Chemistry 888

Section II

Intermolecular Forces

These arise from electromagnetic interactions — from the charged particles: electrons and protons that make up a molecule.

There is some arbitrariness in what divides intra- from intermolecular forces.

(The terms "forces" and "potentials" tend to be used interchangeably though of course force is the space derivative of potential.)

It is known that intermolecular potentials are repulsive at short distances and attractive at large distances.

Repulsive Overlap Forces

The Pauli exclusion principle says that electron clouds of two molecules cannot overlap. So, the electron density between them is reduced. This means that the positively charged nuclei are incompletely shielded and exert a repulsive force.

Attractive Forces — There are three such potential contributions:

1. **Electrostatic**. When, e.g., a molecule possesses a permanent dipole moment (e.g. HCl), then there is an electrostatic interaction between the HCl's. There is no distortion of the charge distribution on interaction (by assumption) — a first order effect.

For example, the interaction of two point (d<<r, with d dipole dimension and separation between the two) dipoles is

$$U = -\frac{\mu^2}{4\pi\varepsilon_0 r^3} J(\theta_1 \theta_2 \phi); \quad J(\theta_1 \theta_2 \phi) = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi$$

$$\mu = Q_2 d_2 + Q_1 d_1 \qquad \text{(ind of origin).} \langle U \rangle = \frac{\int d\Omega_1 d\Omega_2 U \, e^{-\beta U}}{\int d\Omega_1 d\Omega_2 e^{-\beta U}}$$

Since $U - \langle U \rangle \leq k_B T$ expand to evaluate the integral.



Averaging over angles leads to $U = -\frac{c}{r^6}$; attractive $\sim \frac{1}{r^6}$. $c = \frac{2}{3} \frac{\mu_a^2 \mu_b^2}{k_B T}$ (NB c depends on T)

2. **Induction energy**.

An electric field **E** polarizes the atom (or molecule) (separates charge).



E is the field from another molecule — *treated as a dipole (see the following page)*.

 $\mathbf{p} = \alpha \mathbf{E}$ α is polarizability of the atom (or molecule but then the polarizability is a second rank tensor – a 3X3 matrix).

When a molecule with permanent moment μ is placed in the field **E**, the amount of work is not only the potential V_m of the total moment

$$V_m = -(\boldsymbol{\mu} + \mathbf{p}) \cdot \mathbf{E}.$$

There is the work W_{pol} required to form the induced dipole against the internal forces of the molecule. For an infinitesimal change in the induced moment, $d\mathbf{p}$, this work is

$$dW_{pol} = \mathbf{E} \cdot d\mathbf{p}.$$

The total work is obtained as

$$W_{pol} = \int_0^{\mathbf{p}} \mathbf{E}' \cdot d\mathbf{p}' = \frac{1}{\alpha} \int_0^{\mathbf{p}} \mathbf{p}' \cdot d\mathbf{p}' = \frac{p^2}{2\alpha}$$

where we used $\mathbf{p}' = \alpha \mathbf{E}'$. The prime denotes the induced polarization and field for the stage of the (reversible) process.

Then,
$$U = V_m + W_{pol} = -(\boldsymbol{\mu} + \mathbf{p}) \cdot \mathbf{E} + \frac{1}{2}\mathbf{p} \cdot \mathbf{E} = -\boldsymbol{\mu} \cdot \mathbf{E} - \frac{1}{2}\mathbf{p} \cdot \mathbf{E}$$

Therefore, $U_{ind} = -\frac{1}{2}\mathbf{p} \cdot \mathbf{E} = -\frac{1}{2\alpha}p^2 = -\frac{\alpha}{2}E^2$.

We want to work out the induction energy corresponding to a field from a permanent dipole that falls on the atom of interest whose polarizability is α . The field **E** that induces the dipole in the atom is from a permanent dipole. Consider the potential ϕ that a dipole sets up at point P (We will get the field **E** that corresponds to this potential):



$$\phi = \frac{1}{4\pi\varepsilon_0} \left[\frac{Q_1}{r_1} + \frac{Q_2}{r_2} \right]$$

Expand in powers of d_1/r , d_2/r .

$$\phi = \frac{1}{4\pi\varepsilon_0} \left\{ \frac{Q_1 + Q_2}{r} + \frac{\mu}{r^2} \cos\theta + \frac{\Theta}{2r^3} \left(3\cos^2\theta - 1 \right) + \ldots \right\}$$

$$Q_1 + Q_2 = 0$$
 $\Theta = Q_1 d_1^2 + Q_2 d_2^2$

$$\phi(P) = \frac{1}{4\pi\varepsilon_0} \frac{\mu\cos\theta}{r^2}.$$

The field is given by $\mathbf{E} = -\nabla \phi$. The magnitude of the field is

$$E = \left| \mathbf{E} \right| = \left[\left(\frac{\partial \phi}{\partial r} \right)^2 + \left(\frac{1}{r} \frac{\partial \phi}{\partial \theta} \right)^2 \right]^{\frac{1}{2}}$$

Working this out:

$$U_{ind} = -\frac{\alpha}{2}E^2 = -\frac{\alpha}{2}\frac{\mu^2}{r^6}\frac{3\cos^2\theta + 1}{(4\pi\varepsilon_0)^2}.$$

Attractive for all configurations ~ $1/r^6$.

Dispersion Energy — This is an essentially quantum phenomenon. Roughly speaking, the fluctuating dipoles from the charge distributions of the molecules are correlated. (N.B. - this interaction exists for atoms and *nonpolar* molecules.) See any QM text for a derivation based on second order time independent perturbation theory.

$$U_{disp} = \frac{C_6}{r^6}$$
 to leading order in inverse powers.

 $C_6 < 0.$ (For molecules in their ground electronic state).

Based on an oscillator model for each molecule, a simple approximation is

 $C_6 = -\frac{3}{4} \frac{\alpha^2 E_I}{(4\pi\epsilon_0)^2}$, where E_I is the ionization energy of molecule.

(Note that $\alpha \approx e^2/k \approx e^2 r_{eff}^2/E_I$, where r_{eff} is an effective distance for the electrons. Thus, $C_6 \approx \alpha^2 E_I \approx 1/E_I$, as one might expect.)

For most molecules $|U_{disp}| >> |U_{el}|, |U_{ind}|$.



But H_2O is an important exception — here, U_{el} dominates.

Data from: Hirschfelder, J.O., Curtiss, C.F. and Bird, R.B. "Molecular Theory of Gases and Liquids," John Wiley, New York, 1954, 1964. (A superb book on intermolecular forces).

 $C_6 (10^{-60} \text{ erg cm}^6)$

molecule	electrostatic	dispersion	induction
CO	0.003	67	0.06
HI	0.35	382	1.7
H20	190.	47	10.0

Putting this together for atoms, use a Lennard-Jones (LJ) potential,

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

where $\sigma = 2^{-1/6} r_m$. $\sim .9r_m \quad \varepsilon \sim 100{\text{-}}200 \text{ K}, \quad \sigma \sim 3{\text{-}}4 \text{ Å}$. The first term's form is not fundamental. It actually is more exponential – but this form is historical and captures the basic features.

The attractive part is from the dispersion energy contribution. The repulsion is a fit to the quantum chemical calculations for electron overlap effects. (Other powers than 12 are sometimes used.)

Many more flexible potentials have been proposed. They are more flexible because they involve more (fitting) parameters.

Non-spherical molecules — approaches:

1. Could write the potential specific to an orientation. But this would involve many functions.

2.
$$U(r, \omega_1, \omega_2) = U_0(r) + \sum_{n=1}^{\infty} U_n(r) f_n(\omega_1, \omega_2)$$

 ω_1, ω_2 : give the orientation in space of molecules 1 and 2. f_n : some angular basis functions (spherical harmonics) $U_n(r)$: coefficients that only depend on r.

In principle, this expansion is exact, but need rapid convergence of the series, which may not occur.

3. Site-Site approach. It is the one most popular for simulations. Decompose the energy for a molecular pair into a sum of site-site interactions. (The sites often coincide with the atomic nuclei, but they do not have to) The site-site interactions are central (only depend on distance between the sites).



Example:
$$U(r, \omega_1, \omega_2) = \sum_{\alpha\beta} u(r_{\alpha\beta})$$

 $r_{\alpha\beta}$ is the separation of atom α in molecule 1 and atom β in molecule 2.

Use, e. g., LJ for $u(r_{\alpha\beta})$

For N_2 - N_2 , there are 4 such atom-atom terms. For CH₄-CH₄, there are 25 such atom-atom terms.

This will become impractical for a 'large' molecule.

Use 'fused' atom approaches; e. g., CH₃OH (methanol) fuse CH₃ unit to one 'effective' atom (site).

Can put point dipoles/quads on sites too



Electrostatic (Charge) Interactions (for Molecules)

In order to model the interactions as electrostatic, we need to first discuss why an electrostatic picture of a molecule is appropriate. By electrostatic, we mean that the molecule can be described as a classical distribution of charge. A molecule is a quantum object, *but*, an implication of the Born-Oppenheimer approximation is that a molecule in a definite electronic state does act like a classical charge distribution. This may be best appreciated from the Hellmann-Feynman theorem [Hellman "Einfuhrung in der Quantumchemie," 1937; Feynman, *Phys. Rev.* **56**, 340 (1939)]

This states that

$$\frac{\partial E_{k}}{\partial \lambda} = \left\langle \psi_{k} \left| \partial H \right| \left\langle \partial \lambda \right| \psi_{k} \right\rangle$$

where ψ_k is an exact eigenfunction of the system in state *k*, E_k its corresponding energy, and λ a parameter.

If we take $\lambda = R_{AB}$, the separation between two molecules, then $\frac{\partial E_k}{\partial R_{AB}} = -f_{AB}$, the force between the two molecules. And $E_k(R_{AB})$ follows by integration.



We will apply this to the BO energy [cf. 'Quantum Chemistry,' I. Levine, Vol. I, Sec. 14.5]

$$\left(\hat{T}_{el} + V\right)\psi_{el} = U\psi_{el}$$

where $V = V_{el} + V_{NN}$ and $U = U(\mathbf{R}^N)$, the BO potential energy surface.

The Electrostatic theorem, (the Helmann-Feynman theorem applied to $\partial U / \partial R_{\mu}$) with R_{μ} a nuclear coordinate for the μ th nucleus in molecule A, reads:

$$\nabla_{\mu}U = -F_{\mu} = -Z_{\mu}\int \gamma_{B}(\mathbf{r})\frac{1}{\left|\mathbf{r}-\mathbf{R}_{\mu}\right|}d^{3}r$$

where $\gamma_B = -\rho_B(\mathbf{r}) + \sum_{\nu \in B} Z_{\nu} \delta(\mathbf{r} - \mathbf{R}_{\nu})$

 $\rho_{\rm B}(\mathbf{r})$ is the electronic density of molecule B obtained by a Q. M. calculation. The second term arises from the nuclear charges. The nucleus μ in molecule A feels a force F_{μ} arising from all the nuclei in molecule B, and from the electronic density in B.

Then, the interaction energy between those two charge distributions is given from electrostatics as

$$E_{es}(AB) = \iint \frac{\gamma_A(\mathbf{r}_1 | \{R_A\}) \gamma_B(\mathbf{r}_2 | \{R_B\})}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3 r_1 d^3 r_2$$

(This is just a fancy form of Coulomb's law - appropriate to continuous charge distributions)

Define
$$\phi_A(\mathbf{r}_2) = \int \frac{\gamma_A(\mathbf{r}_1|\{R_A\})}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3 r_1.$$
 $\gamma_A = -\rho_A(\mathbf{r}_1) + \sum_{\mu \in A} Z_\mu \delta(\mathbf{r}_1 - \mathbf{R}_\mu)$

It is an integral version of Poisson's equation,

$$\nabla^2 \phi_A = -\frac{1}{4\pi} \gamma_A,$$

which follows, since

$$\nabla_{r_1}^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = -\frac{1}{4\pi} \delta(\mathbf{r}_1 - \mathbf{r}_2).$$

Then, $E_{es}(AB) = \int \phi_A(r_2) \gamma_B(r_2 | \{R_B\}) d^3 r_2$.

 ϕ_A is the potential set up by molecule A at r_2 . γ_B is the charge distribution of molecule B.

Now, it is very lengthy, as a practical matter, to have to integrate over a charge distribution. So, what is done is to replace γ_A and γ_B by a distribution of point charges that will lead to the same result as E_{es} .

Thus, we simplify E_{es} to U_{es} as

$$U_{es} = \iint \frac{\sum_{\alpha} q_{\alpha} \delta(\mathbf{r}_{1} - \widetilde{\mathbf{R}}_{\alpha}) \sum_{\beta} q_{\beta} \delta(\mathbf{r}_{2} - \widetilde{\mathbf{R}}_{\beta})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d^{3}r_{1} d^{3}r_{2} = \sum_{\beta} \sum_{\alpha} \frac{q_{\alpha} q_{\beta}}{\widetilde{\mathbf{R}}_{\alpha\beta}}$$

where $\tilde{\mathbf{R}}_{\alpha\beta}$ is distance between charge site α and charge site β on molecule A and B, respectively. The charges q_{α} are not the same as the atomic charges Z_{μ} . The charge locations $\tilde{\mathbf{R}}_{\alpha}$ are not the same as the nuclear sites \mathbf{R}_{μ} .

Therefore, as a model for the intermolecular potential, we write

$$U = U_{LJ} + U_{es}.$$

How to know which charge values and locations to pick? Certainly sounds non-trivial but there are two general procedures. Also, the multipole expansion idea tells you that the details of a charge distribution "disappear" the further you get from the charge distribution. (FIX FIGURE distance designations wrong.)



Write
$$\widetilde{\mathbf{R}}_{\alpha\beta} = \mathbf{R} + \mathbf{r}_{\alpha} + \mathbf{r}_{\beta}$$
.

R is the vector between the centers of the

charge distributions. Expand $1/\widetilde{\mathbf{R}}_{\alpha\beta}$ in powers of

$$l/R$$
, as on page 2.

Then, get
$$U_{es} = \frac{C_1 C_2}{R} - \frac{C_1 \mu_2}{R^2} \cos \theta_2 - \frac{\mu_1 \mu_2}{R^3} (\text{angles}) + \dots$$

with
$$C_1 = e \sum_{\alpha} q_{\alpha}$$
 and $\mu = \sum_{\alpha} q_{\alpha} e \mathbf{r}_{\alpha}$ $Q = \sum_{\alpha} q_{\alpha} e \mathbf{r}_{\alpha} \mathbf{r}_{\alpha}$

corresponding to charge-charge, charge-dipole, dipole-dipole, . . . , interactions. This is the multipole expansion (in inverse powers of R).

Note that since all we can measure are the multipolar moments: C, μ , Q, etc., if we pick the charges $\{q_{\alpha}\}$ to fit known data, then we have done as well as we can.

Or, pick the $\{q_{\alpha}\}$ to fit the results of full-blown *ab initio* quantum chemical calculations in the sense of successfully reproducing, e. g., the potential surfaces for the interaction between a dimers, the dimerization energy, the geometry, etc. The RESP procedure used in AMBER does this. Gaussian has Merz-Kollman method to fit *ab initio* charge distributions to point charges. See e.g. Kollman et al. J. Phys. Chem. 97, 10269 (1993) for methods developments.

Using these charges to define the electrostatic part of the potential along with the LJ parts defines the force field.

Then, consider statistical mechanical properties: Heat capacity, heat of vaporization, radial distribution functions, hydrogen bond analysis (if appropriate), self-diffusion coefficients, NMR relaxation times, orientational correlation functions.

TIPS (Transferable Intermolecular Potentials)

Want parameters of the intermolecular potential that can be transferred from, e.g., methanol to ethanol, to . . .

$$U = \sum_{\alpha} \sum_{\beta} \left(\frac{q_{\alpha} q_{\beta}}{r_{\alpha\beta}} + \frac{A_{\alpha} A_{\beta}}{r_{\alpha\beta}^{12}} - \frac{C_{\alpha} C_{\beta}}{r_{\alpha\beta}^{6}} \right)$$

Note: this introduces parameters $A_{\alpha}(B_{\beta})$ and $C_{\alpha}(C_{\beta})$ specific to the two interacting atoms. i.e., not e.g. $C_{\alpha\beta}/r_{\alpha\beta}^6$ that is dependent on a particular pair of sites, $\alpha\beta$. See Jorgensen *JACS* **103**, 335-350-(1981).

Sometimes, use Lorentz-Berthelot combining rules (see McQuarrie, Statistical Mechanics):

In order to do methanol, aggregate CH₃ into a united atom 3-site model, as above.

Rigid object; no vibrational motion. This assumption permits bigger MD time steps, as we don't have to worry about the fast vibrational time scale.

Geometry from:	gas phase values
	liquid phase values

Dipole moment enhanced due to dispersion forces (see below for a discussion).

Charges do not have to be on the atomic sites. For example, a quadrupole model for Nitrogen is as follows: (See Allen & Tildesely Nitrogen model)

The charges and distances are chosen to give the correct Nitrogen quadrupole moment $Q = \sum q_{\alpha} r_{\alpha}^2$



A lot of force-field development deals with the *intramolecular* part of the potential.

Fit quantum chemistry data on: vibrational frequencies, dipole moments, derivatives of the energy...

There is a great deal of freedom (for better of worse) in designing an internal force field. To see some of the problems consider water.

For water, a harmonic approximation would give (3N-6=3 internal degrees of freedom)

$$V = \frac{1}{2} k_{HO} (\delta r_{HO})^{2} + \frac{1}{2} k_{HO} (\delta r_{H'O})^{2} + \frac{1}{2} k_{HH'} (\delta r_{HH'})^{2} + k_{HO,H'O} (\delta r_{HO}) (\delta r_{H'O}) + k_{HO,HH'} (\delta r_{HO}) (\delta r_{HH'}) + k_{HO,HH'} (\delta r_{H'O}) \delta r_{HH'}$$

Would be 4 force constants Only 3(3) - 6 = 3 vibrational frequencies observed experimentally.

Two approaches:

1. "Physicists" central force field. Force constant and square of internuclear separation

$$V \approx \frac{1}{2} k_{HO} \left(\delta r_{HO} \right)^2 + \frac{1}{2} k_{HO} \left(\delta r_{H'O} \right)^2 + \frac{1}{2} k_{HH} \left(\delta r_{H'H} \right)^2$$

Two constants, k_{HO} , k_{HH}

2. "Chemists" valence-bond force field. Use bond lengths and bond *angles*

$$V = \frac{1}{2} k_{HO} \left(\delta r_{HO}\right)^2 + \frac{1}{2} k_{HO} \left(\delta r_{HO}\right)^2 + \frac{1}{2} k_a \left(\delta\alpha\right)^2$$
$$\delta\alpha = \theta - \theta_0 \qquad \qquad \theta_0 \text{ is equilibrium angle.}$$

Two constants, k_{HO} , k_{α}

(Last term often written as $\frac{1}{2}k'_{\alpha}(r_0\delta\alpha)^2$, with r_0 a length to make k'_{α} have same units as stretch.)

Neither approach is completely satisfactory, but valence-bond seems better than central.

Can add terms, when data available; e. g.,

$$\frac{1}{2}k_{HO,\alpha}\left(\delta\alpha\,\delta r_{HO}+\delta\alpha\,\delta r_{H'O}\right)$$

bond stretching-angle bending interaction.

MD programs adopt the valence-bond approach.

(ALL Force Fields ARE A COMPROMISE BETWEEN SPECIFICITY AND GENERALITY)

A typical force field will have terms schematized as follows:



Polarizable Liquids

Nonadditivity of the intermolecular potential is a consequence of the electronic polarizability (α) of atoms and molecules. Consider the following: The gas phase dipole moment of water is about 1.8 D; in liquid water, the experimental dipole moment is about 2.4 D. Why? In the liquid, the total dipole moment is $\mu + \langle p \rangle$, the sum of the permanent moment μ , plus the averaged induced moment.

Nonadditivity from polarization is particularly important when dealing with nonuniform systems. For example, around an ion.

The induced dipole on the *i*th site in a particular molecule is

$$\mathbf{p}_i = \alpha_i \mathbf{E}_i$$

where the field falling on this site is \mathbf{E}_i .

The equations for these fields are:

$$\mathbf{E}_{i} = \mathbf{E}_{i}^{0} - \sum \mathbf{T}_{ij} \cdot \mathbf{p}_{j}$$
$$\mathbf{p}_{i} = \alpha_{i} \mathbf{E}_{i} = \alpha_{i} \mathbf{E}_{i}^{0} - \sum_{j \neq i} \alpha_{i} \mathbf{T}_{ij} \cdot \mathbf{p}_{j}$$

where the field on the *i*th site from the charges at the q_i sites in the other molecules is

$$\mathbf{E}_i^0 = -\nabla_i \sum_{j \neq i} q_j \frac{1}{r_{ij}} = \sum_{j \neq i} q_j \frac{\mathbf{r}_{ij}}{r_{ij}^3}$$

The induced-dipole-induced-dipole interaction tensor between the *ij* sites is (this form is just another way of writing what we wrote in terms of angles before.)

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3} \Big[1 - \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} \Big] \qquad \hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij} / |\mathbf{r}_{ij}|$$

The polarization energy from these induced dipoles then is (see Section I) (remember, it was the moment induced by a dipole field)

$$U_{pol} = -\frac{1}{2} \sum_{i=1}^{N} \mathbf{p}_i \cdot \mathbf{E}_i^0$$

Solve this scheme either by matrix inversion or by iteration to self-consistency. That is, given a configuration of molecules, solve the above linear equations for the p_i .

From these p_i evaluate U_{pol} .

For water, if such a scheme is pursued, with the *gas* phase polarizibility of the water molecule approximated by using its value on the oxygen site, then the average total dipole moment per molecule is about 2.4 D.



Diffusion Coefficient

Tagged particle (tracer)



 $(\mathbf{r}(t) - \mathbf{r}(0)) \cdot (\mathbf{r}(t) - \mathbf{r}(0))$ $\delta \mathbf{r}(t) \equiv \mathbf{r}(t) - \mathbf{r}(0)$ $\delta \mathbf{r}(t) \cdot \delta \mathbf{r}(t) = \delta x^{2}(t) + \delta y^{2}(t) + \delta z^{2}(t)$

 $D = \frac{\left(\delta \mathbf{r}(t)\right)^2}{6t}$ means add up over many trajectories and divide by number of such trajectories.

So for 256 Argon atoms, it is easy to do this. Add the independent records.

For one atom, you get

Averaging over 256 atoms you get

