

The stability of thin (soft) films

Lecture 4 – Dispersion-force contributions November 13, 2009

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Review of Lecture 1



The disjoining pressure is a jump in pressure at the boundary. It does not vary between the plates.

$$\Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h} \bigg|_{T,P,\sigma_1,\sigma_2,N_i}$$



Force between 2 spheres: $F_{s-s}(y) \cong \frac{2\pi R_1 R_2}{R_1 + R_2} \int_{y}^{\infty} \Pi(h) dh$ $\Pi(h) = -\frac{\partial G(h)}{\partial h}$ $G(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S$ $G(\infty) = 0$ $\int_{y}^{G(h)} \frac{1}{2} \int_{y}^{1} \frac{Curve \ 1 - Stable}{Curve \ 2 - Metastable}$ $Curve \ 3 - Unstable$

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$$\Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h} \bigg|_{T,P,\sigma_1,\sigma_2,N_i}$$

$$dG = -S^{s}dT + \sum_{i=1,r} \mu_{i}dN_{i}^{s} + A(\Psi_{1}d\sigma_{1} + \Psi_{2}d\sigma_{2}) - A\Pi dh$$

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

$$\Pi = \frac{1}{A} \int_{h}^{\infty} \left(\frac{\partial N_{i}^{s}}{\partial h} \right)_{\mu_{i},\dots,\Psi_{1},\Psi_{2}} d\mu_{i}$$

is a 'modified" $\left(-d\sigma = \sum \frac{n_i^{\sigma}}{A} d\mu_i = \sum \Gamma_i d\mu_i\right)$

$$\frac{N_i^s}{A} - \Gamma_i = A \int_h^\infty \left(\frac{\partial \Pi}{\partial \mu_i} \right)_{h...} dh$$

is the excess adsorption due to disjoining pressure. Note that we do not know how much excess is on either plate!

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Review of Lecture 3



For the approach of surfaces at constant potential, Φ_0 is constant.

For the approach of surfaces at constant surface charge density Φ_0 is:

$$\sigma_{s} = \frac{2zen}{\kappa} \sqrt{2(\cosh \Phi_{0} - \cosh \Phi_{m})}$$

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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 (1**894**); collected works, Moscow (**1913**), p. 56



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Hamaker's model (1937)





- 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.



"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.

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- 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.



Data for dielectric functions

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_{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:

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

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 $\mathcal{E}(i\xi_n)$



$\varepsilon(i\xi) = 1 + \sum_{j} \frac{d_{j}}{1 + \xi\tau_{j}} + \sum_{j} \frac{f_{j}}{\omega_{j}^{2} + g_{j}\xi + \xi^{2}}$ Sample spectral parameters

	Polystyrene	
Four-term fit	UV frequencies only	
6.35	14.6	0.65
14.0	96.9	5.0
11.0	44.4	3.5
20.1	136.9	11.5
	Gold	
Four-term fit	To absorption data	
-	9.7	3.21
2.9	4.95	0.67
4.0	41.55	2.22
8.9	207.76	8.50
Four-term fit	To absorption data	
-	40.11	-
3.87	59.61	2.62
8.37	122.55	6.41
23.46	1031.19	27.57
Four-term fit	To absorption data	
-	53.0	1.8
3.0	5.0	0.8
4.8	104.0	4.4

Parsegian, 2006, pp 268



Lifshitz theory

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

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

$$A_{123} = \frac{3kT}{2} \sum_{n=0}^{\infty} \Delta_{12} \Delta_{32} \times \operatorname{Rel}_{n}(l)$$

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:

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

The sampling frequencies are:

$$\xi_n = n \frac{4\pi^2 kT}{h}$$

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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.

The first sampling frequency corresponds to an IR frequency.

$$\hbar \xi_n \equiv 2\pi kTn$$
$$\xi_n \equiv \frac{2\pi kT}{\hbar}n$$

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

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)

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$$kT_{room} = 4.05 \ zJ$$



Lifshitz coefficients

Material	A _{Ham} across water (zJ)	A _{Ham} across vacuum (zJ)	
Organics			
Polystyrene ²⁶	13	79	
Polycarbonate ²⁷	3.5	50.8	
Hydrocarbon (tetradecane, Level 1)	3.8	47	
Polymethyl methacrylate ²⁷	1.47	58.4	
Protein ^{28, 29}	5–9, 12.6	n/a	
Inorganics			
Diamond (IIa) ³⁰	138	296	
Mica (monoclinic) ³⁰	13.4	98.6	
Mica (Muscovite) ³¹	2.9	69.6	
Quartz silicon dioxide ³¹	1.6	66	
Aluminum oxide ³¹	27.5	145	
Titanium dioxide rutile ³¹	60	181	
Potassium chloride (cubic crystal) ³⁰	4.1	55.1	
Water ³²	n/a	55.1	
Metals			
Gold ³³	90 to 300	200 to 400	
Silver ³³	100 to 400	200 to 500	
Copper ³³	300	400	

Interaction	$A_{\rm Am/Am}(l=0)^a$		
Hydrocarbon across water	$0.95 \ kT_{\rm room} = 3.6 \ z$ J		
Mica across hydrocarbon	$2.1 \ kT_{\rm room} = 8.5 \ z$]		
Mica across water	$3.9 \ kT_{\rm room} = 15. \ z$		
Gold across water	$28.9 \ kT_{\rm room} = 117.$		
Water across vacuum	$9.4 \ kT_{\rm room} = 40. \ z$		
Hydrocarbon across vacuum	$11.6 kT_{\rm room} = 46.9$		
Mica across vacuum	$21.8 \ kT_{\rm room} = 88. \ z_{\rm r}$		
Gold across vacuum	$48.6 kT_{\rm room} = 196 z$		
_{IN/water/AIN} = 102.2 zJ I _{2O3/water/AI2O3} = 58.9 zJ (27.5 zJ ¹⁵)	$A_{AIN/vac/AIN} = 228.5 \text{ zJ}$ $A_{AI_2O_3/vac/AI_2O_3} = 168.7 \text{ zJ} (145 \text{ zJ}^1)$		
$_{\rm IgO/water/MgO} = 26.9 \rm zJ$	$A_{MgO/vac/MgO} = 114.5 \text{ zJ}$		
$c_{\rm r}/water/sic_{\rm r} = 6.0 \text{zI} (1.6 \text{zI}^{15})$	$A_{SiO_2}/vac/SiO_2 = 66.6 zJ (66 zJ^{15})$		

 $A_{Si/vac/Si} = 212.6 \text{ zJ}$

Parsegian, 2006, pp 19, 64, 265

 $A_{Si/water/Si} = 112.5 zJ$

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Derjaguin, B.V.; Churaev, N.V.; Muller, V.M. Surface forces; Consultants Bureau: New York; 1987.



The first results - Derjaguin et al



-3-4 -4 -1 -0,6 -0,2 0

log F

-2

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)

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Calculation vs measurement

Generally:





direction	ε (0)	ω _{IR} (rad/s)	C_{IR}	$\omega_{\text{UV}}(\text{rad/s})$	C_{UV}
perpendicular	86	1 x 10 ¹⁴	80	7.49 x 10 ¹⁵	4.77
parallel	170	1 x 10 ¹⁴	163	7.24 x 10 ¹⁵	6.01



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





For pair-wise interactions:

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

in modern notation, *i.e.* Hamaker constants
$$A_{acb} = A_{ab} + A_{cc} - A_{ac} - A_{cb}$$

when $a = b$:
$$A_{aca} = A_{aa} + A_{cc} - 2A_{ac}$$

Derjaguin, B. (with Obuchov, E.) Ultramicrometric analysis of solvate layers and elementary expansion effects. *Acta Phys.-Chim.*, **1936**, 5(1), 1-22.

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Parsegian, V.A. van der Waals forces; Cambridge University Press: New York; 2006



Hamaker geometries



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 $\frac{A}{6}\frac{R}{l}$