Statistical Molecular Thermodynamics

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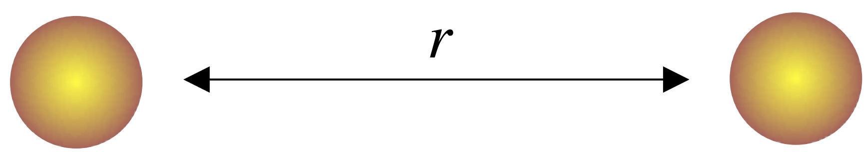
Video 2.7

Other Intermolecular Potentials

Molecular Interaction

The virial expansion derives from *exact relationships between virial coefficients and intermolecular interactions*



If 2 molecules interaction according to a potential energy function that depends only on their separation r, then B_{2V} can be expressed as:

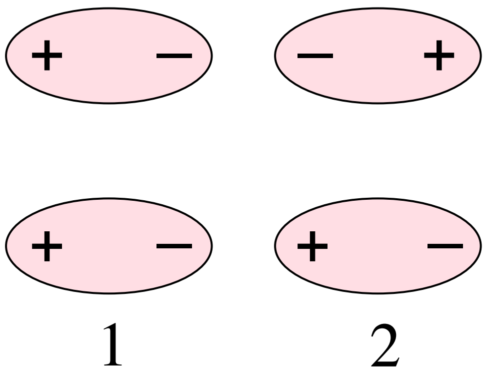
$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[e^{-u(r)/k_B T} - 1 \right] r^2 dr$$

Understanding Attraction

We can understand the r^{-6} attraction term in the L-J potential

dipole-dipole interactions

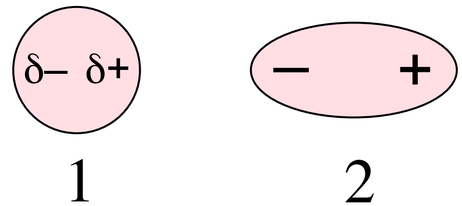
averaged over all orientations



$$u_{d,d}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2(3k_\mathrm{B}T)}\frac{1}{r^6}$$

All terms have same r^{-6} behavior, but for nonpolar molecules only the *dispersion interactions* are relevant

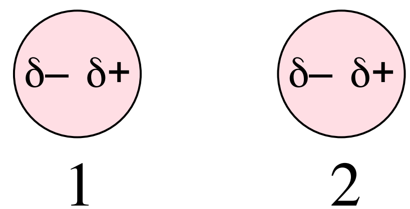
dipole-induced dipole interactions



$$u_{\mathrm{induced}}(r) = -\frac{\mu_1^2\alpha_2}{(4\pi\varepsilon_0)^2 r^6} - \frac{\mu_2^2\alpha_1}{(4\pi\varepsilon_0)^2 r^6}$$

dispersion interactions

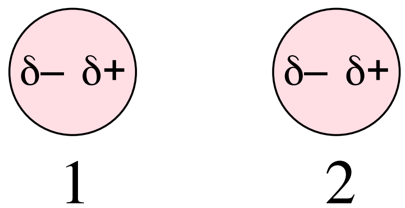
induced dipole-induced dipole interactions



$$u_{\mathrm{disp}}(r) = -\frac{3}{2}\frac{I_1 I_2 \alpha_1 \alpha_2}{(I_1 + I_2)(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

Quantum Mechanical Dispersion

This is a quantum mechanical effect associated with the correlated motion of the electrons in the atoms, which leads to a reduction in energy.



Fritz London

ionization energy (J)

polarizability (C•m²•V⁻¹)

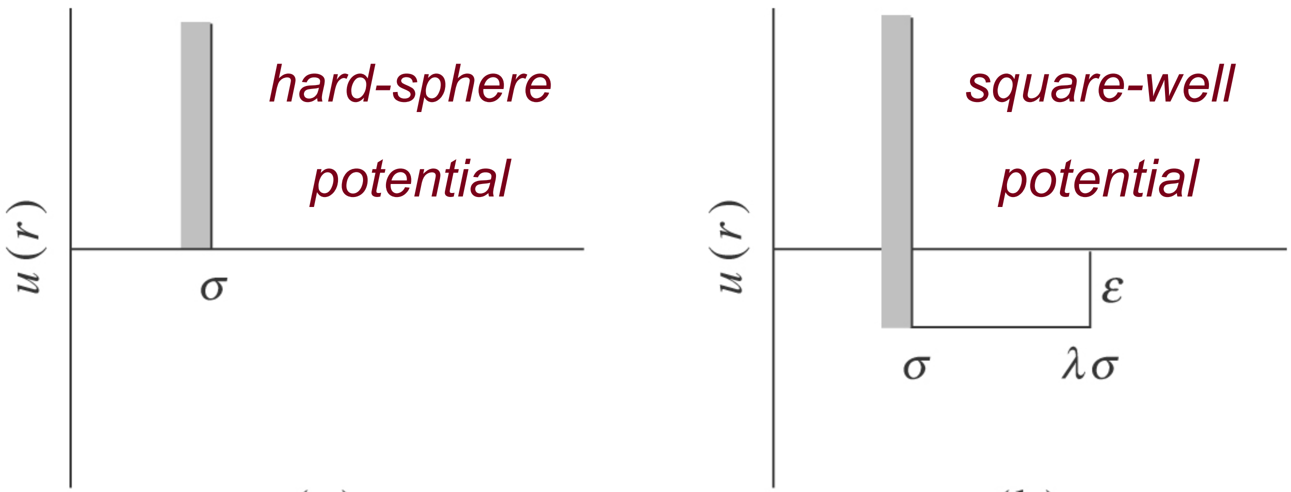
$$u_{\mathrm{disp}}(r) = -\frac{3}{2}\frac{I_1 I_2 \alpha_1 \alpha_2}{(I_1 + I_2)(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

permittivity of vacuum (C²•J⁻¹•m)

Dispersion is generally the dominant contribution to the r^{-6} term

Other Intermolecular Potentials

Simpler $u(r)$ models lead to analytical solutions for the integral that defines $B_{2V}(T)$



(a) (b)

$$u(r < \sigma) = \infty$$
$$u(r > \sigma) = 0$$

$$u(r < \sigma) = \infty$$
$$u(\sigma < r < \lambda\sigma) = -\varepsilon$$
$$u(r > \lambda\sigma) = 0$$

The Hard Sphere Model

Good for very high T relative to ε/k_B

$$u(r < \sigma) = \infty$$
$$u(r > \sigma) = 0$$

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[e^{-u(r)/k_B T} - 1 \right] r^2 dr$$

$$= -2\pi N_A \int_0^\sigma [0 - 1] r^2 dr - 2\pi N_A \int_\sigma^\infty [e^0 - 1] r^2 dr$$

$$= \frac{2\pi\sigma^3 N_A}{3}$$

This is 4 times the volume of N_A *spheres (*σ *in this case can be thought of as the sphere diameter)*

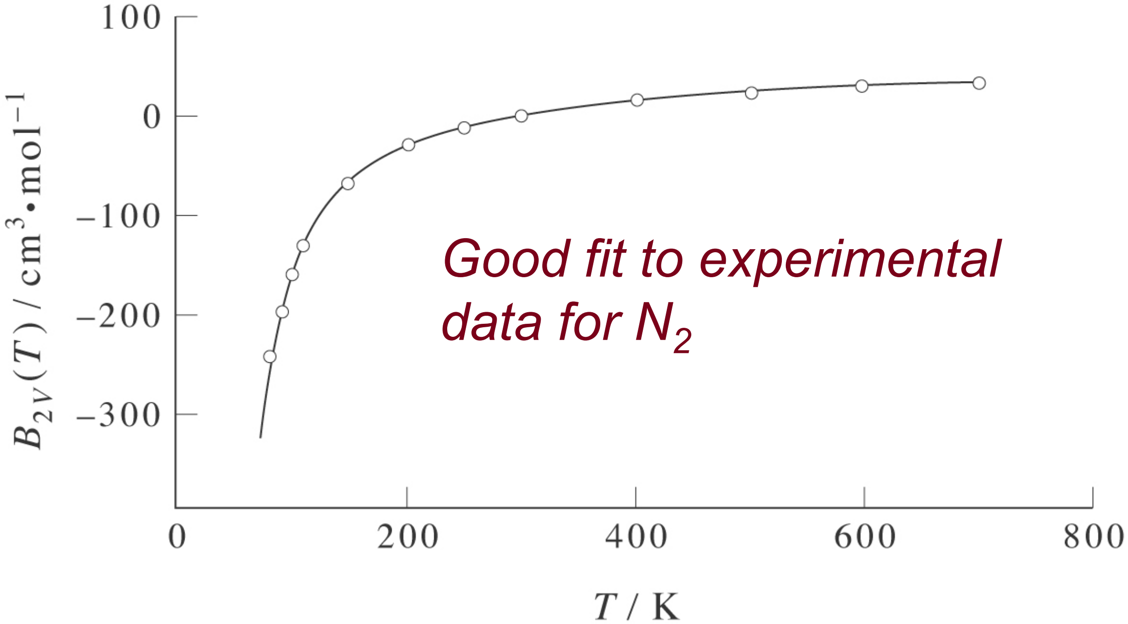
Independent of T, but $B_{2V}(T)$ vs T plot *is* reasonably flat at high T

The Square Well Model

$$u(r < \sigma) = \infty$$
$$u(\sigma < r < \lambda\sigma) = -\varepsilon$$
$$u(r > \lambda\sigma) = 0$$

same as hard sphere

$$B_{2V}(T) = \frac{2\pi\sigma^3 N_A}{3}\left[1 - \left(\lambda^3 - 1\right)\left(e^{\varepsilon/k_BT} - 1\right)\right]$$



Good fit to experimental data for N_2

	sqwm	L-J
σ (pm)	328	370
ε/k_B (K)	95.2	95.1
λ	1.58	—