Intermolecular interactions

Monday, October 10, 2016
SBU:CHE/PHY/BME 558, Physical & Quantitative Biology
Rutgers University: Chemical Thermodynamics
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Molecular interaction potentials

Potential energy (kJ/mol)

Internuclear distance, $r$ (pm)

Observed bond distance in $\text{H}_2$

$r = 45$

$r = 74$

$r = 150$

$r = 300$

$-432$
Uncharged molecules and atoms can interact

Uncharged atoms and molecules can interact! They participate in covalent and noncovalent interactions:

- Particles **attract** each other when they are close
- Particles **repel** each other when they are **too** close, due to the Pauli exclusion principle.

Interactions between particles can be described through a potential \( u(r) \) and the corresponding force \( f(r) \):

\[
 u(r) = \frac{\text{const}}{r^p} \\
 f(r) = -\frac{du(r)}{dr} = p\frac{\text{const}}{r^{p+1}}
\]
Atomic Force Microscopy (AFM)

Molecular interactions can be directly observed by Atomic Force Microscopy (AFM).
Inter- and intramolecular forces by AFM

Intermolecular interaction forces by AFM

Intramolecular interaction forces by AFM

Molecular structure by AFM
Short-range versus long-range interactions

Interaction potentials are typically described by power functions:

\[ u(r) = \alpha r^{-p} = \frac{\alpha}{r^p} \]

Interactions are considered:

- short-ranged if \( p > 1 \)
- long-ranged if \( p \leq 1 \)

(This tells whether flux decreases with distance)
Electrostatic origins of short-range interactions

Charged particles have long-ranged electrostatic interactions ($p=1$).

Particles without net charge interact by **short-ranged interactions** ($p>1$), for three reasons:

1) Atoms and molecules interact as multipoles;

2) Multipolar atoms or molecules orient freely;

3) They become multipoles under external induction

We will discuss these effects one by one.
Multipole expansion
Multipole expansion of scalar functions

Scalar angular functions can be expanded into a series of spherical harmonics.

\[ f(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_l^m Y_l^m(\theta, \varphi) \]

\( Y_l^m(\theta, \varphi) \) are spherical harmonics:

- **l = 0**
- **l = 1**
- **l = 2**
- **l = 3**
Spatial charge distributions $\rho(x, y, z) = \rho(r)$ can be described by a multipole expansion.

<table>
<thead>
<tr>
<th>Moment</th>
<th>Description</th>
<th>Mathematical Expression</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th</td>
<td>monopole (charge, a scalar)</td>
<td>$\int_V \rho(r) dV = q$</td>
<td>Monopole</td>
</tr>
<tr>
<td>1st</td>
<td>dipole (dipole moment, a vector)</td>
<td>$\int_V r \rho(r) dV = qd = \mu$</td>
<td>Dipole</td>
</tr>
<tr>
<td>2nd</td>
<td>quadrupole (quadruple moment, a tensor)</td>
<td>$\int_V [3r_i r_j - (r_i)^2 \delta_{ij}] \rho(r) dV = [Q_{ij}]$</td>
<td>Quadrupole</td>
</tr>
<tr>
<td>3rd</td>
<td>octupole (a 3-dimensional tensor)</td>
<td></td>
<td>Octupole</td>
</tr>
</tbody>
</table>
Multipole expansion: Electricity and magnetism

Dipole

Quadrupole

Octupole
Pivoting shortens the range of interactions

The potential energy of a dipole oriented at angle $\theta$ relative to an external field of a charge is:

$$u(r, \theta) = -\frac{q\mu}{4\pi\varepsilon_0 Dr^2} \cos(\theta) = -E\mu \cos(\theta) = u_0 \cos(\theta)$$

If the dipole can freely rotate in all directions, it sweeps over a sphere, giving an average:

$$\langle u(r) \rangle = \frac{\int_0^\pi u(r, \theta) e^{-\frac{u(r,\theta)}{kT}} \sin(\theta) d\theta}{\int_0^\pi e^{-\frac{u(r,\theta)}{kT}} \sin(\theta) d\theta}$$

Using the approximation:

$$e^{\pm \frac{u}{kT}} \approx 1 \pm \frac{u}{kT}$$

$$\langle u(r) \rangle = -\frac{u_0^2}{3kT} = -\frac{1}{3kT} \left( \frac{q\mu}{4\pi\varepsilon_0 D} \right)^2 \frac{1}{r^4}$$
## Multipole-multipole interaction ranges

### Multipoles with fixed orientation:

<table>
<thead>
<tr>
<th>Multipole Type</th>
<th>Interaction Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monopole-monopole</td>
<td>$1/r$</td>
</tr>
<tr>
<td>Monopole-dipole</td>
<td>$1/r^2$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$1/r^3$</td>
</tr>
<tr>
<td>N-pole with M-pole</td>
<td>$1/r^{(N+M-1)}$</td>
</tr>
</tbody>
</table>

### Multipoles that are free to rotate:

<table>
<thead>
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<th>Multipole Type</th>
<th>Interaction Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monopole-monopole</td>
<td>$1/r$</td>
</tr>
<tr>
<td>Monopole-dipole</td>
<td>$1/r^4$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$1/r^6$</td>
</tr>
</tbody>
</table>
London dispersion forces and polarizabilities

Attractive interactions exist everywhere, even between particles lacking net charge. This is because uncharged objects can polarize by redistributing their charges. These forces are called **London** (or **dispersion**) **forces**.

The dipole moment induced by a small external electric field is proportional to the field:

\[ \mu_{\text{ind}} = \alpha E \]

If the external electric field is strong, higher-order terms appear in the induced electric dipole moment:

\[ \mu_{\text{ind}} = \alpha E + \beta E^2 + \gamma E^3 + \ldots \]
Charge polarizes a neutral atom and attracts it

If a charge approaches a neutral atom, it polarizes and attracts it. Assume that a charge $Q$ is at distance $r$ from the center of a neutral atom. It causes a polarization – effectively, charges $+q$ and $-q$ separated by a distance $\Delta r$.

The force acting on the polarized atom is:

$$f = -qE \left( r - \frac{\Delta r}{2} \right) + qE \left( r + \frac{\Delta r}{2} \right) \approx q\Delta r \frac{dE}{dr} = \mu_{ind} \frac{dE}{dr} = \alpha E \frac{dE}{dr}$$

$$f = -2\alpha \left( \frac{Q}{4\pi \varepsilon_0 D} \right)^2 \frac{1}{r^5}$$

$$u(r) = -\frac{\alpha}{2} \left( \frac{Q}{4\pi \varepsilon_0 D} \right)^2 \frac{1}{r^4}$$

This is a short-range interaction (since $p>1$)
The Lennard-Jones potential

Two neural atoms can induce polarization in each other and interact electrostatically.

The energy of polarized atom #2 is:
\[ u_2 = \mu_2 E_1 = -\alpha E_1^2 = -\frac{\alpha \mu_1^2}{(4\pi\epsilon_0 D)^2 r^6} \]

For polarized atom #1:
\[ u = \mu_1 E_2 = -\alpha E_2^2 = -\frac{\alpha \mu_2^2}{(4\pi\epsilon_0 D)^2 r^6} \]

Then the total interaction energy is:
\[ u(r) = \frac{u_1 + u_2}{2} = -\frac{\alpha \mu^2}{(4\pi\epsilon_0 D)^2 r^6} \]

This is a possible attractive term in the widely used Lennard-Jones potential (in addition to rotating dipoles):

\[ u(r) \approx \frac{a}{r^{12}} - \frac{b}{r^6} \]
Real gas. Van der Waals model

Johannes Diderik van der Waals (1837 –1923)
Towards the real gas law

The ideal gas model assumes no interactions between the particles. This assumption is relaxed in real gas models. What is the total energy of all interactions? Our goal will be to derive the “real gas law”. We need $U$ and $S$ for this because...

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

Choose a particle and calculate $U'$, the total energy of all interactions it has. We consider shells of radius $r$ and sum up all interaction energies, assuming energies $= u(r)$.

For a single shell: 
\[
dU' = \rho 4\pi r^2 u(r)dr
\]

For all shells: 
\[
U' = 4\pi \rho \int r^2 u(r)dr
\]

For all atoms: 
\[
U = 2\pi N \rho \int r^2 u(r)dr
\]
The real gas: Internal energy

Assume that the interaction potential takes the form:

\[ u(r) = \begin{cases} 
\infty, & r < r^* \\
-u_0 \left( \frac{r^*}{r} \right)^6 & r \geq r^* 
\end{cases} \]

Therefore, the internal energy of the real gas is:

\[ U = -2\pi u_0 \frac{N^2}{V} (r^*)^6 \int_{r^*}^{\infty} \frac{dr}{r^4} = -\frac{2\pi u_0 (r^*)^3}{3} \frac{N^2}{V} \]

where

\[ a = \frac{2\pi u_0 (r^*)^3}{3} \]
## The real gas: Entropy

We will use a lattice model to derive the entropy of a real gas. Starting with the multiplicity $W$:

\[
W = \frac{M!}{N!(M-N)!} \quad \Rightarrow \quad \frac{S}{k} = -N \ln \left( \frac{Nb_0}{V} \right) - \left( \frac{V}{b_0} - N \right) \ln \left( 1 - b_0 \frac{N}{V} \right)
\]

Above we substituted $M = V/b_0$ because $V/M = b_0$ is the volume of a lattice site.

Reminder:

<table>
<thead>
<tr>
<th>Case</th>
<th>Configuration</th>
<th>Volume</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Diagram A" /></td>
<td>5 cells</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Diagram B" /></td>
<td>4 cells</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Diagram C" /></td>
<td>3 cells</td>
<td>1</td>
</tr>
</tbody>
</table>
The real gas law; van der Waals equation

Now we use free energy to establish the real gas law: \( F = U - TS \)

\[
F = -a \frac{N^2}{V} + kT \left[ N \ln \left( \frac{Nb_0}{V} \right) + \left( \frac{V}{b_0} - N \right) \ln \left( 1 - b_0 \frac{N}{V} \right) \right]
\]

We calculate the pressure from:

\[
p = \left( \frac{\partial F}{\partial V} \right)_{T,N} = -a \frac{N^2}{V^2} + \frac{kT}{b_0} \ln \left( 1 - b_0 \frac{N}{V} \right)
\]

Approximate:

\[
\ln(1 - x) \approx -x - \frac{x^2}{2}
\]

Ideal gas law

\[
p \approx kT \frac{N}{V} + \frac{1}{2} \frac{kT}{b_0} \left( \frac{b_0 N}{V} \right)^2 - a \frac{N^2}{V^2}
\]

Approximate: \( 1 + \frac{x}{2} \approx \frac{1}{1 - \frac{x}{2}} \)

This is the van der Waals equation.
The van der Waals fluid exhibits phase transition

Series of isotherms based on the van der Waals equation:

\[ p \approx \frac{NkT}{V - Nb} - a \frac{N^2}{V^2} \]

Notice that there are 3 \( V \) values corresponding to some \( p \) values.

Two are stable – these are phases.
Radial distribution functions: bulk structure

We assumed that particles are evenly distributed in space: \( \rho(x, y, z) = \frac{N}{V} = \text{const} \).

In reality, interacting particles can cluster in space. This is expressed as: \( \rho g(r) \)

Radial distribution function or pair correlation function \( g(r) = \frac{\text{actual density}}{\text{mean density}} \)

Particles in a single shell: \( 4\pi r^2 \rho g(r)dr \)  Nearest neighbors: \( N_1 = 4\pi \rho \int_0^B r^2 g(r)dr \)

Total energy of all interactions for 1 particle: \( U' = 4\pi \rho \int r^2 u(r) g(r)dr \)
Potentials of mean force

Another perspective: consider how often two solvent molecules are found at distance $r$.

This is actually the radial distribution function $g(r)$.

We can define a free energy corresponding to $g(r)$: $w(r) = -kT \ln[g(r)]$

Are nearest-neighbor approximations good? If $u(r) \propto r^{-6}$ \[ \Rightarrow U(r) \propto r^{-4} \]

\[ N \propto 4\pi r^2 \]

Nearest neighbors give 92.4% of total energy.
Appendix: Derivation, tumbling dipole

\[
\langle u(r) \rangle \approx \frac{\int_{0}^{\pi} u(r, \theta)[1 - \frac{u(r, \theta)}{kT}] \sin(\theta) d\theta}{\int_{0}^{\pi} [1 - \frac{u(r, \theta)}{kT}] \sin(\theta) d\theta} = \\
\int_{0}^{\pi} \cos(\theta) \sin(\theta) d\theta - \frac{u_{0}^{2}}{kT} \int_{0}^{\pi} \cos^{2}(\theta) \sin(\theta) d\theta \\
\int_{0}^{\pi} \sin(\theta) d\theta - \frac{u_{0}^{2}}{kT} \int_{0}^{\pi} \cos(\theta) \sin(\theta) d\theta \\
\left. -u_{0} \int_{1}^{1} xdx + \frac{u_{0}^{2}}{kT} \int_{1}^{1} x^{2}dx \right] = -\frac{u_{0}^{2}}{3kT} \\
\left. [-\cos(\pi) + \cos(0)] + \frac{u_{0}}{kT} \int_{1}^{1} xdx \right]
\]