Lecture 6
Interaction forces II –
Tip-sample interaction forces

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<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-ion electrostatic</td>
<td>$U(r) = \frac{Q_1 Q_2}{4\pi \varepsilon_0 r}$</td>
</tr>
<tr>
<td>Dipole-charge electrostatic</td>
<td>$U(r) = -\frac{Q p \cos(\theta)}{4\pi \varepsilon_0 r^2}$</td>
</tr>
<tr>
<td>Dipole-dipole electrostatic</td>
<td>$U(r) = -\frac{p_1 p_2 [2 \cos(\theta_1) \cos(\theta_2) - \sin(\theta_1) \sin(\theta_2) \cos(\phi)]}{4\pi \varepsilon_0 r^3}$</td>
</tr>
<tr>
<td>Angle-averaged electrostatic (Keesom force)</td>
<td>$U_{\text{Keesom}}(r) = -\frac{p_1^2 p_2^2}{3 (4\pi \varepsilon_0)^2 k_B T r^6}$</td>
</tr>
<tr>
<td>Angle-averaged induced polarization force (Debye force)</td>
<td>$U_{\text{Debye}}(r) = -\frac{p_1^2 \alpha_{02} + p_2^2 \alpha_{01}}{(4\pi \varepsilon_0 \varepsilon)^2} \frac{1}{r^6}$</td>
</tr>
<tr>
<td>Dispersion forces act between any two molecules or atoms (London force)</td>
<td>$U_{\text{London}}(r) = -\frac{3 \alpha_{01} \alpha_{02}}{2 (4\pi \varepsilon_0 \varepsilon)^2} \frac{(I_1)(I_2)}{I_1 + I_2} \frac{1}{r^6}$</td>
</tr>
</tbody>
</table>

Adapted from J. Israelachvilli, “Intermolecular and surface forces".
Relative values of Van der Waals force components are presented in **Table 1** [3].

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\chi, m^3 \times 10^{18}$</th>
<th>$d, \text{D}$</th>
<th>$I, \text{eV}$</th>
<th>$C_{\text{Keesom}} \times 10^{79} \text{J.m}^6$</th>
<th>$C_{\text{Debye}} \times 10^{79} \text{J.m}^6$</th>
<th>$C_{\text{London}} \times 10^{79} \text{J.m}^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.667</td>
<td>0</td>
<td>13.6</td>
<td>0</td>
<td>0</td>
<td>6.3</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.57</td>
<td>0</td>
<td>13.6</td>
<td>0</td>
<td>0</td>
<td>41.3</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.74</td>
<td>0</td>
<td>15.8</td>
<td>0</td>
<td>0</td>
<td>59.3</td>
</tr>
<tr>
<td>Ar</td>
<td>1.6</td>
<td>0</td>
<td>15.8</td>
<td>0</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>He</td>
<td>0.2</td>
<td>0</td>
<td>24.7</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>1.99</td>
<td>0.12</td>
<td>14.3</td>
<td>0.0034</td>
<td>0.057</td>
<td>67.5</td>
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<tr>
<td>HCl</td>
<td>2.63</td>
<td>1.03</td>
<td>13.7</td>
<td>18.6</td>
<td>5.4</td>
<td>105</td>
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<tr>
<td>H$_2$O</td>
<td>1.48</td>
<td>1.84</td>
<td>18.0</td>
<td>197</td>
<td>10</td>
<td>48.8</td>
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<tr>
<td>NH$_3$</td>
<td>2.24</td>
<td>1.5</td>
<td>11.7</td>
<td>87</td>
<td>10</td>
<td>72.6</td>
</tr>
</tbody>
</table>

**Table 1.** Magnitudes of polarizability, dipole moment, ionization potential and energies of different weak interactions between various atoms and molecules.

Summary of Coulombic Intermolecular Forces

System of interacting atoms and/or molecules and/or ions

- Is H bonded to O, N or F (permanent dipoles)?
  - NO
  - YES
  - Dipole – dipole Interactions (hydrogen bonding)
    - Dipoles fixed
    - Dipole rotating
    - Ion – dipole Interaction
      - Dipole fixed
      - Coulomb Energy

- Ions Involved?
  - YES
  - Dipole rotating
  - Ion – dipole Interaction
    - Dipole fixed
    - Coulomb Energy

- Are there any atoms or molecules?
  - YES
  - Do the atoms or molecules have a permanent dipole?
    - YES
    - Dipole fixed
    - Coulomb Energy
    - van der Waals Forces
  - NO
  - Induced dipole-induced dipole only
    - London Dispersion
    - Keesom
    - Debye
Interaction between electrically NEUTRAL objects!

Dispersive or van der Waals Force

Uncharged sphere, radius $R$

Uncharged Insulating plate

an Electrodynamic effect!

$F(D) = -A \frac{2R^3}{3D^2(2R+D)^2}$

$A$ = Hamaker’s constant
Putting in some numbers

R = 10 nm; Q = 8 electrons

Attractive Force (nN)

D Surface-to-Surface Separation (nm)

Neutral sphere
Charged sphere

Dielectric plate
Metal plate

Uncharged plate
Implications for AFM

- In AFM the tip usually has native oxide on the tip within which small trapped charges or permanent dipoles can exist. As debris accumulates more permanent dipoles and charges accumulate on tip.

- Dispersion potential $U(r)$ scales as $r^{-6}$ while electrostatics scales as $r^{-1}$ (ion-ion), or $r^{-2}$ (ion-dipole), or $r^{-3}$ (dipole-dipole).

- In reality attractive forces are due to combination of vdW and short range electrostatics (i.e. covalent forces).