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5.62 Physical Chemistry II
Spring 2008

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5.62 Lecture #18: Model Intermolecular Potentials

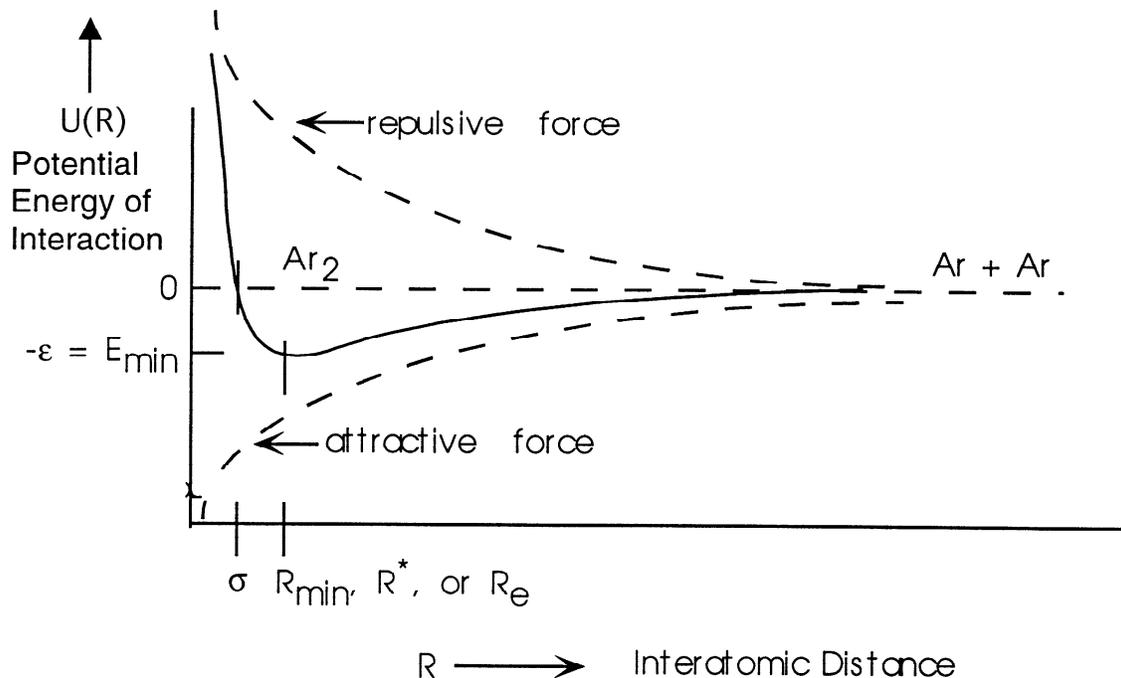
Readings: Hill, pp. 261-274

Intermolecular potentials are interactions between molecules — up to this point, particles are treated as independent, ideal particles that do not interact.

Approximation okay for gas molecules at low pressure

All atoms and molecules interact with one another, even inert gas atoms.

Interaction potential between *non-polar* atoms



Attractive forces:

$$U(r) \propto \frac{1}{r^6}$$

can be derived by QM perturbation theory

London dispersion or van der Waals force. Induced dipole interaction due to fluctuations in electron distribution: Charge distribution on one atom is “off center” due to fluctuation. The resulting electric dipole induces a temporary dipole on the other atom. Dipole-dipole attraction.

Repulsive forces:

Due to electron orbital overlap (“overlap” or “Pauli” repulsion) Difficult to derive explicit distance dependence: usually treated as strongly repulsive, e.g.

$$U(r) \propto \frac{1}{r^{12}} \quad \text{OR} \quad U(r) \propto \exp[-a(r - R_{\min})^d] \quad (d \text{ is odd integer})$$

Add attractive and repulsive portions of potential — resulting interaction potential looks like that for a diatomic molecule!! Two Ar atoms form a non-covalent "bond", but the binding energy is $\epsilon \approx 0.8$ kJ/mol, which is much smaller than kT at room temperature. This "van der Waals molecule" is stable only at low temperature.

Lennard-Jones "6-12" Potential – empirical fit

Computationally useful and physically plausible approximate interaction potential

$$U_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

\uparrow well depth (show this) \uparrow repulsion dominates at small r \uparrow attraction dominates for larger r

where is minimum of U_{ij} ?
 r_{\min} ? $U(r_{\min})$?

This is the interaction between atoms. For interaction between molecules "I" and "J":

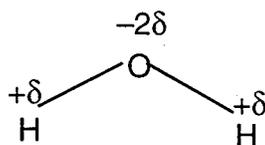
$$U_{IJ}(\vec{q}_I, \vec{q}_J) = \sum_{i \in I} \sum_{j \in J} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (\text{pairwise interactions between all atoms})$$

– requires σ_{ij} (sum of radii of i^{th} and j^{th} particles) and ϵ_{ij} between all atom pairs (parameters)

Polar and Charged Atoms

charged atoms (ions) bear a full formal charge (e.g., Na^+ , Cl^- , Mg^{+2} , etc.)

atoms in polar bonds can sometimes be thought of as bearing a partial atomic charge:



Interactions between charges treated by Coulomb's Law

$$U_{ij} = \frac{q_i q_j}{D r_{ij}} \quad \begin{array}{l} q_i, q_j \text{ are atomic charges} \\ D = \text{dielectric constant (1 for vacuum)} \end{array}$$

NOTE: All atoms interact via van der Waals potential. Polar or charged atoms also subject to Coulombic interaction potential.

Two Molecules with no net charge but permanent dipole moment μ :

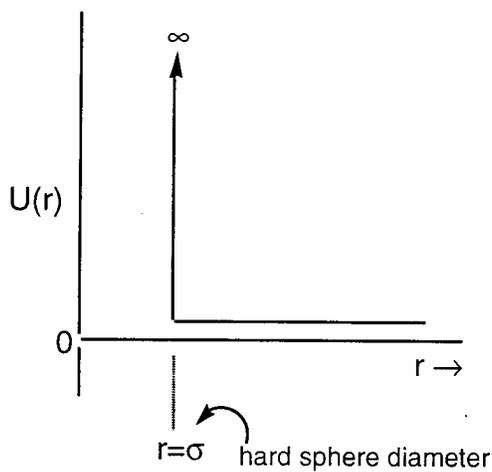
Dipole-dipole interaction:

$$U \propto \frac{\mu_1 \mu_2}{r^3} \quad \text{dipole-dipole interaction (also has angle dependence)}$$

For atoms and simple molecules, molecular beam scattering can be used to obtain information about the interaction potential. Can also fit potential to structural (e.g., spectroscopic data or crystal ionic radii) and thermodynamic data (e.g., heats of sublimation). Finally, detailed quantum mechanical calculations can be fit in order to model an interaction potential.

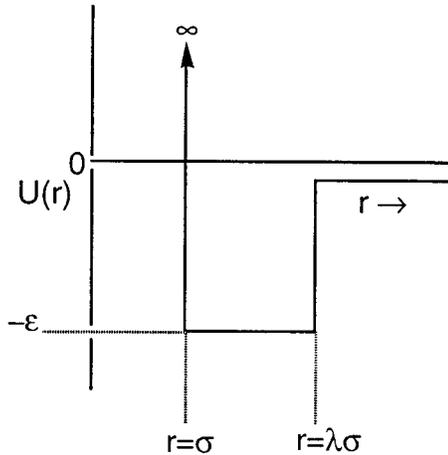
Simplified Empirical Potentials (convenient for Statistical Mechanical calculations)

1. Hard Sphere Potential



$$U(r) = \infty \quad r < \sigma$$

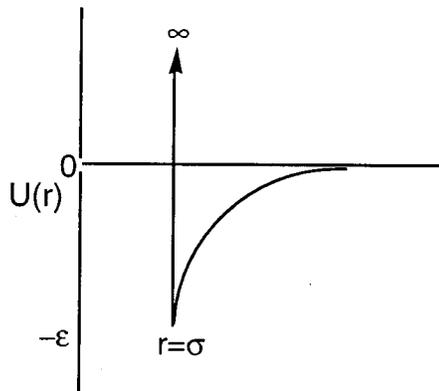
$$U(r) = 0 \quad r \geq \sigma$$

2. Square Well Potential

$$U(r) = 0 \quad (r \geq \lambda\sigma)$$

$$U(r) = -\epsilon \quad (\sigma \leq r < \lambda\sigma)$$

$$U(r) = \infty \quad (r < \sigma)$$

3. Sutherland Potential

$$U(r) = \infty \quad (r < \sigma)$$

$$U(r) = -\epsilon \left(\frac{\sigma}{r} \right)^6 \quad (r \geq \sigma)$$

How do INTERMOLECULAR INTERACTIONS affect macroscopic properties?

Let's check by seeing how Ideal Gas Law (which is exact for non-interacting point particles) is "modified" by including interaction potential.

$$q = \sum_i e^{-\epsilon_i/kT} ; \epsilon_i = \text{C-O-M kinetic} + \text{internal} + \text{interaction energy}$$

$$pV = nRT + \text{corrections}$$

↑
from kinetic
energy alone

↑
from interaction potential energy (internal energy
does not contribute to pressure because it has no
volume dependence). These are the terms that we
have so far left out.

—LET'S FIND THESE CORRECTIONS—

$$\epsilon = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\underline{q}^{3N})$$

To solve for Q while including the full interaction potential, $U(\underline{q}^{3N})$, we will use classical description because energy levels are closely spaced.

exp. of sum is product of exponentials

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int \dots \int d^3 \underline{p}_1 \dots d^3 \underline{p}_N d^3 \underline{q}_1 \dots d^3 \underline{q}_N \exp \left[- \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U(\underline{q}^{3N}) \right) / kT \right]$$

$$= \frac{1}{N! h^{3N}} \left(\int d^3 \underline{p} e^{-p^2/2mkT} \right)^N \int \dots \int d^3 \underline{q}_1 \dots d^3 \underline{q}_N e^{-U(\underline{q}^{3N})/kT}$$

$$= \frac{(2\pi mkT)^{3N/2}}{N! h^{3N}} \underbrace{Z(N, V, T)}$$

from $d^3 \underline{p}$ integral

everything left over from $d^3 \underline{q}$ integral

where

$$Z(N, V, T) \equiv \int d\underline{q}^{3N} e^{-U(\underline{q}^{3N})/kT}$$

Configurational Integral or Configurational Partition Function

As a simple check that we've set this up correctly, should find no corrections to Ideal Gas Law if we set $U(\underline{q}) = 0$.

$$U(\underline{q}) = 0 \Rightarrow Z = \int d\underline{q}^{3N} = V^N$$

Thus,

$$Q(N, V, T) = \frac{(2\pi mkT)^{3N/2}}{N! h^{3N}} V^N = \frac{q_{\text{trans}}^N}{N!}$$

where $q_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V.$

So

$$p = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = +kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{kTN}{V} = \frac{nRT}{V}$$

$$pV = nRT$$

Of course, our check worked.

But now the idea is to evaluate $Z(N,V,T)$ for each of the four special model $U(\tilde{q}^{3N})$ potentials.