right) \rho 4\pi r^2 = \frac{N}{2} u\left(r^*\right) z = \frac{Nwz}{2}$$

$$\xrightarrow{\hspace{6cm}}$$

sum over nearest neighbors only

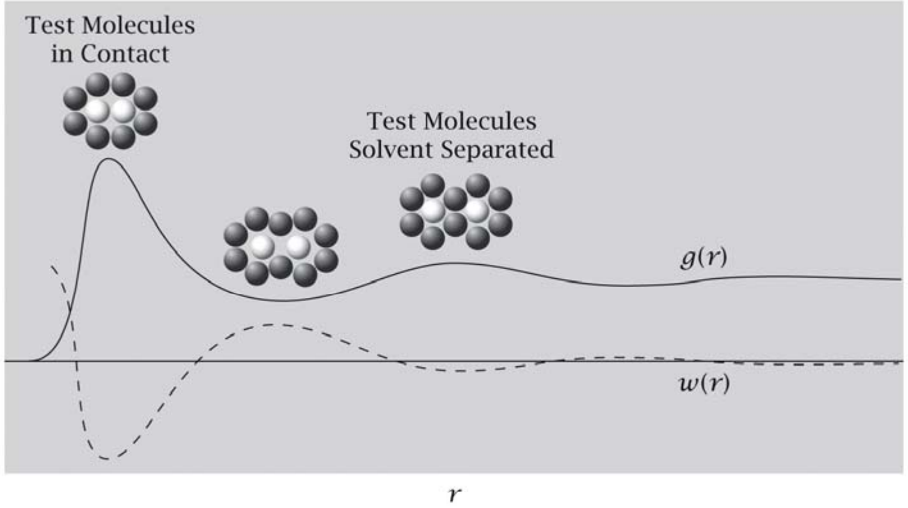


Figure 24.11 Molecular Driving Forces 2/e (© Garland Science 2011)

For molecules for which van der Waals (dispersion) interactions dominate:

$$w_{AA} = -c\alpha_A^2 \qquad w_{BB} = -cw_B^2 \qquad w_{AB} = -c\alpha_A\alpha_B$$

c = constant ~ equal for molecules of ~ same size