Intermolecular Interactions

- the fact that all molecules aggregate at low enough $T$ reflects the universal presence of attractive interactions between molecules or between parts of a single molecule

- estimate the strength of intermolecular attractions à la Stone* using only the boiling point, $T_b$:

$$\Delta_{vap} H \approx 10RT_b \approx \frac{1}{2} N_A z \varepsilon$$

which predicts a pair interaction strength $\varepsilon$ of:

$$\varepsilon \approx \frac{20}{z} k_B T_b$$

Some Values of $\varepsilon$

<table>
<thead>
<tr>
<th>System</th>
<th>$T_b$ / K</th>
<th>$z$</th>
<th>$(20T_b/z)$ / K</th>
<th>$\varepsilon_{obs}/k_B$ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.2</td>
<td>12</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Xe</td>
<td>166</td>
<td>12</td>
<td>277</td>
<td>281</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>111.5</td>
<td>12</td>
<td>186</td>
<td>144</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>352.3</td>
<td>12</td>
<td>587</td>
<td>~428</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>373.2</td>
<td>4</td>
<td>1866</td>
<td>~2400</td>
</tr>
</tbody>
</table>

• intermolecular interactions can be approximately grouped into four categories:

1. **electrostatic (+/-)**
   - interactions between the permanent charge distributions of molecules (i.e. dipole-dipole, dipole-quadrupole, etc.)

2. **dispersion (-)**
   - interactions due to the instantaneous correlations between the electronic motions in two molecules

3. **short-range repulsion (+)**
   - interactions due to the overlap of filled electronic orbitals & atomic cores

4. **inductive (-)**
   - interactions between the permanent charge distribution of one molecule and the electronic polarizability of a second molecule (e.g. dipole-induced dipole, etc.)
1. Electrostatic Interactions; Multipole Expansion

• Leech considers the electrical potential $\phi_{el}$ at a distant point B that is created by a pair of charges near A:

$$\phi_{el}(B) = \frac{1}{4\pi\varepsilon_0} \left( \frac{q_1 + q_2}{r_1} + \frac{q_1}{\sqrt{r^2 + z_1^2 + 2rz_1\cos\theta}} + \frac{q_2}{\sqrt{r^2 + z_2^2 - 2rz_2\cos\theta}} \right)$$

$$= \frac{1}{4\pi\varepsilon_0} \left( \frac{q_1 + q_2}{r} + \frac{(q_2z_2 - q_1z_1)}{r^2} + \frac{(q_1z_1^2 + q_2z_2^2)}{2r^3} + \ldots \right) \quad r > z_1, z_2$$

• the last expression shows that $\phi_{el}(B)$ can be expressed in terms of the multipole moments of the A charge distribution: the net charge $q$, the dipole moment $\mu$, the dipole moment, the quadrupole moment $\Theta$, etc.
more generally, for a distribution of charge due to a molecule centered at A:

\[
\phi^A_{el}(B) = \frac{1}{4\pi\varepsilon_0} \sum_a \frac{q_a}{|R - \vec{a}|}
\]

\[
\simeq T q - T_\alpha \mu_\alpha + \frac{1}{3} T_{\alpha\beta} \mu_{\alpha\beta} - \frac{1}{15} T_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} + \ldots \quad \vec{R} > \vec{a}
\]

where \( \alpha, \beta, \gamma \) are cartesian coordinates \((x, y, z)\), repeated indices imply summation, and the \( T \)s are the spatial derivatives:

\[
T^{(n)}_{\alpha\beta\ldots\nu} = \frac{1}{4\pi\varepsilon_0} \frac{\partial}{\partial R_\alpha} \frac{\partial}{\partial R_\beta} \ldots \frac{\partial}{\partial R_\nu} \quad \text{i.e.} \quad T = \frac{1}{4\pi\varepsilon_0} \quad T_{xy} = \frac{1}{4\pi\varepsilon_0} \frac{\partial}{\partial x} \frac{\partial}{\partial y} \quad \text{etc.}
\]

this expansion enables the electrostatic interaction between two molecules A and B to be expressed:

\[
V_{el}^{AB} = q^B \phi^A_{el} + \mu^B_\alpha \frac{\partial}{\partial \alpha} \phi^A_{el} + \Theta^B_{\alpha\beta} \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} \phi^A_{el} + \Omega^B_{\alpha\beta\gamma} \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} \frac{\partial}{\partial \gamma} \phi^A_{el} + \ldots \quad \vec{R} > \vec{a}, \vec{b}
\]

1st moment of B charge
1st deriv. of el. potential from A
no overlap of A and B charge dists.
• the multipole moments of a molecule are given by:

\[ q = \sum_{\text{charges } a} q_a \quad \text{charge} \]

\[ \mu_\alpha = \sum_{\text{charges } a} q_a a_\alpha \quad (\alpha = x, y, \text{or } z) \quad \text{dipole moment} \]

\[ \Theta_{\alpha\beta} = \sum_{\text{charges } a} q_a \left( \frac{3}{2} a_\alpha a_\beta - \frac{1}{2} a^2 \delta_{\alpha\beta} \right) \quad \text{quadrupole moment} \]

\[ \Omega_{\alpha\beta\gamma} = \sum_{\text{charges } a} q_a \left\{ \frac{5}{2} a_\alpha a_\beta a_\gamma - \frac{1}{2} a^2 \left( a_\alpha \delta_{\beta\gamma} + a_\beta \delta_{\alpha\gamma} + a_\gamma \delta_{\alpha\beta} \right) \right\} \quad \text{octopole moment} \]

• For a continuous charge distribution \( \rho(\mathbf{r}) \) the summations in these equations are simply replaced by integrals. For example:

\[ \mu_x = \sum_a q_a x_a = \int \rho(\mathbf{r}) x d\mathbf{r} \quad \Theta_{xy} = \sum_a \frac{3}{2} q_a x_a y_a = \int \frac{3}{2} \rho(\mathbf{r}) x y d\mathbf{r} \]

\[ \Theta_{zz} = \sum_a q_a \left( \frac{3}{2} z_a^2 - \frac{1}{2} r_a^2 \right) = \int \rho(\mathbf{r}) r^2 \left( \frac{3}{2} z^2 - \frac{1}{2} r^2 \right) d\mathbf{r} \]

• “2^n-poles”:

\[ q \quad (n=0) \quad \mu \quad (n=1) \quad \Theta \quad (n=2) \quad \Omega \quad (n=3) \]
Electrical Potentials of Multipoles $n=0-2$

\[ \phi_q \propto \frac{1}{r} \]

\[ \phi_{\theta z} \propto \frac{3 \cos^2 \theta - 1}{3r^3} \]

\[ \phi_{\mu z} \propto \frac{\cos \theta}{r^2} \]
• some examples of quadrupole moments of molecules

\[ \Theta_{zz} = \int \rho(\vec{r})r^2 \left( \frac{3}{2} \cos^2 \theta - 1 \right) d\vec{r} \]

(node) \( \frac{1}{2}(3\cos^2\theta - 1) \)

(a) \( +1 \)

(b) CO_2

(c) HF

(d) HCCCH

(e) C_6H_6

(f) H_2O

Fig. 2.1 from A. J. Stone, *The Theory of Intermolecular Forces* (Oxford, 1996)

• some important units:

charge \( q \): \( 1e = 1.6022 \times 10^{-19} \) C

dipole moment \( \mu \): \( 1 \text{ } ea_0 = 8.478 \times 10^{-30} \) C m = 2.5418 D

quadrupole moment \( \Theta \): \( 1 \text{ } ea_0^2 = 4.487 \times 10^{-40} \) C m^2 = 1.354 D Å
• some explicit forms for interaction energy:

\[ V_{\mu\nu} = \frac{\mu_A \mu_B}{4\pi\varepsilon_0 r^3} \{2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \phi\} \]

\[ V_{\mu\Theta} = \frac{\mu_A \Theta_B}{4\pi\varepsilon_0 r^4} \frac{3}{2} \{\cos \theta_A (3 \cos^2 \theta_B - 1) - \sin \theta_A \sin 2\theta_B \cos \phi\} \]

\[ V_{\mu\Theta} = \frac{\Theta_A \Theta_B}{4\pi\varepsilon_0 r^5} \frac{3}{4} \{1 - 5 \cos^2 \theta_A - 5 \cos^2 \theta_B - 15 \cos^2 \theta_A \cos^2 \theta_B \]

\[ + 2(4 \cos \theta_A \cos \theta_B - \sin \theta_A \sin 2\theta_B \cos \phi)\} \]

Note: \( \theta_A = \theta_1, \theta_B = \theta_2; \phi = \phi_1 - \phi_2 \) in figure.

• quadrupole forms assume a linear quadrupole with the symmetry axis chosen as \( z \) with: \( \Theta_{zz} = \Theta \) and \( \Theta_{xx} = \Theta_{yy} = -\frac{1}{2} \Theta \)

• the factor: \( 4\pi\varepsilon = 1.11265 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2} \) is appropriate for the SI unit system
2. Dispersion Interactions

- also “London” dispersion forces after F. London (1930) who first gave QM explanation
- long-range attraction, universally present
- dominant in nonpolar systems like He, Xe, CH₄, CCl₄...
- due to correlated electron motions on two molecules
- understand using Drude model of harmonically bound es:

\[ V(r) \approx -\frac{3\hbar \omega e^4}{4(4\pi\varepsilon_0)^2 k^2} \frac{1}{r^6} \quad r \to \infty \]

- London formula is:

\[ V(r) \approx -\frac{3 I_1 I_2 \alpha_1 \alpha_2}{2 I_1 + I_2} \frac{1}{r^6} \]

molecules 1 & 2, \( \alpha = \) polarizability, \( I = \) ionization energy

- leading term in expansion in 1/r:
3. Short-Range Repulsion

- also called “exchange-repulsion” or just “exchange” energy
- 2 effects: electron exchange between two molecules (-) and Pauli repulsion between $e$ of like spin (+)
- net is repulsive and of exponential form (like overlap of $\Psi$)

$$V_{sr}(r) \approx A \exp(-\beta r)$$

Fig. 6.2 from A. J. Stone, *The Theory of Intermolecular Forces* (Oxford, 1996)
4. Inductive Interactions

- result from permanent charge moments on one molecule inducing an electronic polarization in another molecule
- attractive

\[ V_{q\alpha}(r) = -\frac{q^2 \alpha}{(4\pi\varepsilon_0)^2} \frac{1}{r^4} \]
\[ V_{\mu\alpha}(r) \propto -\frac{\mu^2 \alpha}{r^6} \]
\[ V_{\Theta\alpha}(r) \propto -\frac{\Theta^2 \alpha}{r^8} \]

induction is non-additive:

\[ -2\alpha\mu^2/(4\pi\varepsilon_0)^2R^6 \]
\[ -8\alpha\mu^2/(4\pi\varepsilon_0)^2R^6 \]
\[ 0 \]

Fig. 4.1 from A. J. Stone, *The Theory of Intermolecular Forces* (Oxford, 1996)
• although the interaction between two dipoles varies as $r^{-3}$, thermal averaging leads to

$$< V_{\mu\mu} >_T = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{(4\pi\varepsilon_0)^2 k_B T} \frac{1}{r^6}$$

• thus, all attractive interactions between dipolar molecules scale (at long range) as $r^{-6}$

$$< V_i >_T = -\frac{B_i}{r^6}$$

which allows their magnitudes to be compared in a general manner

Table 4-5  Relative magnitudes of intermolecular forces between two identical molecules at 0°C.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dipole moment (debye)</th>
<th>Dipole</th>
<th>Induction</th>
<th>Dispersion $B \times 10^7$ (J m$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>102</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1460</td>
</tr>
<tr>
<td>c-C$<em>6$H$</em>{12}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1560</td>
</tr>
<tr>
<td>CO</td>
<td>0.10</td>
<td>0.0018</td>
<td>0.0390</td>
<td>64.3</td>
</tr>
<tr>
<td>HI</td>
<td>0.42</td>
<td>0.550</td>
<td>1.92</td>
<td>380</td>
</tr>
<tr>
<td>HBr</td>
<td>0.80</td>
<td>7.24</td>
<td>4.62</td>
<td>188</td>
</tr>
<tr>
<td>HCl</td>
<td>1.08</td>
<td>24.1</td>
<td>6.14</td>
<td>107</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1.47</td>
<td>82.6</td>
<td>9.77</td>
<td>70.5</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.84</td>
<td>203</td>
<td>10.8</td>
<td>38.1</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>2.87</td>
<td>1200</td>
<td>104</td>
<td>486</td>
</tr>
</tbody>
</table>

Table from, Prauznitz et al. *Molecular Thermodynamics of Fluid Phase Equilibria* (Prentice-Hall, 1999)
Ab Initio Calculations of Intermolecular Interactions

Calculated Ne$_2$ Potentials

Ne$_2$ Potentials - Calc & Expt

- calculating dispersion energies is hard; (BSSE)