The stability of thin (soft) films

Lecture 4 – Dispersion-force contributions
November 13, 2009
The disjoining pressure is a jump in pressure at the boundary. It does not vary between the plates.

\[ \Pi(h) = -\frac{1}{A} \frac{\partial G(h)}{\partial h} \]

Force between 2 spheres:

\[ F_{s-s}(y) \approx \frac{2\pi R_1 R_2}{R_1 + R_2} \int_y^\infty \Pi(h) \, dh \]

\[ \Pi(h) = -\frac{\partial G(h)}{\partial h} \]

\[ G(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S \]

\[ G(\infty) = 0 \]
Review of Lecture 2

\[
\Pi(h) = -\frac{1}{A} \left. \frac{\partial G}{\partial h} \right|_{T,P,\sigma_1,\sigma_2,N_i}
\]

\[
dG = -S^s dT + \sum_{i=1,r} \mu_i dN_i^s + A(\Psi_1 d\sigma_1 + \Psi_2 d\sigma_2) - A\Pi dh
\]

\[
dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2) - A\Pi dh
\]

\[
\Pi = \frac{1}{A} \int_h^\infty \left( \frac{\partial N_i^s}{\partial h} \right)_{\mu_i,\ldots,\Psi_1,\Psi_2} d\mu_i
\]

is a ‘modified’ Gibbs equation. \( -d\sigma = \sum \frac{n_i^e}{A} d\mu_i = \sum \Gamma_i d\mu_i \)

\[
\frac{N_i^s}{A} - \Gamma_i = A \int_h^\infty \left( \frac{\partial \Pi}{\partial \mu_i} \right)_{h,\ldots} dh
\]

is the excess adsorption due to disjoining pressure. Note that we do not know how much excess is on either plate!
For the approach of surfaces at constant potential, $\Phi_0$ is constant.

For the approach of surfaces at constant surface charge density $\Phi_0$ is:

$$\sigma_s = \frac{2z en}{\kappa} \sqrt{2 \left( \cosh \Phi_0 - \cosh \Phi_m \right)}$$
Hertz's interpretation of light oscillations as electromagnetic processes, hides another problem, the processes that take place in a molecular vibrator when it emits light energy into the surrounding space.

This problem leads us into the field of spectral analysis it brings us to, the field of molecular forces.

Having accepted the standpoint of the electromagnetic theory of light, we have to conclude that ponderomotive forces must exist between two light-emitting molecules as between two vibrators in which electromagnetic oscillations have been generated.

A nonlinear force that a charged particle experiences in an inhomogeneous oscillating electromagnetic field. (e.wikipedia.org/wiki/Ponderomotive_force) Lebedev, P.N. Wiedemann Ann., 52, 621 (1894); collected works, Moscow (1913), p. 56

\[ F_p = -\frac{e^2}{4m\omega^2} \nabla E^2 \]
Hamaker’s model (1937)

The intermolecular attraction is due to London (dispersion) energies:

\[ U_{11} = -\frac{3}{2} \Lambda_{11} r^{-6} \]

\[ \Delta G = -\frac{A}{12\pi H^2} \]
Planck (1900)  Energy levels of standing, oscillatory EM waves in a vacuous cavity with conducting walls. The temperature derivative gave heat capacity.

Casimir (1948) Energy levels of standing, oscillatory EM waves across a vacuum between two conducting flat plates. The distance derivative gave the force per unit area.

Lifshitz (1954) Energy levels of standing, oscillatory EM waves across any medium between any two flat plates. The distance derivative gave the force per unit area.
Electromagnetic fluctuations

“Empty space” can be considered as a turmoil of electromagnetic waves of all frequencies and wavelengths.

Absorption frequencies: those at which charges naturally dance or those where charge polarization quells the fluctuations and stills the space between the surfaces.

Retardation occurs when the time it takes for perturbations to be sensed by both particles becomes important.
The modern view – “fluctuation-dissipation”

- Electromagnetic fluctuations abound – quantum and thermal
- Producing spontaneous, transient electric and magnetic fields
- Which have the strongest effects at absorption frequencies.
- Net forces are coordinated interactions, averaged over time.
- Calculate “dispersion” forces from optical spectra.
The absorption (or reflection) spectrum is measured. Sometimes a single peak in the UV and an average IR is sufficient.

The dielectric spectrum is calculated from the absorption spectrum. The only additional information needed is the static dielectric constant.
Dielectric permittivity – how a material responds to an electric field

Imaginary frequency – field varies exponentially rather than sinusoidally

Optical data:

\[ \varepsilon''(\omega) = 2n_{ref}\kappa_{abs} \]

Reflectivity

\[ \text{Reflectivity}_{\text{normal}} = \frac{(n_{ref} - 1)^2 + \kappa_{abs}^2}{(n_{ref} + 1)^2 + \kappa_{abs}^2} \]

Kramers-Kronig relation:

\[ \varepsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \varepsilon''(\omega)}{\omega^2 + \xi^2} d\omega \]

Why imaginary frequencies – the functions are smooth. Dielectric constants vary wildly with real frequency (near peaks).

For a system of dipole and resonant-damped oscillators:

\[ \varepsilon(i\xi) = 1 + \sum_{j} \frac{d_j}{1 + \xi\tau_j} + \sum_{j} \frac{f_j}{\omega_j^2 + g_j\xi + \xi^2} \]
Sample spectral parameters

$$\varepsilon(i\xi) = 1 + \sum_{j} \frac{d_j}{1 + \xi \tau_j} + \sum_{j} \frac{f_j}{\omega_j^2 + g_j \xi + \xi^2}$$

<table>
<thead>
<tr>
<th></th>
<th>Polystyrene</th>
<th>Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four-term fit</td>
<td>UV frequencies only</td>
<td>Four-term fit</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.35</td>
<td>14.6</td>
<td>9.7</td>
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<tr>
<td>14.0</td>
<td>96.9</td>
<td>4.95</td>
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<tr>
<td>11.0</td>
<td>44.4</td>
<td>41.55</td>
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<tr>
<td>20.1</td>
<td>136.9</td>
<td>207.76</td>
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<tr>
<td>Four-term fit</td>
<td>To absorption data</td>
<td>Four-term fit</td>
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<td></td>
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<tr>
<td>-</td>
<td>40.11</td>
<td>53.0</td>
</tr>
<tr>
<td>3.87</td>
<td>59.61</td>
<td>5.0</td>
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<tr>
<td>8.37</td>
<td>122.55</td>
<td>104.0</td>
</tr>
<tr>
<td>23.46</td>
<td>1031.19</td>
<td></td>
</tr>
</tbody>
</table>

Parsegian, 2006, pp 268
Lifshitz theory

The Lifshitz constant is a double summation of products of dielectric functions:

\[ \Delta G_{123} = -\frac{A_{123}}{12\pi H^2} \]

\[ A_{123} = \frac{3kT}{2} \sum_{n=0}^{\infty} \Delta_{12}\Delta_{32} \times \text{Re}_n(l) \]

The prime on the summation indicates that the \( n = 0 \) term is given half weight.

The dielectric functions are differences in dielectric constants over a series of imaginary frequencies:

\[ \Delta_{12} = \frac{\varepsilon_1(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_2(i\xi_n)} \quad \text{and} \quad \Delta_{32} = \frac{\varepsilon_3(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_3(i\xi_n) + \varepsilon_2(i\xi_n)} \]

The sampling frequencies are:

\[ \xi_n = n\frac{4\pi^2kT}{h} \]
Sampling (Matsubara) frequencies

The zero frequency term is the static dielectric constant.

Frequencies are evenly spaced such that photon energies, from quantum mechanics, of each frequency is a multiple of thermal energy $kT$, from thermodynamics.

\[ \hbar \xi_n \equiv 2\pi k T n \]
\[ \xi_n \equiv \frac{2\pi k T}{\hbar} n \]

The first sampling frequency corresponds to an IR frequency.

\[ \xi_n (T_{room}) \equiv 2.41 \times 10^{14} n \frac{rad}{s} \]
\[ \lambda_1 = \frac{2\pi c}{\xi_1} = 7.82 \mu m \]

A few more through the IR and visible (excitations are thermal)

Most sampling frequencies are in the UV and x-ray regions (excitations are quantum mechanical)
Lifshitz coefficients

\[ kT_{room} = 4.05 \, \text{zJ} \]

### Lifshitz coefficients

<table>
<thead>
<tr>
<th>Material</th>
<th>( A_{Ham} ) across water (zJ)</th>
<th>( A_{Ham} ) across vacuum (zJ)</th>
<th>Interaction</th>
<th>( A_{Ham}/A_{Ham} (l=0)^{\mu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organics</strong></td>
<td></td>
<td></td>
<td>Hydrocarbon across water</td>
<td>0.95 ( kT_{room} ) = 3.6 zJ.</td>
</tr>
<tr>
<td>Polystyrene(^{26})</td>
<td>13</td>
<td>79</td>
<td>Mica across hydrocarbon</td>
<td>2.1 ( kT_{room} ) = 8.5 zJ.</td>
</tr>
<tr>
<td>Polycarbonate(^{27})</td>
<td>3.5</td>
<td>50.8</td>
<td>Mica across water</td>
<td>3.9 ( kT_{room} ) = 15. zJ.</td>
</tr>
<tr>
<td>Hydrocarbon (tetradecane, Level 1)</td>
<td>3.8</td>
<td>47</td>
<td>Gold across water</td>
<td>28.9 ( kT_{room} ) = 117. zJ.</td>
</tr>
<tr>
<td>Polymethyl methacrylate(^{27})</td>
<td>1.47</td>
<td>58.4</td>
<td>Water across vacuum</td>
<td>9.4 ( kT_{room} ) = 40. zJ.</td>
</tr>
<tr>
<td>Protein(^{28}, 29)</td>
<td>5–9, 12.6</td>
<td>n/a</td>
<td>Hydrocarbon across vacuum</td>
<td>11.6 ( kT_{room} ) = 46.9 zJ.</td>
</tr>
<tr>
<td><strong>Inorganics</strong></td>
<td></td>
<td></td>
<td>Mica across vacuum</td>
<td>21.8 ( kT_{room} ) = 88. zJ.</td>
</tr>
<tr>
<td>Diamond (Iia)(^{30})</td>
<td>138</td>
<td>296</td>
<td>Gold across vacuum</td>
<td>48.6 ( kT_{room} ) = 196 zJ.</td>
</tr>
<tr>
<td>Mica (monoclinic)(^{30})</td>
<td>13.4</td>
<td>98.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica (Muscovite)(^{31})</td>
<td>2.9</td>
<td>69.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz silicon dioxide(^{31})</td>
<td>1.6</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium oxide(^{31})</td>
<td>27.5</td>
<td>145</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide rutile(^{31})</td>
<td>60</td>
<td>181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium chloride (cubic crystal)(^{30})</td>
<td>4.1</td>
<td>55.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water(^{12})</td>
<td>n/a</td>
<td>55.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold(^{33})</td>
<td>90 to 300</td>
<td>200 to 400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver(^{33})</td>
<td>100 to 400</td>
<td>200 to 500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper(^{33})</td>
<td>300</td>
<td>400</td>
<td></td>
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</tr>
</tbody>
</table>

\[ A_{\text{AlN/water/AlN}} = 102.2 \, \text{zJ} \]
\[ A_{\text{Al_{2}O_{3}/water/Al_{2}O_{3}}} = 58.9 \, \text{zJ} (27.5 \, \text{zJ}^{15}) \]
\[ A_{\text{MgO/water/MgO}} = 26.9 \, \text{zJ} \]
\[ A_{\text{SiO_{2}/water/SiO_{2}}} = 6.0 \, \text{zJ} (1.62 \, \text{zJ}^{15}) \]
\[ A_{\text{Si/water/Si}} = 112.5 \, \text{zJ} \]

Parsegian, 2006, pp 19, 64, 265

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Lecture 4 - Dispersion-forces

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The first results – Derjaguin et al

First instrument direct measurements of molecular forces between macroscopic bodies (1951).

Quartz-quartz interactions in vacuum and in air. Lines are for Lifshitz theory (1954).
Calculation vs measurement

Generally:

\[ \varepsilon(i\xi_n) = \frac{c_{ir}}{1 + \left(\frac{\xi_n}{\omega_{ir}}\right)^2} + \frac{c_{uv}}{1 + \left(\frac{\xi_n}{\omega_{uv}}\right)^2} \]

<table>
<thead>
<tr>
<th>direction</th>
<th>(\varepsilon(0))</th>
<th>(\omega_{ir}) (rad/s)</th>
<th>(C_{ir})</th>
<th>(\omega_{uv}) (rad/s)</th>
<th>(C_{uv})</th>
</tr>
</thead>
<tbody>
<tr>
<td>perpendicular</td>
<td>86</td>
<td>(1 \times 10^{14})</td>
<td>80</td>
<td>(7.49 \times 10^{15})</td>
<td>4.77</td>
</tr>
<tr>
<td>parallel</td>
<td>170</td>
<td>(1 \times 10^{14})</td>
<td>163</td>
<td>(7.24 \times 10^{15})</td>
<td>6.01</td>
</tr>
</tbody>
</table>

Larson, I.; et al  
*JACS, 1993, 115, 11885-11890.*

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Lecture 4 - Dispersion-forces  
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Other geometries
Archimedean buoyancy

For pair-wise interactions:

\[ \Sigma_{12} = \Sigma_{12}^{ab} + \Sigma_{12}^{cc} - \Sigma_{12}^{ac} - \Sigma_{12}^{cb} \]

in modern notation, \textit{i.e.} Hamaker constants:

\[ A_{acb} = A_{ab} + A_{cc} - A_{ac} - A_{cb} \]

when \( a = b \):

\[ A_{aca} = A_{aa} + A_{cc} - 2A_{ac} \]

Hamaker geometries

Parallel infinitely extended slabs of fixed thickness \( a \), variable separation \( l \)

\[
- \frac{A}{12\pi l^2} \left( \frac{1}{l^2} - \frac{2}{(l + a)^2} + \frac{1}{(l + 2a)^2} \right)
\]

Infinitely thick wall parallel to cube of finite extent or two parallel cubes of extent \( L \)

\[
- \frac{A}{12\pi l^2} L^2
\]

Spheres, fixed radii \( R_1, R_2 \), near contact

\[
- \frac{A}{6} \left( \frac{R_1 R_2}{R_1 + R_2} \right) \frac{1}{l}
\]

Sphere near a planar thick wall

\[
- \frac{A R}{6} \frac{1}{l}
\]

Spheres, radius \( R \), far apart

\[
- \frac{16A R^6}{9} \frac{1}{z^6}
\]

Small sphere, radius \( R \), far from planar surface of an infinitely thick wall

\[
- \frac{2A}{9} \left( \frac{R}{z} \right)^3
\]

Infinitely long, parallel, circular cylinders, fixed radii \( R \), near contact

\[
- \frac{A R^{1/2}}{24} \frac{1}{l^{3/2}}
\]

Infinitely long thin parallel cylinders

\[
- \frac{3A A_1 A_2}{8\pi} \frac{1}{z'}
\]

Infinitely long cylinders, perpendicular, near contact

\[
- \frac{A R}{6} \frac{1}{l}
\]

Infinitely long cylinders, perpendicular, far apart

\[
- \frac{A A_1 A_2}{2\pi} \frac{1}{z'}
\]