Intermolecular interactions

Wednesday, September 24, 2015
SBU: CHE/PHY558, Physical & Quantitative Biology
Lecturer: Gábor Balázs
Uncharged molecules and atoms can interact

Uncharged atoms and molecules can still participate in covalent and noncovalent interactions.

Particles repel each other when they are very close, due to the Pauli exclusion principle (no 2 fermions in same quantum state).

But they often attract each other when they are close.

Particles interact through a potential $u(r)$ and the corresponding force $f(r)$:

$$f(r) = -\frac{du(r)}{dr} \quad u(r) = (\text{const})r^{-p}$$

Interactions are considered:
- short-ranged if $p>3$
- long-ranged if $p\leq3$
Electrostatic interactions act between particles with net charge and are long-ranged ($p=1$).

However, electrostatic forces can also give rise to short-range interactions, in three different ways:

1) Atoms and molecules may be multipoles with short-range interactions;
2) When multipolar atoms or molecules are free to orient, their interactions are even shorter-ranged;
3) When atoms and molecules become multipoles under external induction, their interactions are even shorter-ranged

We will be discussing these cases one by one.
Multipole expansion of charge distributions

Spatial charge distributions can be described by a multipole expansion.

\[ \rho(x, y, z) = \rho(\mathbf{r}) \]

0\textsuperscript{th} moment: \textit{monopole}. \[ \int_V \rho(\mathbf{r})dV = Q \] (charge, a scalar)

1\textsuperscript{st} moment: \textit{dipole}. \[ \int_V \mathbf{r}\rho(\mathbf{r})dV \] (dipole moment, a vector)

2\textsuperscript{nd} moment: \textit{quadrupole}. \[ \int_V [3r_ir_j - (r_i)^2 \delta_{ij}] \rho(\mathbf{r})dV \] (quadruple moment, a tensor)

...
Spatial charge distributions can be described by a multipole expansion.

\[ \rho(x, y, z) = \rho(r) \]

- 0th moment: **monopole**.
  \[ \int_V \rho(r) dV = Q \]  (charge, a scalar)

- 1st moment: **dipole**.
  \[ \int_V \mathbf{r} \rho(r) dV \]  (dipole moment, a vector)

- 2nd moment: **quadrupole**.
  \[ \int_V [3r_i r_j - (r_i)^2 \delta_{ij}] \rho(r) dV \]  (quadruple moment, a tensor)

A dipole can be: **permanent** or **induced**.

Dipole is characterized by:
- dipole moment: \( \mathbf{\mu} = q \mathbf{d} \)
The potential created by two opposite charges is:

\[
\psi(r) = -\frac{q}{4\pi\varepsilon_0 Dr_-} + \frac{q}{4\pi\varepsilon_0 Dr_+}
\]

The charges are at distances \( r_- \) and \( r_+ \) from the center:

\[
r_- = \left(x + \frac{d}{2}\right)^2 + y^2 = x^2 + y^2 + xd + \left(\frac{d}{2}\right)^2 \approx r^2 \left(1 + \frac{dx}{r^2}\right) \quad \text{and} \quad r_+ \approx r^2 \left(1 - \frac{dx}{r^2}\right)
\]

\[
\psi(r) \approx q \frac{\left(\frac{dx}{r^2}\right)}{4\pi\varepsilon_0 Dr} = \frac{\mu \cos \theta}{4\pi\varepsilon_0 Dr^2}
\]

\[
\psi(r) = \frac{\mu}{4\pi\varepsilon_0 Dr^2} \frac{r}{r}
\]
The energy of a dipole in an electric field

Consider a dipole that can rotate around a fixed center in an electric field \( E \). We calculate the energy needed to rotate it from angle \( \pi/2 \) (perpendicular to field) to angle \( \theta \):

\[
w = \int fda \quad f_c = f\sin(\theta) \text{ is the force component against which work rotates one charge.}
\]

The displacement of each charge as the dipole turns is: \( ad\theta \)

\[
\delta w = fda = -f_c (ad\theta) = -qEa\sin(\theta)d\theta
\]

The total work (and potential energy) is:

\[
w = -2Eqa\int_{\pi/2}^{\theta} \sin(\theta') d\theta' = E\mu \cos(\theta)
\]
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:

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

If the dipole can freely rotate in all directions, it sweeps and averages over a sphere:

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

Using the approximation: $e^{\pm \frac{u}{kT}} \approx 1 \pm \frac{u}{kT}$

$$\langle u(r) \rangle = -\frac{u_0^2}{3kT} = -\frac{1}{3kT} \left( \frac{q \mu}{4\pi \varepsilon_0 D} \right)^2 \frac{1}{r^4}$$
Shortening the range of interactions

**Fixed orientation:**

- Monopole-monopole: $1/r$
- Monopole-dipole: $1/r^2$
- Dipole-dipole: $1/r^4$

**Free to rotate:**

- Monopole-monopole: $1/r$
- Monopole-dipole: $1/r^4$
- Dipole-dipole: $1/r^6$
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:

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

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

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

This is a short-range interaction ($p>3$)
The Lennard-Jones potential

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

The force acting on each polarized atom is:

\[ f \approx -\alpha \frac{\mu}{2\pi \varepsilon_0 D r^3} \frac{dE}{dr} \]

Then the potential is:

\[ u(r) \approx -\frac{\alpha}{2} \left( \frac{\mu}{2\pi \varepsilon_0 D} \right)^2 \frac{1}{r^6} \]

This is the attractive term in the widely used Lennard-Jones potential:

\[ u(r) \approx \frac{a}{r^{12}} - \frac{b}{r^6} \]
The real gas: Internal energy

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? 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: $\rho 4\pi r^2 u(r) dr$

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

For all atoms: $U = 2\pi N \rho \int r^2 u(r) dr$

Assume: $u(r) = \begin{cases} \infty, & r < r^* \\ -u_0 \left( \frac{r^*}{r} \right)^6 & \end{cases}$

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

Therefore, the internal energy of the real gas is:

$U = -a \frac{N^2}{V}$

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 assumed that $V/M = b_0$ is the volume of a lattice site.

<table>
<thead>
<tr>
<th>Case</th>
<th>Configuration</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>3</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:

\[
1 + \frac{x}{2} \approx \frac{1}{1 - \frac{x}{2}}
\]

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

This is the van der Waals equation.
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 \( g(r) = \text{(actual density)}/\text{(mean density)} \)

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 $u(r) \propto r^{-6}$, then $U(r) \propto r^{-4}$

$N \propto 4\pi r^2$

Nearest neighbors give 92.4% of total energy.