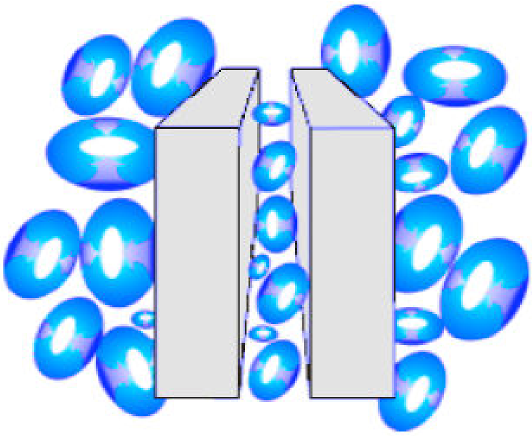
UNIVERSITY OF LJUBLJANA
Faculty of Mathematics and Physics
Department of Physics

VAN DER WAALS FORCES



Franci Bajd

Advisor: prof. dr. Rudolf Podgornik

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Abstract

Hictoric overwiev of van der Waals interaction will be presented in the following seminar and different approaches will be discussed. Pairwise Hamaker approach is first approximation for van der Waals interactions, but can be rigorously complemented by Lifshitz theory, introducing harmonic oscillator surface modes. In stead of exact but complicated Lifshitz theory, the derivations are based on heuristic simplificated approach. Next to theory, some interesting experimental examples and calculations are in the second part of seminar.

1. Contents

2. Introduction

The origin of van der Waals interactions are transient electric and magnetic field arising spontaneously in material body or in vacuum. Fluctuation of charge are governed in two different ways. Besides thermal agitation there are also quantum-mechanical uncertaintes in positions and momenta. Thermal agitation can be neglected in the limit of zero temperature, but Heissenberg quantum uncertainty principle ($\Delta E \Delta t \approx h$) is unavoidable. Van der Waals interactions stand for collective coordinated interactions of moving charges, instantaneous current and field, averaged over time. Due to origin, van der Waals interactions are allways present.

3. Historic overwiev

The theory of van der Waals interactions gradually developed. Interactions are named by Dutch physisist van der Waals, however there are important contibutions of other scientists. Van der Waals formulation of non-ideal gas equation (1870) was revolutiuonary idea for interaction between particles, in well known equation of state for non ideal gas, iteractions (r^{-6}) are implicitely included. That time equation for electric and magnetic field were set by Maxwell. Hertz showed that electromagnetic oscillation could create and absorb electromagnetic waves. Meantime, the pairwise interparticle interactions were considered and the foundations for modern theory of electromagnetic modes between interacting media across other media were established. When van der Waals interaction between two particles were taken into acount, it tended to be generalized on interactions between huge bodies (mesoscopic, 100nm – 100um) comparing to one atom.

One direction of devlopment is summation of pairwise interactions over all constituent atoms and was done by Hamaker (1937). The knowlege of dilute gases, where pairwise interactions could be applied, was applied to solids and liquids. He generalised conviniently known types of two-particle interactions with three sub grups regarding to character of involved diploles: the contribution among permanent dipoles is Keesom interaction, Debye interaction betveen one permanent and one induced dipole and London or dispersion interaction between two induced dipoles. The idea that incremental parts of large bodies interact by $-C/r^6$ energies as though the remaining material were absent is well-intentioned approximation for liqiuds and solids, although the correspondence to reallity is not satisfactory. The pairwise summation is disputable, but it was the first attemption how to consider van der Waals forces between large bodies occuring in scientific and technological processes. Nevertheless Hamaker calculated the significant decreasing in power of distance dependance of free energies from 6 to 2 for planar geometry. The influence of van der Waals interactions is thus larger within mecoscopic bodies.

Another approach is based on Maxwell electrodynamics and problem of blackbody. To solve the problem of heat capacity of blackbox, Planck postulated famous statement, that the fileds of blackbody radiation can be expressed as emission and absorbtion of oscillatory standing waves in walls of the cavity. Changes of energy occur at discrete units (photons hν) with finite value of Plank constant ($h = 6,63\cdot10^{-34}$ Js). Casimir theory (1948), based on electromagnetic modes, benefited from blackbody properties; the force between ideally conducting media was considered as the force in a box having two opposite faces with infinite dimensions. There exist vacuum fluctuations with all allowed frequencies outside the box, but fewer modes within it. The inequality in number of modes results into depletion force as shown on Fig. 1. The most important advantage of this idea was in turning from microscopic thinking about atoms to macroscopic whole. Additional advantage of Casimir work is that zero point electromagnetic fluctuations in vacuum are as valid as fluctuations in charge motions. Heissenberg uncertainty principle predict infinitely large energies for infinitesimaly short fluctuations. We are bathed in physically imposible infinities and therefore effects of divergence is cancelled.

Clear classical analogy of van der Waals interaction in connection with electromagnetic modes is consideration of two boats in rough water (Fig. 1). Empirically, boats are pushed together by waves from all directions except that of wave-quelling neighbour. Van der Waals interactions behave in similar way. The share of quelling is in proportion to the material-absorption spectra. Absorption frequencies are those, at which charges naturally dance and those at which charge polarization quells the vacuum fluctuation. This is the concept of fluctuation-disipation theorem, which states, that the spectrum over which charges in a material spontaneously fluctuate is directly connecs with the spectrum of their ability to absorb electromagnetic waves imposed on them.

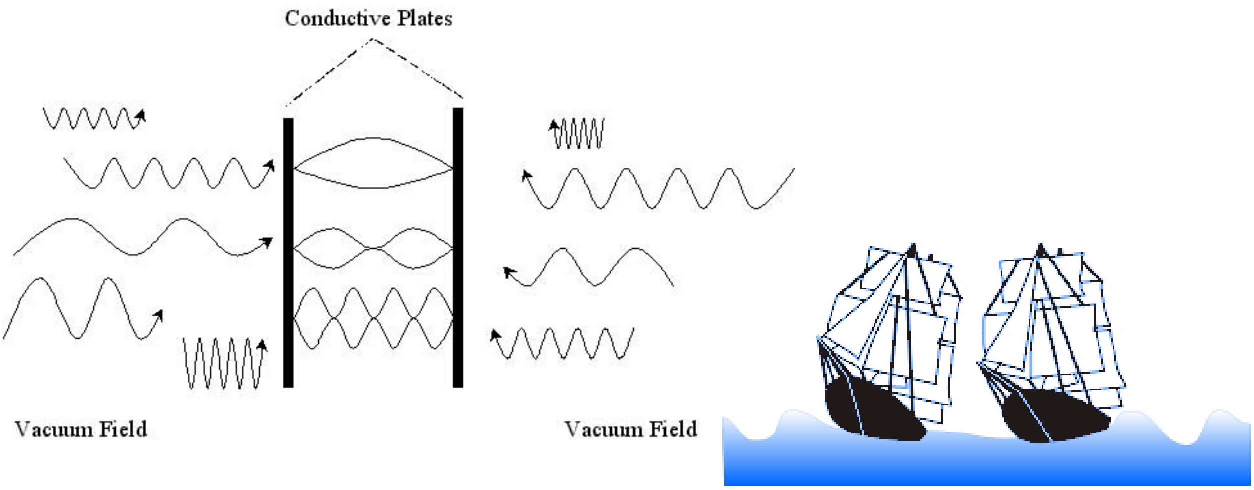


Fig 1: Depletion pressure between Casimir plates [1] and classical analogy with ship attracting on undulating sea level [2].

Another conceptual supplement, which is neglected in Hamaker calculations, is retardation effect. This concept was introduced by Casimir and Polder in the same year (1948) as the use of Planck´s blackbox idea. At large distance between fluctuating charges, the infinite speed of light can not be assumed. It takes finite time for electromagnetic field come from one charge across space to another; meantime the first charge changes its configuration when the second one responses. However there is no first and second corresponding charge, but only the coordinated fluctuation of charges. The intensity of interaction is always reduced, the power in distance of separation for point particles increases from 6 to 7.

The step closer to more common van der Waals interactions was by Lifshitz, Dzyaloshinskii and Pitaevskii (~ 1960). Vacuum gap was replaced by real materaial with its own absorption properties. Following to Casimir work, Lifshitz theory involves macroscopic quantities instead of microscopic. It limits the validity of theory to the scale, where materials look like cotinuua. For determining the stability of mesoscopis solution (colloids), Lifshitz theory is good approximation. In Lifshitz approach the only fluctuations contributing to the force between two media across third one are surface modes, which are alowwed to penetrate the outer media. In gap not all modes are allowed, but outside, what results in depletion force.

Being loyal to historical development of the theory of van der Waals interaction, Lifshitz formulae are tended to be writen in form with Hamaker constant ($G = A_{HAM}/12\pi l^2$ for planar system). Direct proportionality between the magnitude of van der Waals interaction is important. If Hamaker constant is accurately appointed, then the free energy in well defined, as Hamaker constant measures the strength of van der Waals interactions. Van der Waals forces are relatively strong compared to thermal energy. The rule of thumb is, that Hamaker constant is within $1k_BT_{room}$ to $100k_BT_{room}$ for most materials interacting across vacuum and lower for non-vacuum intermediate media. An interesting estimation for strength of van der Waals forces is the case of fly on the ceiling. Fly with downcast head opposes the gravity with van der Waals adhesion. For $A_{HAM} = 10\ k_BT_{room}$, $l = 10$ nm (~ 70 interatomic distance), the forces are balanced if cubically approximated fly has volume 8 cm^3 ($\rho \sim 1\ kg/m^3$) For spherically approximated fly, radius comes to 10^{-3} cm. But why is it impossible to glue 8cm^3 cube on the celing? This principle is in reality used by many animals (Gecko) and was evolutionary developed. To faciliate downcast head living, fly should use golden coated legs and habitate on metal surface, but migration from the surface would be more energy consuming.

Van der Waals interactions are attractive, Hamaker constant is positive. On contrary, there exist examples, where Hamaker constant is negative, leading to repulsion van der Waals interaction. It happens, when dielectric function are $\varepsilon_A > \varepsilon_m > \varepsilon_B$, i.e. dielectric functions of interacting media embrace the dielectric function of intemediate medium. A good example is liquid helium, flowing out the container. Helium is interacting media, air and any container with $\varepsilon_A > \varepsilon_m$ mutually repels if liquid helium is mediator. Helium tends to spread all over the container surface. The thickness of liquid helium depends on the height of liquid. Momentary thickness is run by balance between gravitation and van der Waals contribution, but for shallow container equilibrium thickness is inaccessable, because outside the container liquid helium drops away.

4. Heuristic derivation of Lifshitz´s general result

The interaction between two bodies across an intermediate substance or vacuum is rooted on the electromagnetic fluctuations, which occur in material and also in vacuum. The frequency spectrum of fluctuations is uniquely related to absorbtion spectrum and electrodinamic forces can be calculated from these spectra. Lifshitz (1954) derived the force between the two bodies across vacuum gap from teh Maxwell stress tensor corresponding to the spontaneous electromagnetic fields that arise the gap between boundary surfaces. The gap is Planck-Casimir box. The presentation of original formulation is out of this seminar, but the heuristic (Ninham, Parsegian Weiss, van Kampen) method will be presented, where Lifshitz´s procedure with Green function is omitted and free energy concept is used instead. In the simplified approach the electromagnetic interaction is considered as enery of electromagnetic waves of allowed modes. The allowed frequencies are defined by the material properties and boundary conditions for electromagnetic field. After deriving the interaction energy for one mode, the summation over all allowed modes has to be done. The heuristic approach is an example of elegant theory involving some mathematics and modern concepts in physics (integration per partes, contour integral, imaginary frequencies, eigenfrequencies), although the assumption of pure oscillators even in absorbtion region is far from away from reality. Nevertheless, the results are frequently used ([3], [4], [5], [6], [7]) especialy in limiting forms (1 → 0, c → ∞).

In derivativation for planar system (it can be easily generalized to other geometries [3]) we assume the exsistence of pure sinusoidal oscillations extending over disipative media. Taking into account equidistant eigenenergies for simple harmonic oscillator (HO) we can calculate the free energy from the partition function. The index j designates the j-th oscillation mode across the gap.

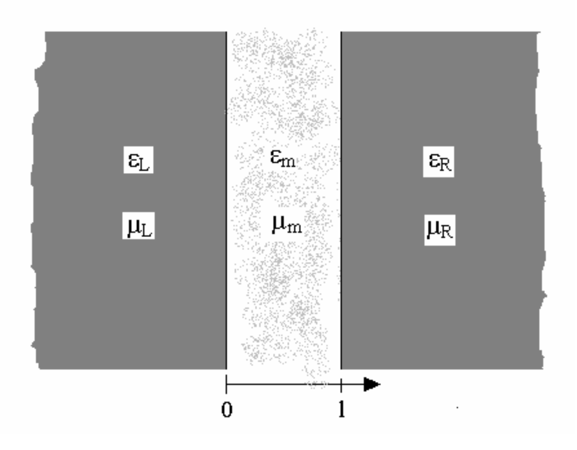


Fig. 2: Two semi-infinite media with a gap.

$$Z(\omega_j) = \sum_{n=0}^{\infty} \exp(\hbar\omega_j (n + \frac{1}{2}) / kT), \qquad \text{Eq. (1)}$$

$$g(\omega_j) = -kT \ln[Z(\omega_j)] = -kT \ln[2\sinh(\hbar\omega_j / 2kT)]. \qquad \text{Eq. (2)}$$

The total free interacting energy is the summation over modes ω_j. Before summation all the eigenmodes have to be found.

Electromagnetic waves obey wave eguation for both electric and magnetic filed. For sake of simplicity and due to evident similarity between both fields, the clear derivation for electric field satisfy and can be applied to magnetic field equations as well.

Electric field is expanded in terms of Fourier components

$$E(t) = \mathrm{Re}\left(\sum_{\omega} E_{\omega} e^{-i\omega t}\right). \qquad \text{Eq. (3)}$$

Which rewrites the wave equation in frequency dependent form

$$\nabla^2 \vec{E} + \frac{\varepsilon\mu\omega^2}{c^2}\vec{E} = 0. \qquad \text{Eq. (4)}$$

In a simple planar system decomposition of electric field vector in components is made

$$\vec{E} = E^x \hat{i} + E^y \hat{j} + E^z \hat{k}. \qquad \text{Eq. (5)}$$

By symmetry we can guess, that the ansatz has the form of free wave in x-y direction because, the system is not limited in x and y directions. The proportional constant in dependent on direction z

$$E_i^j = f_i^j(z) e^{i(ux+vy)}. \qquad \text{Eq. (6)}$$

Index j stands for conponent in coordinate system and index i designates media. It yields to

$$f''(z) - \rho_i^2 f(z) = 0. \qquad \text{Eq. (7)}$$

This diferential equation is solved by exponent functions($f(z) = Ae^{\rho z} + Be^{-\rho z}$) with

$$\rho_i^2 = (u^2 + v^2) - \frac{\varepsilon_i \mu_i \omega^2}{c^2} = \rho^2 - \frac{\varepsilon_i \mu_i \omega^2}{c^2}. \qquad \text{Eq. (8)}$$

The quantity ρ_i^2 is dependent on susceptibilities of certain media. Eigenmodes are defined by boundary conditions. Additional assumptions is made, i.e. there are no free charges present on boundaries, the first Maxwell equation is equal to zero

$$\vec{\nabla} \cdot \vec{E} = 0. \qquad \text{Eq. (9)}$$

Boundary conditions for electromagnetic field are, that tranversal components of E (B) to the wave vector and parallel components of D (H) are preserved. It is obvious that far away from the gap the fields must not diverge. Therefore A_R and B_L are set zero in the solution for amplitude equation.

Considering all boundary condition for electric field we obtain from secular determinant

$$D_E(\omega) \equiv 1 - \left(\frac{\rho_L \varepsilon_m - \rho_m \varepsilon_L}{\rho_L \varepsilon_m + \rho_m \varepsilon_L}\right)\left(\frac{\rho_R \varepsilon_m - \rho_m \varepsilon_R}{\rho_R \varepsilon_m + \rho_m \varepsilon_R}\right) e^{-2\rho_m l} = 0 . \qquad \text{Eq. (10)}$$

Similar expression is obtained for magnetic field as well. New defined function (*dispersion function*) is

$$D(\omega) \equiv D_E(\omega) \cdot D_M(\omega) . \qquad \text{Eq. (11)}$$

It conects magnetic and electric allowed wave modes and has property

$$D(\omega_j) = 0 . \qquad \text{Eq. (12)}$$

Till now we looked for eigenmodes and calculated free energy for one oscillator. To describe interaction between semi-infinite efficintly, we have to sum over all states and to integrate over all wave vectors. We desire to have such an result at the end

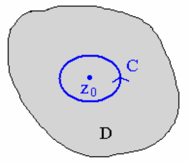
$$G_{LmR}(l) = \frac{1}{(2\pi)^2} \operatorname{Re}\left\{ \int_0^\infty 2\pi\rho [G_l(\rho) - G_\infty(\rho)] d\rho \right\}, \qquad \text{Eq. (13)}$$

where is

$$G_l(\rho) = \sum_{\{\omega_j\}} g(\omega_j) . \qquad \text{Eq. (14)}$$

Usually the free energy at infinite separations between media is zero and we can omit second term of integral over wave vectors. If the calculation was straightforward, we could skip it, but there are still some details to be mentioned. The connection between free energy for harmonic oscillators and dispersion function damands use of *Cauchy integral formula (argument theorem)*

$$\tilde{g}(z_0) = \frac{1}{2\pi i} \oint_C \frac{\tilde{g}(z)}{z - z_0} dz ,$$



Eq. (15)

where $\tilde{g}(z)$ is analytic in a simply conected domain D. For any point z_0 in D and any simple closed path C in D the Cauchy integral formula is valid.
Equation (1) has logaritmic singularities for those frequencies, where sinus hyperbolicus is zero. It occurs at imaginary numbers, so called Matsubara frequencies

$$\omega = i\xi = i\frac{2\pi kT}{\hbar} n .$$

Eq. (16)

The introduction of imaginary frequencies is purely mathematical procedure, helping us sufficiently perform van der Waals interaction with surface modes.
Cauchy integral formula for HO free energies rewrites into

$$\sum_{\{\omega_j\}} g(\omega_j) = \frac{1}{2\pi i} \oint_C g(\omega) \frac{d \ln[D(\omega)]}{d\omega} d\omega . \qquad \text{Eq. (17)}$$

Definition of dispersion relation Eq. (11) with property Eq. (12) suggests, that we can write

$$D(\omega) = \prod_j \left(\omega - \omega_j\right) \qquad \text{Eq. (18)}$$

and the application of Cauchy integral formula seems reasonable.
The path of integration is aroud semicircle (Fig. 3).

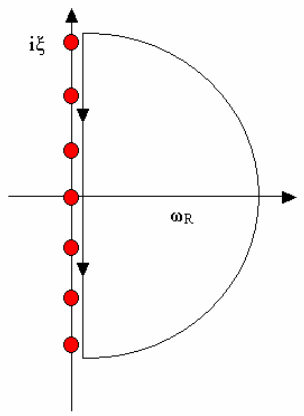


Fig. 3: Path of contour integration for HO partition function.

At integrating on the semicircle the dependence of dielectric response on frequency is taken into account. As frequency approaches to infinity the sistem is not able to follow the excitation and dielectric function is equal to 1 for all materials. Dispersion relation is thus equal to1 in this case and the integrand is zero. The remaining term of integral is

$$G_l(\rho) = \sum_{\{\omega_j\}} g(\omega_j) = \frac{1}{2\pi i} \int_{\infty}^{-\infty} g(i\xi) \frac{d \ln[D(i\xi)]}{d\xi} d\xi \,. \qquad \text{Eq. (19)}$$

After tedious calculations [3, p. 288] the simple form is obtained

$$G_l(\rho) = \frac{kT}{2} \sum_{n=-\infty}^{\infty} \ln[D(i\xi_n)] \,. \qquad \text{Eq. (20)}$$

Although it is not correct, practically we assume that ε is an even function of frequency. Therefore we write another summation, where the prime stands for multiplying n = 0 term by ½.

$$G_l(\rho) = kT \sum_{n=0}^{\infty'} \ln[D(i\xi_n)] \,. \qquad \text{Eq. (21)}$$

The total free energy per unit surface can be expreesed as an integral over all wave numbers. Regarding to the Eq. (8), the low integral boundary is not zero.
Free energy of interaction has different forms, depending on different integral substitutions. The most famous are with wave number as an integral variable or with dimensionless integral variable x. Equations (11), (12) and (22) for free energies are fundamental for calculating van der Waals interactions in heuristic approach of Lifshic theory of van der Waals interactions.

$$G_{LmR}(l) = \frac{kT}{2\pi}\sum_{n=0}^{\infty'}\int_{\varepsilon_m^{1/2}\mu_m^{1/2}\xi_n/c}^{\infty}\rho_m \ln\left[\left(1-\overline{\Delta}_{Lm}\overline{\Delta}_{Rm}e^{-2\rho_m l}\right)\left(1-\Delta_{Lm}\Delta_{Rm}e^{-2\rho_m l}\right)\right]d\rho_m \quad \text{Eq. (22)}$$

$$\overline{\Delta}_{ji} = \frac{\varepsilon_j\rho_i - \varepsilon_i\rho_j}{\varepsilon_j\rho_i + \varepsilon_i\rho_j}, \qquad \Delta_{ji} = \frac{\mu_j\rho_i - \mu_i\rho_j}{\mu_j\rho_i + \mu_i\rho_j} \quad \text{Eqs. (23)}$$

$$\rho_i^2 = \rho_m^2 + \frac{\xi_n^2}{c^2}\left(\varepsilon_i\mu_i - \varepsilon_m\mu_m\right),$$

$$r_n = \frac{2l(\varepsilon_m\mu_m)^{1/2}\xi_n}{c},$$

$$G_{LmR}(l) = \frac{kT}{8\pi l^2}\sum_{n=0}^{\infty'}\int_{r_n}^{\infty} x\ln\left[\left(1-\overline{\Delta}_{Lm}\overline{\Delta}_{Rm}e^{-x}\right)\left(1-\Delta_{Lm}\Delta_{Rm}e^{-x}\right)\right]dx \quad \text{Eq. (24)}$$

Let us mention the third form that is commonly used:

$$G_{LmR}(l) = \frac{kT}{2\pi c^2}\sum_{n=0}^{\infty'}\varepsilon_m\mu_m\xi_n^2\int_1^{\infty} p\ln\left[\left(1-\overline{\Delta}_{Lm}\overline{\Delta}_{Rm}e^{-r_n p}\right)\left(1-\Delta_{Lm}\Delta_{Rm}e^{-r_n p}\right)\right]dp, \quad \text{Eq. (25)}$$

where are

$$s_i = \sqrt{p^2 - 1 + (\varepsilon_i\mu_i/\varepsilon_m\mu_m)}, \qquad \overline{\Delta}_{ji} = \frac{\varepsilon_j s_i - \varepsilon_i s_j}{\varepsilon_j s_i + \varepsilon_i s_j} \quad \text{Eqs. (26)}$$

In the second form of free energy Eq. (24) is the distance of separation explicit. Following to the Hamaker work, it is possible to define free energy as

$$G_{LmR}(l) = -\frac{A_{LmR}}{12\pi l^2} \quad \text{Eq. (27)}$$

Hence the heuristic Lifshitz procedure also produces the Hamaker constat of the form

$$A_{LmR}(l) = -\frac{3kT}{2}\sum_{n=0}^{\infty'}\int_{r_n}^{\infty} x\ln\left[\left(1-\overline{\Delta}_{Lm}\overline{\Delta}_{Rm}e^{-x}\right)\left(1-\Delta_{Lm}\Delta_{Rm}e^{-2x}\right)\right]dx \quad \text{Eq. (28)}$$

Hamaker constant is function of dielectric responses but also distance of separation. In general the Hamaker constant changes with distence of separation.

Till now we did not mention the simplification of infinite velocity of light in heuristic approach. *Pertinent ratio* r_n, the travel time to the fluctuation time ratio, becomes zero for infinite velocity of light. The low integral boundary is then zero and Δ functions are independent on wave number. This approximation is valid for small distances of separation. This approximation is also useful just to estimate the interaction free energy but is less reliable for exact calculations.

Another common simplification in nonretarded limit is to replace logarithm with infnite summation for small Δ functions. It holds for many cases at finite frequencies. It is also possible to expand logarithm for n = 0, where Δ functions are larger (especially if water is solvent, $\Delta \approx 1$), if exponential factor takes care for small argument of logarithm. In this approximation, the integral is solved *per partes*, which leads to additional k^2 in denominator.

$$A_{LmR} = \frac{3kT}{2} \sum_{n=0}^{\infty}{}' \sum_{k=1}^{\infty} \frac{\left(\overline{\Delta}_{Lm} \overline{\Delta}_{Rm}\right)^k}{k^3} \qquad \text{Eq. (29)}$$

The result is rapidly converging summation in k ($k_{max} \sim 30$ instead of infinity) but for the summation in sampling frequencies is better to use larger number for upper boundary of summation ($n_{max} \sim 3000$). This requirement is also physically justified: the first Matsubara frequency starts in IR ($\xi_1 \sim 2.46 \cdot 10^{14}$rad/s ~ 0.162 eV) and to include all frequency range, where the Δ is significant, the n_{max} has to be at least 1000 ($10^3 \cdot \xi_1 \sim 10^{17}$rad/s).

This is the result of Lifshitz´heuristic approach, introduced by Parsegian *et al* [3]. We derived total free energy of interaction and can be used for different geometries and response-functions-dependancies on frequencies.

5. Derjaguin transformation

Refered to Hamaker, Derjaguin (1934) derived equations for non planar geometries. He was aware of complications in curved systems comparing to planar one. Under certain simplifications and assumptions he modified equations for planar system with Derjaguin transformation (Derjaguin approximation), which was applied in nuclear physics as proximity force theorem. The transformation holds when three conditions are fulfilled: The smallest separation between curved surfaces must be small and curvarure radii large (l/R → 0), electromagnetic excitement in one patch are so weak and localized, that they do not perturb excitations in neighbouring patches, and interaction between opposite patches fall off enough with patch separation that closest patches contributions dominate.

As common nonplanar geometry spherical one will be presented in Derjaguin transformation. As it will be shown, term for planar geomery free energy in included in interactions between two spheres. The three assumptions justify small-angle limit. Therefore trigonometric functions, connecting geometric parameters, can be properly expanded in Taylor series.

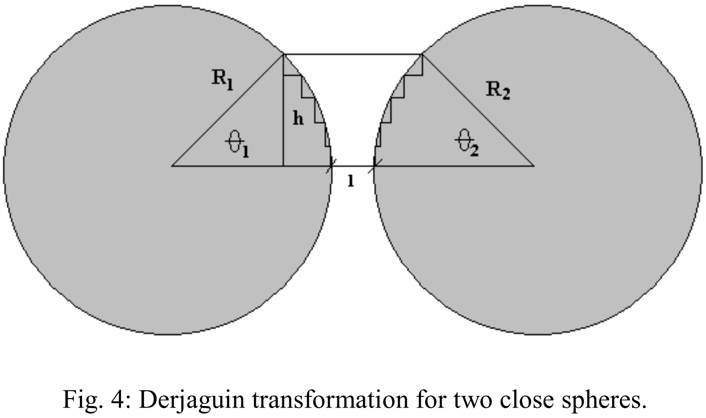


Fig. 4: Derjaguin transformation for two close spheres.

$$h = l + R_1(1-\cos\theta_1) + R_2(1-\cos\theta_2) \approx l + \frac{R_1}{2}\left(1+\frac{R_1}{R_2}\right)\theta_1^2 = l + \alpha\theta_1^2, \qquad \text{Eqs. (30)}$$

$$R_1 \sin\theta_1 = R_2 \sin\theta_2, \qquad R_1\theta_1 \approx R_2\theta_2 .$$

Bringing some new substitutins in, $h = l + \alpha t$, $t = \theta_1^2$ the force between two spheres with radii R_1 and R_2 and the smallest separation *l* is expressed as an integral over all infinitesimaly small planar patches. Assumed rapid convergence of planar patches allows us to set the upper integral boundary to infinity

$$G_{SS}(l; R_1, R_2) = \pi R_1^2 \int_0^\infty G_{PP}(l + \alpha t)dt . \qquad \text{Eq. (31)}$$

where G_{PP} is Eq. (31). Since the force is negative derivative of free energy with respect to separation, the force between two spheres is

$$F_{SS}(l; R_1, R_2) = -\frac{\partial G_{SS}}{\partial l} = \pi R_1^2 \int_0^\infty G'_{PP}(l + \alpha t)dt = \frac{2\pi R_1 R_2}{(R_1 + R_2)} G_{PP}(l) \qquad \text{Eq. (32)}$$

This is famous large quoted Derjaguin transformation for spherical geometry. For interactions between parallel cylindres another but evident geometric expressions are used within the same transformation procedure [3].

6. Derivation of van der Waals interactions in layered planar systems

Approaching to reality, interacting media are not homogenous and isotropic. Special case are basic material coated with thin layers of different absorbtion spectra. The thickness of layers and absorbtion properties of layers are important parameters. On first hand, large metal layers screen interactions between substract media, but on the other side, thin layers with similar spectra as substrat media can be neglected in first approximation.

To express the interaction between layered system we can use the Lifshitz free energy Eq. (24), but secular determinat has to be properly modified [3].

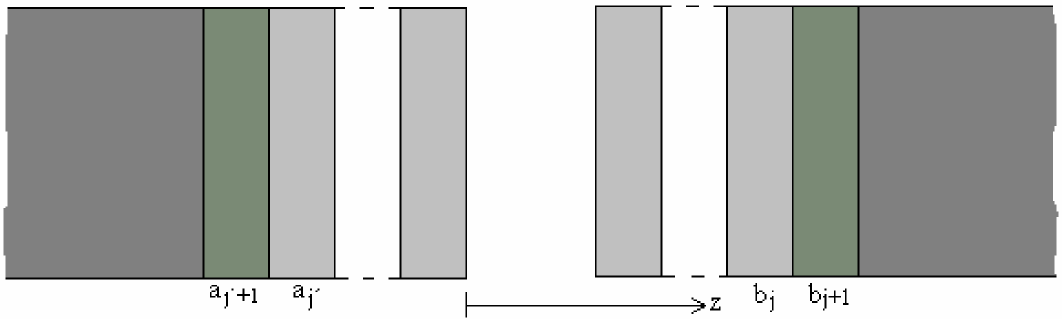


Fig. 5: Van der Waals interaction between two layered media.

Four boundary conditions for Maxwell electrodynamics equation give two equations for coeficients A and B in two successive layers. Exponential terms are not equal to zero, as the origin of coordinate system is positioned as shown on Fig. 5,

$$\left(-A_{i+1}e^{\rho_{i+1}l_{i/i+1}}+B_{i+1}e^{-\rho_{i+1}l_{i/i+1}}\right)\rho_{i+1}=\left(-A_{i}e^{\rho_{i}l_{i/i+1}}+B_{i+1}e^{-\rho_{i}l_{i/i+1}}\right)\rho_{i}, \qquad \text{Eqs. (33)}$$

$$\left(A_{i+1}e^{\rho_{i+1}l_{i/i+1}}+B_{i+1}e^{-\rho_{i+1}l_{i/i+1}}\right)\varepsilon_{i+1}=\left(A_{i}e^{\rho_{i}l_{i/i+1}}+B_{i+1}e^{-\rho_{i}l_{i/i+1}}\right)\varepsilon_{i}.$$

It can be rewriten in matrix form,

$$\begin{pmatrix} A_{i+1} \\ B_{i+1} \end{pmatrix}=\underline{\underline{M}}_{i+1/i}\begin{pmatrix} A_{i} \\ B_{i} \end{pmatrix}, \qquad \text{Eq. (34)}$$

where M is transition matrix. For finite dimension of layer on semi-infinite media, all coeficients A and B in coated layers are nonzero.

The simplest case is one layered semi-infinite media interacting wit another uncoated semi-infinite media. To consider boundary conditions that field components do not diverge, the certain coeficients ($A_R = 0 = B_L$) are zero. Multiplication of matrices is successive and effective transition matrix for right side is used in stead of product of two matrices

$$\begin{pmatrix} 0 \\ B_{R} \end{pmatrix}=\underline{\underline{M}}_{RB_1}\underline{\underline{M}}_{B_1m}\underline{\underline{M}}_{mL}\begin{pmatrix} A_{L} \\ 0 \end{pmatrix}=\underline{\underline{M}}^{eff}_{Rm}\underline{\underline{M}}_{mL}\begin{pmatrix} A_{L} \\ 0 \end{pmatrix}. \qquad \text{Eq. (35)}$$

After exact multiplication of matrices in effective matrix, Rm interface is split into two interfaces, the dispersion relation D has the same form, but Δ function for right side is changed.

$$D_{LmB\,R}(i\xi_n)=\left(1-\overline{\Delta}_{Lm}\overline{\Delta}^{eff}_{Rm}e^{-2\rho_m l}\right)\left(1-\Delta_{Lm}\Delta^{eff}_{Rm}e^{-2\rho_m l}\right), \qquad \text{Eq. (36)}$$

$$\overline{\Delta}^{eff}_{Rm}=\frac{\overline{\Delta}_{RB_1}e^{-2\rho_{B1}b_1}+\overline{\Delta}_{B_1m}}{1+\overline{\Delta}_{RB_1}\overline{\Delta}_{B_1m}e^{-2\rho_{B1}b_1}}.$$

For multilayer systems Δ functions have recursion form [3]. It is proper to mention the attention to distances when calculating, because they differ from layer to layer. The origin of coordinate system is usually placed in the boundary bwtween the intermediate media and first layer on the left medium.

Inhomogenous media in absorption spectrum are treated as coated system with infinitesimaly small layers. The procedure is the same as for system with homogenous and finite large layers, however in nonretarded limit electric waves satisfy the first Maxwell equation with dielectric function inside the braket, on which derivative operator acts. It results in modificated Eq. (7) and qualitatively new form of force versus separation.

$$f''(z)+\frac{d\varepsilon/dz}{\varepsilon(z)}f'(z)-\rho^2 f(z)=0 \qquad \text{Eq. (37)}$$

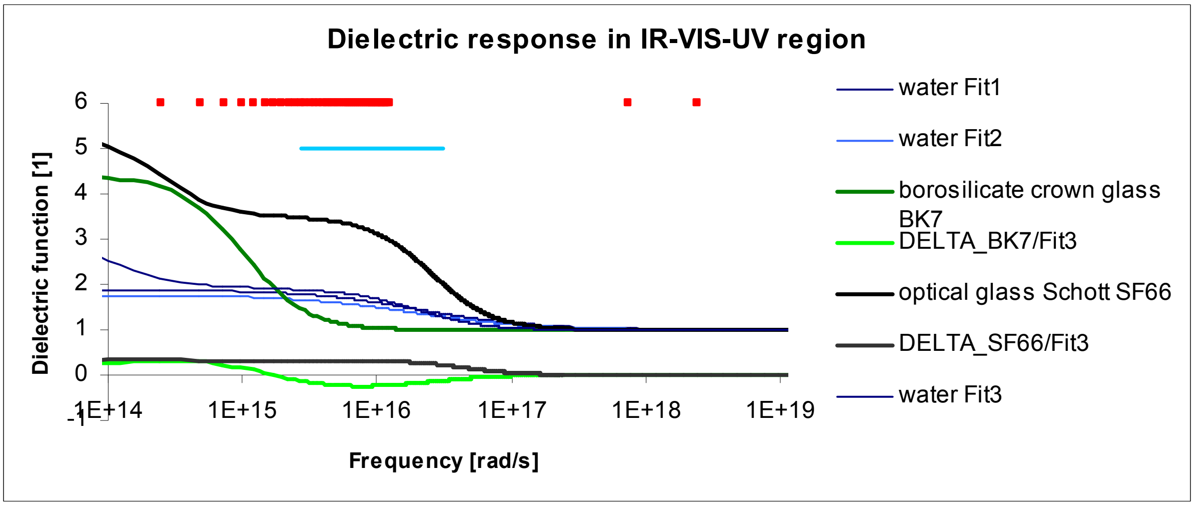
The change compared with Eq. (7) is in additional second term, containing derivative of dielectric function. For homogenous though layerder system with constant dielectric function, second term in Eq. (7) vanish. Another change in procedure for calculating interaction free energy in homogenous media is conversion of diferences into derivatives for the thickness of slice going to zero.

7. Dielectric function

In free energy for planar system Eq. (24), Δ functions of dielectric properties appear. Beacause other geometries are closely connected with planar system, Δ functions must be known for all van der Waals interactions, irrespective of geometry. For fast estimations for interactions A-m-B, where B = A, thus A-m-A, in nonretarded approximation the summation is of order $\sum_{n=0}^{\infty'} \overline{\Delta}_{Am}^{2} \approx 1$. However, for exact calculations dielectric spectroscopic data are needed. Dielectric response function is mathematically performed as complex function. The real part represent the magnitude of (induced) polarization and the imaginary part is directly proportional to Joule heating, which dramatically increases near absorption frequencies. In the same frequency region, real part decreases. Dielectric functions versus frequency are meassured and data are available as fiting parameters of different models. The most widespread is dipole and damped-resonant oscillator model (Sellmeier; Ninham, Parsegian).

$$\varepsilon(i\xi) = 1 + \sum_{i=1}^{M} \frac{d_i}{1+\tau_i \xi} + \sum_{j=1}^{N} \frac{f_j}{1+g_j \xi + \xi^2} \qquad \text{Eq. (38)}$$

Model enables that for infinitely large frequencies dielectric response is equal to 1. First term is contribution of permanent dipole orientation. For some materials dielectric responses are shown od Graph 1. Dielectric response for water is calculated for different fitting parameters ([3], [4], [5], [8]).



Graph 1: Dielectric permittivity function for two glasses and water; Δ are reasonablely small.

For water is common 6 UV/5IR damped-resonant oscillator model and was used as *waterFit3* on Graph 1 [5]. In Graph 1 are shown Δ functions, although in dispersion function Δ^2 is present. Figure show the evidence that $\Delta^2 << 1$. Simplified summation, Eq. (29), based on Taylor expansion of log[D] can be used. Visible region is marked with bright blue.
Sampling frequencies are quantizated, remarkably, there is enormous difference between ξ_0 and ξ_1 in log scale. Zero-frequency contribution is not shown on Graph 1, nevertheless it is not ignorable, as water is dipolar solution and has extraordinary high static dielectric cosntant (~ 80). In red belt in the Graph 5 are 50 Matsubara frequencies. The last red points correspond to 3000-th Matsubara frequency, at which the cummulative function of upper summation boundary

$$f(M) = A_{LmR}(M) = \frac{3kT}{2} \sum_{n=0}^{M'} \sum_{k=1}^{\infty} \frac{\left(\overline{\Delta}_{Lm} \overline{\Delta}_{Rm}\right)^k}{k^3} \qquad \text{Eq. (39)}$$

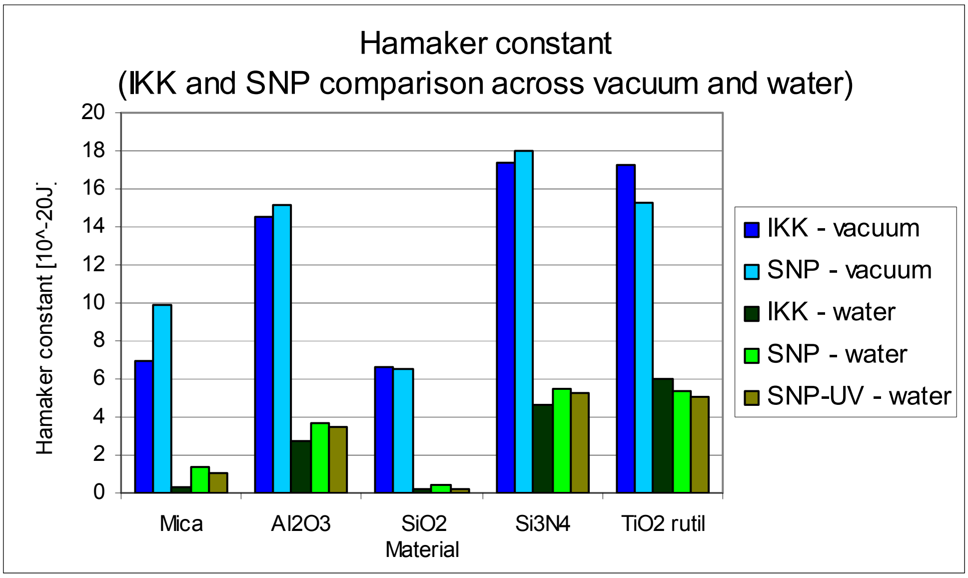
is well saturated, and 10000-th Matsubara frequency. First Massubara frequency belongs to IR at room temperature; despite possible extreme differences in absorbtion spectra (e.g complete frequency range spectrum for water demontrates enormous Debye relaxation in microwave region), van der Waals interactions are not governed by these differences at room temperature. But they have to be taken into account at lower temperature.
Real part of permitivity function can be calculated from imaginary part of permitivity via Kramers-Kronig relation. Absorption spectra are integrated to obtain real permittivity, which must be evaluated at imaginary sampling frequencies to calculate van der Waals interactions.

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{x \varepsilon''(\omega)}{x^2 - \omega^2} dx . \qquad \text{Eq. (40)}$$

For imaginary argument, Kramers-Kronig relation is rewritren in adequate form

$$\varepsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{x \varepsilon''(i\xi)}{x^2 + \xi^2} dx . \qquad \text{Eq. (41)}$$

On Graph 2 Hamaker constants are shown for representative materials, where van der Waals attraction can not be neglected [5]. The strength of interaction evidentely depends on intermediate media. Polar water molecule are not as transparent for charge fluctuations of exampling oxides as vacuum. Graph 2 includes comparison between different methods to determine absorption spectra from meassured data. IKK stands for integral Kramer-Kronig method (Eq. (38)) and SNP for summation Ninham-Parsegian method (Eq. (36)). SNP-UV means, that IR damped-resonant oscillators in Eq. (36) are omitted. There is no as significant changes between different approaches as in influence of intermediate media. These Hamaker constants are valid for limit c → ∞ (nonretarded) or equvivalently for small distances of separation.



Graph 2: Hamaker constant across vacuum and water.

8. Field-flow fractionation

Although Hammaker constants depend on amount of dipol in media, they can be meassured directly, avoinding dielectric spectroscopy. Let us mention atomic force microscopy (AFM) and surface force apparatus (SFA), the last one is in detail described in [9]. However fast but efficient sedimentation field-flow fractionation (SdFFF) is also useful technique to determine Hamaker constant [6]. SdFFF is sub-technique of field-flow fractionation (FFF), where the separation of the suspended particles is accomplished with a centrifugal force field and is applicable to colloids analysis. Colloids are charged by nature and additional repulsion term appears in potential. First term in Eqs. (42) is outer force due to applied centrifugal force field.

$$V_{tot} = V_{SdFFF} + V_A + V_R \qquad \text{Eqs. (42)}$$

$$V_{tot} = \frac{4}{3}\pi\left(\frac{d}{2}\right)^2 (\rho_S - \rho)Gx - \frac{A_{132}}{6}\left[\frac{d(d+2h)}{2h(d+h)} - \ln\left(\frac{d+h}{h}\right)\right] + 16\varepsilon\frac{d}{2}\left(\frac{kT}{e}\right)^2 \tanh\left(\frac{e\psi_1}{4kT}\right)\tanh\left(\frac{e\psi_2}{4kT}\right)e^{-\kappa h}$$

d is diameter of spheriacal particle (stokes diameter) for non-spherical particles, ρ density of dispesing medium and ρ_S density of particles, G sedimatation field strenght (acceleration), ε dielectric constant of liquid phase, x coordinate position of the centre of mass and ψ_1, ψ_2 surface potential of the particle and the chanell wall. κ is reciprocial double-layer thicknes. Sample colloid solution is exposed do external gravitational and cetrifugal force field. SdFFF is chromatographic technique, where time of moving for certain particles is measured and output volume is analysed. Schematically FFF is ilustrated in Fig. 6. Hamaker constant is estimated as fitting parameter.

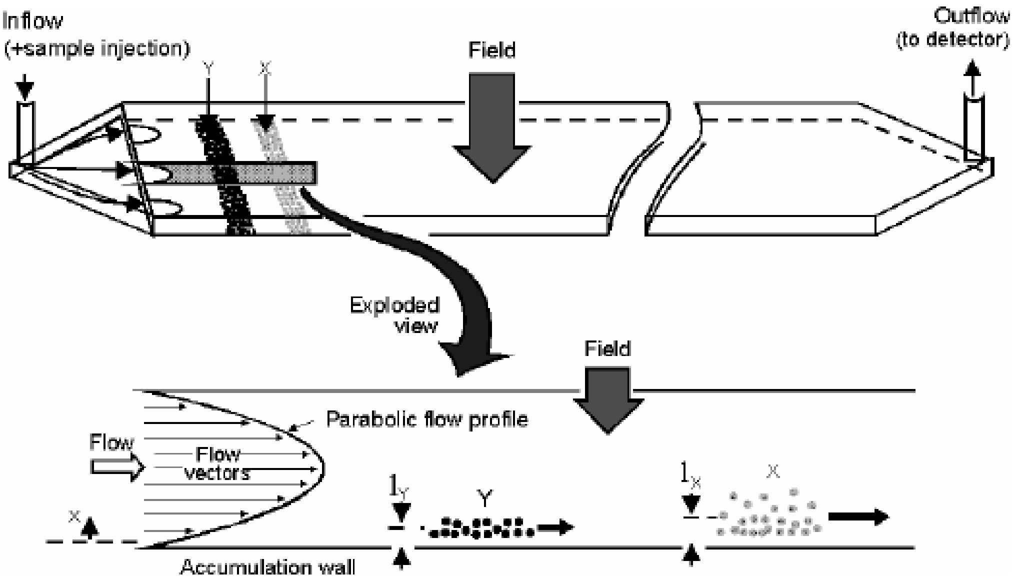
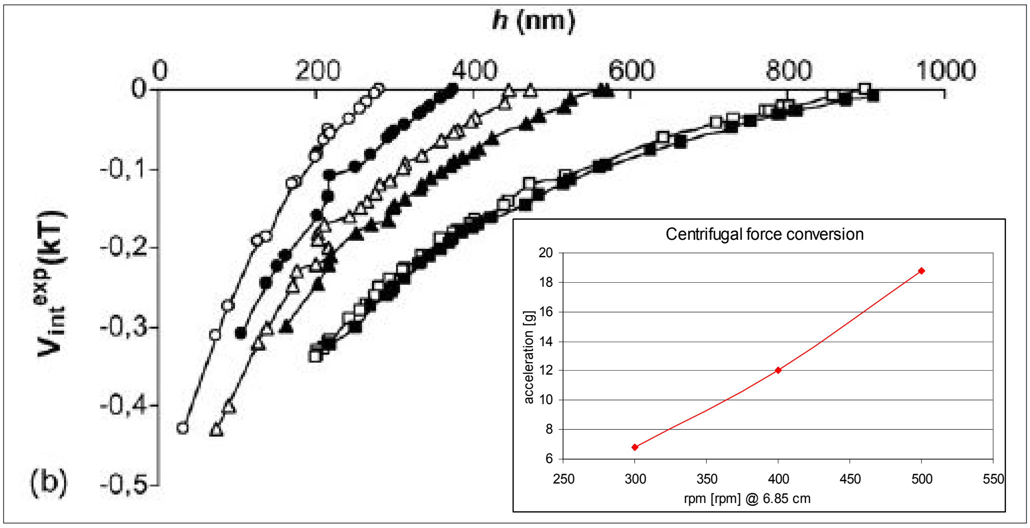


Fig. 6: Princple of FFF technique [10].

When dispezion of SiO_2 particles (490 nm) was meassured, three different cetrifugal forces were applied in SdFFF [6]. Electrostatic repulsion was estimated $10^{-80}k_BT$ and thus neglected. Attractive term in Eqs. (42) can be expressed as difference between V_{tot} and V_{SdFFF}. h_{eff} is the distance of the particle surface from accumulation wall of the SdFF with added electrolyte and h_{eff}^0 the same distance in absence of added electrolyte.

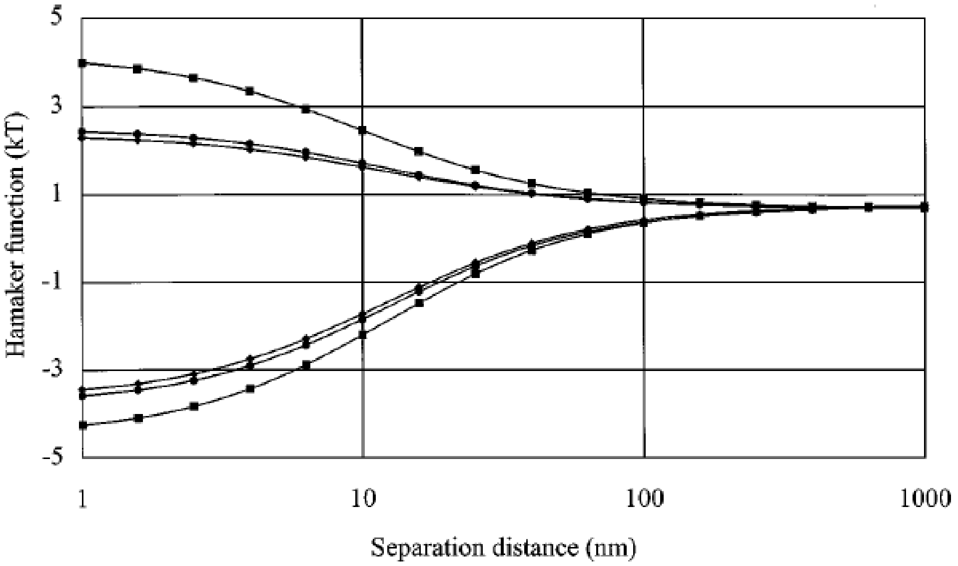
$$V_{\text{int}} = \frac{4}{3}\pi\alpha_{true}^3 \Delta\rho\left(G_{app}h_{eff} - G_{SdFFF}h_{eff}^0\right) \qquad \text{Eq. (43)}$$



Graph 3: Interaction potential for SiO2, measured by SdFFF ((■,□): 300 rpm, (○,●): 400 rpm, (▲,Δ): 500 rpm) [6]. Insert: Rpm (rotations per minute) conversion into acceleration for cetrifugal force.

9. Calculations

Graph (4) confirms, that Hamaker constant (as proportional factor in Lifshitz theory of van der Waals interactions) depends on distance of separation.
For quartz-water-quartz (upper) and quartz-water-air (lower) curve Hamaker constant is computed using complete, improved approximate (anothe Sellmeier constant with different number of dumped-resonant oscillators) and Cauchy plot analysis [4]. Quartz attracts itself across water, the smaller distance the stronger attraction. For large distance, quartz attracts air across water, but repells it at small distances. Negative Hamaker constant is an indicator for repulsive van der Waals interaction. This case is familiar to liquid helium in container; water tends to spread over all available quartz surface.



Graph 4: Exact calculation of retarded Hamaker constant for quartz-water-quartz (upper) and quartz-water-air (lower). Curves differ on method to obtain spectra: complete (circles), improved approximate (diamonds) and Cauchy plot analysis (squares) spectra.

For lipid-water bilayers-coated semi-infinite mica (R) in front of bare semi-infinite mica (L) or free standing succesive layer of lipid-water bilayers in water (R) in front of bare semi-infinite mica (L) van der Waals interaction was calculated numerically [11]. N = 100 bilayers (blue curve) screen the effect of right semi-infinite media as seen on Graph (5); from gap separation 200 nm further there is no significant change in free energy for both mica (full curve) and water (dashed curve) right semi-infinite media. For one bilyer (N = 1, black curve) and ten bilayers (N = 10, red curve), the the effect of right can not be neglected. Van der Waals forces are long range interactions (up to 1 µm). Applied parameters were: thickness of tetradecan (lipid, a = 5 nm), thicknes of water in bilayer (b = 2 nm), T = 300 K. Absorbtion spectra were obtained from resonant-damped oscillator model and certain parameters.

Interesting is comparison between exact retarded regime and nonretarded approximation of Eq. (22) in system with three bilayers on mica semi-infinite media on Graph (6). Approximation predicts longer range as retarded calculation. Free energy for retardend case is flater, derivative is nearly equal to zero, hence the range is shorter. Nonretarded approximation can be used at small distances of separation; both curves coincide up to ~ 50 nm.

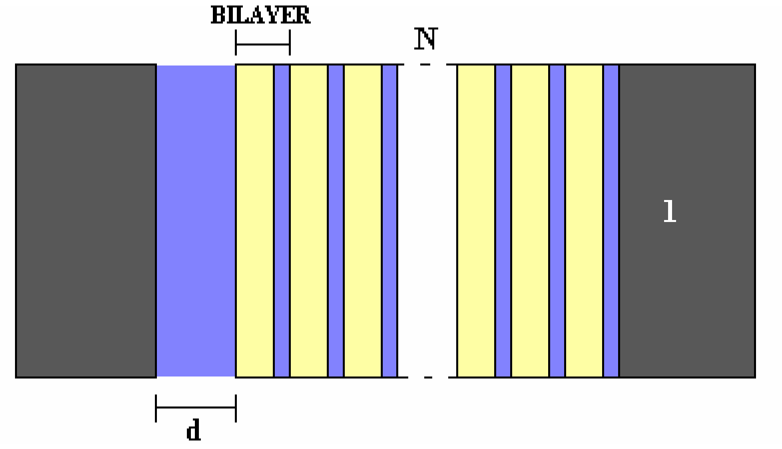
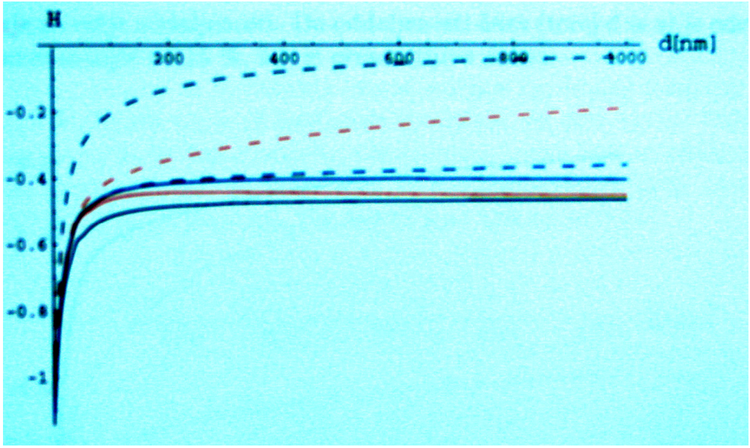
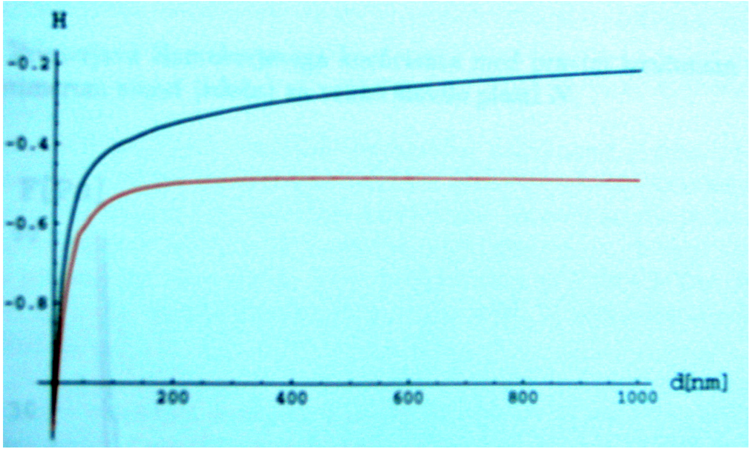


Fig. 7: The set for bilayers-coated-system (1 – mica or water) in front of mica semi-infinite media in [11].



Graph (5): Free energy for interacting mica and coated mica (full) and water (dashed) across water gap for N = 1 (black), N = 10 (red) and N = 100 (blue) bilayers.



Graph (6): Exact retarded and approximated nonretarded free energies are compared for interaction between mica bilayers-coated mica across water gap. It confirms decreasing of energy in retarded system.

10. Van der Waals interaction *in vivo*

In everyday life we experience upside down standing insects. They take advantage of van der Waals interactions between their legs and grounding. Moreover, there are bigger animals, whose ceiling walking is based on fundamental van der Waals forces, although physiological mechanisms are diverse. Many species of small lizards, named geckos (*Pachydactylus bibroni*), have specialized toe pads that enable them to climb smooth vertical surfaces and even cross indoor ceilings with ease. Their toes adhere to wide variety of surfaces with finely divided *spatulae*. If gecko had every one of his *spatulae* in contact with a surface, it would be capable of holding a 120 kg man. In Fig. 8, gecko climbs on surface down ahead.

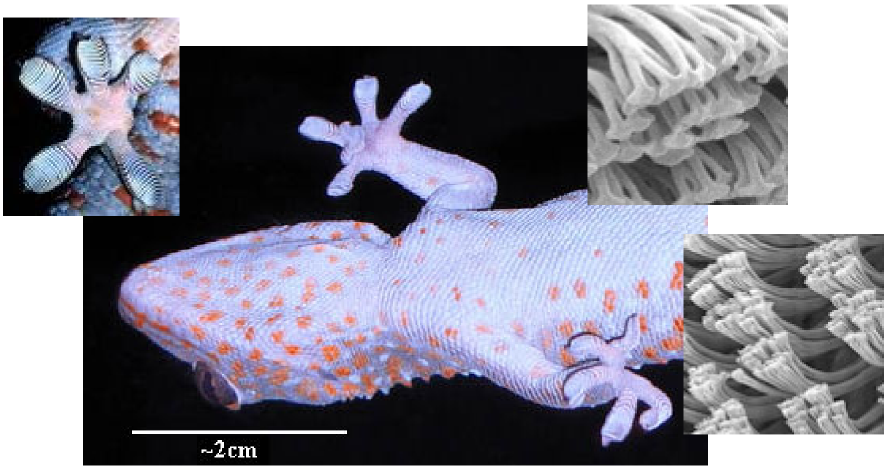


Fig. 8: Down ahead climbing gecko on transparent smooth surface and clusters of spatulae [12].

11. Conclusion

Van der Waals interactions are based on thermal and quantum charge fluctuations. As they are unavoidable (*in vitro* and *in vivo*), they deserve special consideration. In the first attempts in theory, microscopic quantities of gases were applied to liquid and solid media via pairwise summation. In Lifshitz theory interacting media are treated as continuum and permittivity functions are taken into account in stead of polarizabilities. Several experimantal techniques were developed to meassure the strenght of van der Waals interaction (Hamaker constant), fast methods as FFF appropriate merely for estimations, however if we want precise values of it, we have to include absorption spectra, as in seminar it was derived in detail in heuristic derivation of Lifshitz´general result for two semi infinite media interacting across a gap. For further reading, i recommend ecyclopedic rewiev for diferent geometries, available in [3].

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