"van der Waals" "Hamaker" "Casimir" "Lifshitz" "fluctuation" "electrodynamic" Where now? What next?

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Desiderata

Solve for more geometries and for real materials (pure Casimir is not questionable as an idea, but does it ever really exist?)

Piece apart the "zero-frequency" term

(dominates at long distances, especially at room temperature)

(important with polar materials, always with water)

Control conditions of measurements

-- to see if we are measuring what we think we are measuring

(high vacuum for clean surfaces)

(optical data, on samples themselves, to go with measurement)

Design shapes and materials so as to modify forces

Talk with each other! Nicely!!

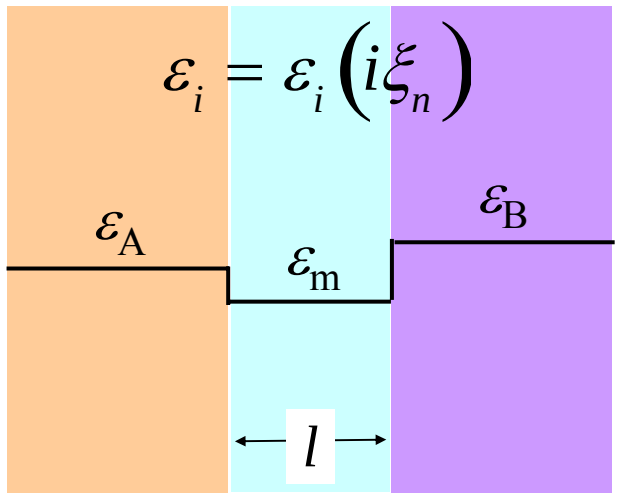
Lifshitz et al.: half-spaces A and B across medium m

$$G_{AmB}(l) = -\frac{A(l)}{12\pi l^2} \qquad A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n}{}' \left(\frac{\varepsilon_A - \varepsilon_m}{\varepsilon_A + \varepsilon_m}\right)\left(\frac{\varepsilon_B - \varepsilon_m}{\varepsilon_B + \varepsilon_m}\right) \times R_n(l)$$

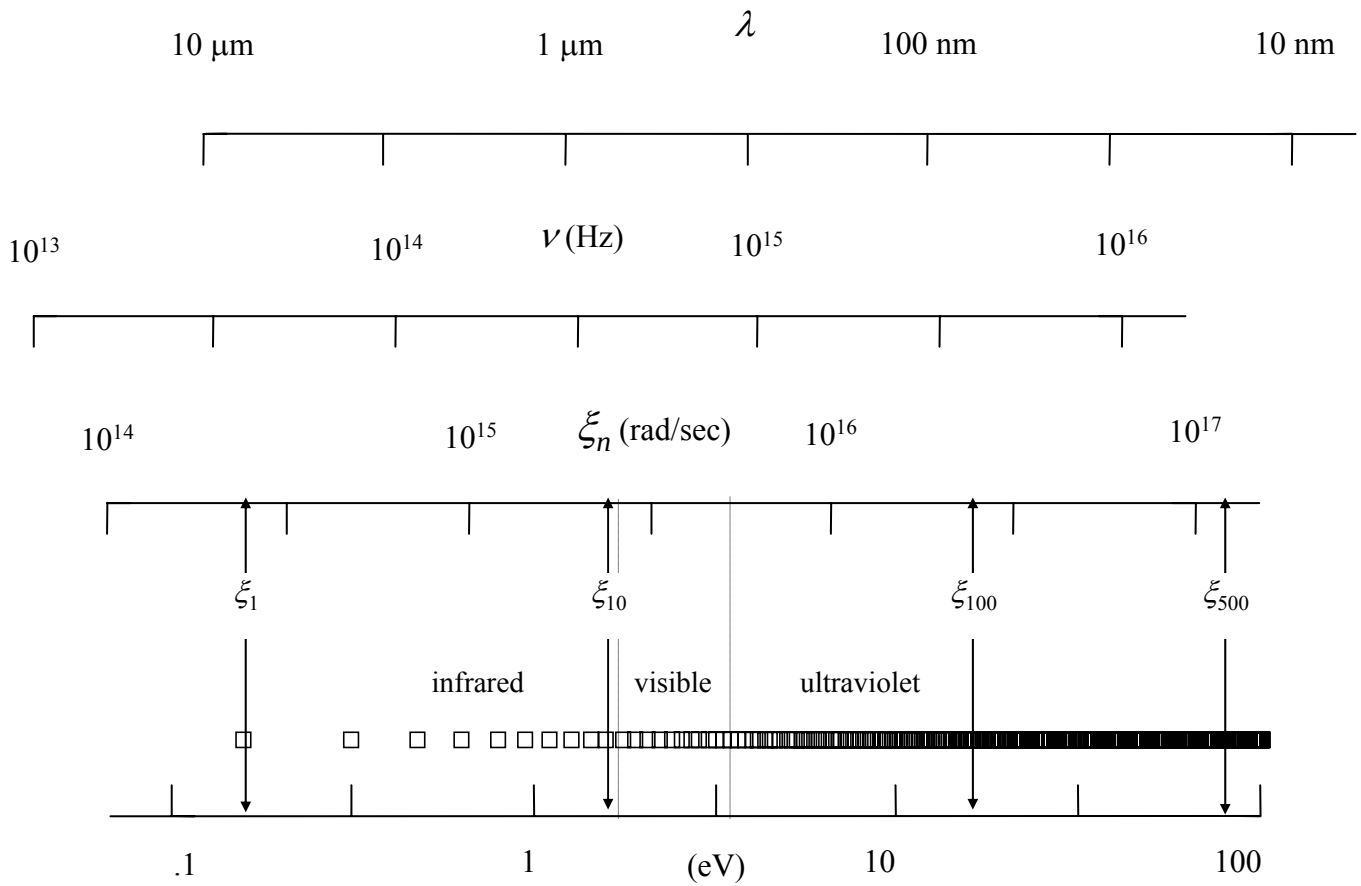
$$h\xi_n \equiv 2\pi kTn \qquad R_n \approx (1 + r_n)e^{-r_n}$$

$$r_n = \left(\frac{2l}{c}\right) \Big/ \left(\frac{1}{\xi_n}\right) = \frac{2l}{\lambda_T} n; \; \lambda_T \equiv \frac{hc}{2\pi k_B T_{room}} = 1.2\,\mu m$$

l =	100 nm	1μm	10 μm
n: $r_n = 1$	n = 6	n = .6	n <<1
r_1 =	.16	1.6	16
R_1 =	~1	< 1/2	zero!



Matsubara frequencies at T_{room}, as λ, ν, and ξ_n □ □ $\pi\nu$



The first sampling frequency after $\xi_0 = 0$, corresponds to IR vibrations.

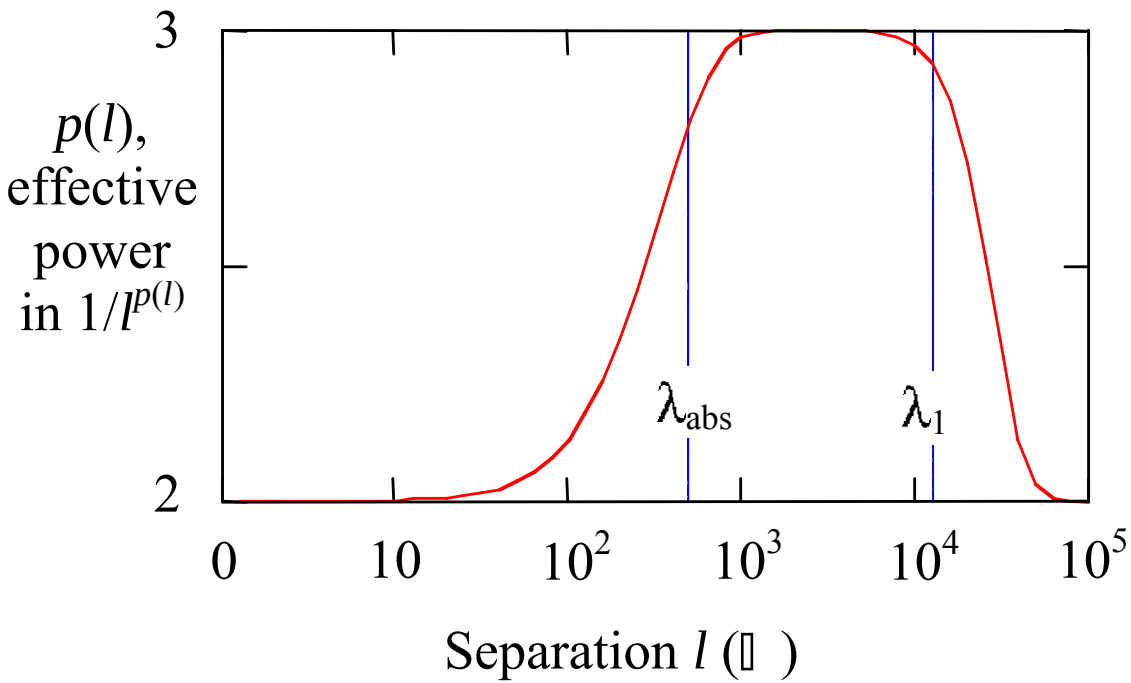
$\lambda_1 = 2\pi c/\xi_1 = 7.82 \times 10^{-4}$ cm $= 7.82$ μm $= 7.82 \times 10^4$ Angstroms.

"Power law" from a single-oscillator,

$\lambda_{absorption}$ = 500 Angstrom,

$\varepsilon_{left} = \varepsilon_{right}$ across vacuum

$$G_{AmB}(l) = -\frac{A_{Am/Bm}(l)}{12\pi l^2} \qquad p(l) = -\frac{d\ln\left(G_{AmB}(l)\right)}{d\ln(l)}$$



Two metals at T_{room} $l \sim 10$ μm in vacuum, never Casimir

$$A(l) = \frac{3kT}{2} \sum_{\substack{\text{Matsubara sampling} \\ \text{frequencies } \xi_n}}{}' \left(\frac{\varepsilon_A - \varepsilon_m}{\varepsilon_A + \varepsilon_m}\right)\left(\frac{\varepsilon_B - \varepsilon_m}{\varepsilon_B + \varepsilon_m}\right) \times R_n(l) \to \frac{3kT}{4}$$

$$G(l) \approx -\frac{A(l)}{12\pi l^2} = -\frac{3kT}{48\pi l^2} = -\frac{kT}{16\pi l^2}$$ without magnetic terms

$$G(l) \approx -\frac{3kT}{24\pi l^2}\varsigma(3) = -\frac{kT}{8\pi l^2}\varsigma(3)$$ with magnetic terms, and proper summation

vs. Casimir (T = 0 K)

$$G_{\text{Casimir}}(l) \approx -\frac{hc\pi^2}{720 l^3}; P_{\text{Casimir}}(l) \approx -\frac{hc\pi^2}{240 l^4}$$

Skinny cylinder parallel to plane,
separation z, radius R, thermal de Broglie wavelength λ_T
traditional pairwise sum vs. Collective fluctuations

Pairwise summation

$$E(z): \; -kT\frac{R^2}{z^3}\,\mathrm{L}$$

Metallic wire

Emig Jaffe Kardar, Scardicchio

PRL 96: 080403 (2006)

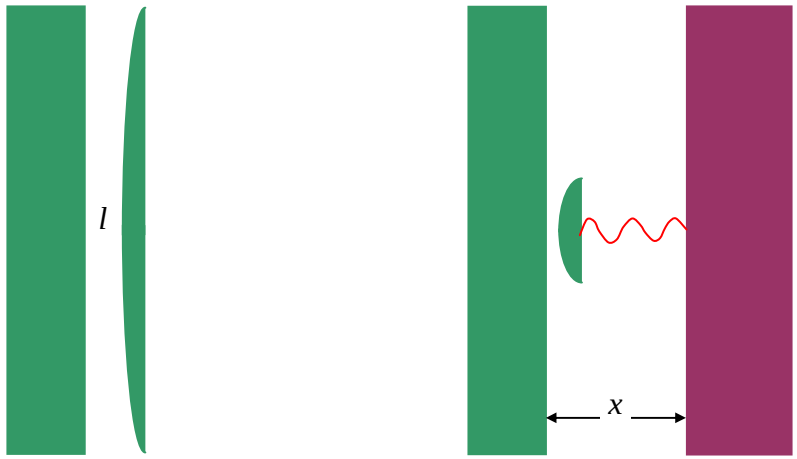
$$E(z): \; \frac{kT}{z\ln\left(R/\lambda_T\right)}\,\mathrm{L}; \quad \mathrm{R} = \lambda_T = z$$

Measurements not often noticed

Force balances (room temparture)

Glass (Derjaguin, Lifshitz, Abrikosova, 1950's)

Mica (Tabor, Winterton, Israelachvili, 1970's)



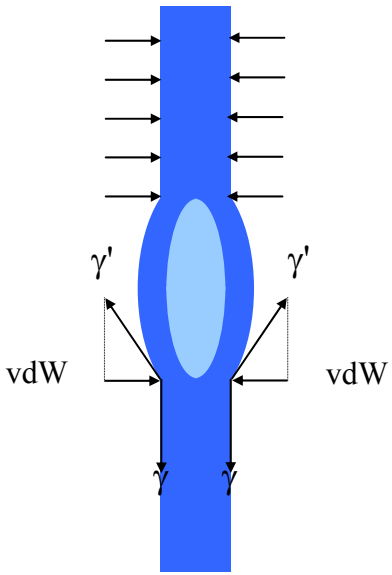
B. V. Derjaguin, "The force between molecules" Scientific American, 203:47 - 53 (1960);

B. V. Derjaguin, I. I. Abrikosova & E. M. Lifshitz, "Direct measurement of molecular attraction between solids separated by a narrow gap" Quarterly Reviews (London), 10: 295 - 329 (1956).

J. N. Israelachvili & D. Tabor, Van der Waals Forces: Theory and Experiment, vol. 7, pp. 1-55, Progress in Surface and Membrane Science, 1973

Forces across bilayers (Haydon & Taylor, 1968)

water



water

Hydrocarbon membrane

~ 4 nm thick layer with trapped hc drop

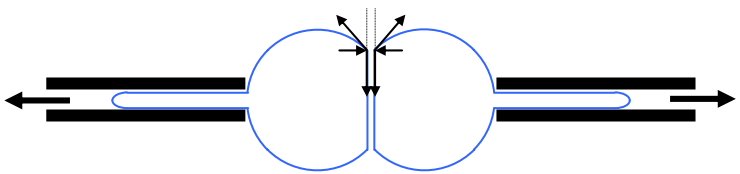
By the strength with which they flatten against each other, two juxtaposed bilayers create a measurable contact angle.

D. A. Haydon & J. L. Taylor, "Contact angles for thin lipid films and the determination of London-van der Waals forces" Nature, 217: 739 - 740 (1968)

Parsegian, V.A, Ninham B.W.: Application of the Lifshitz theory to the calculation of van der Waals forces across thin lipid films. Nature 224: 1197-1198 (1969)

Forces between bilayer vesicles (Evans, Rand)

Water inside and outside

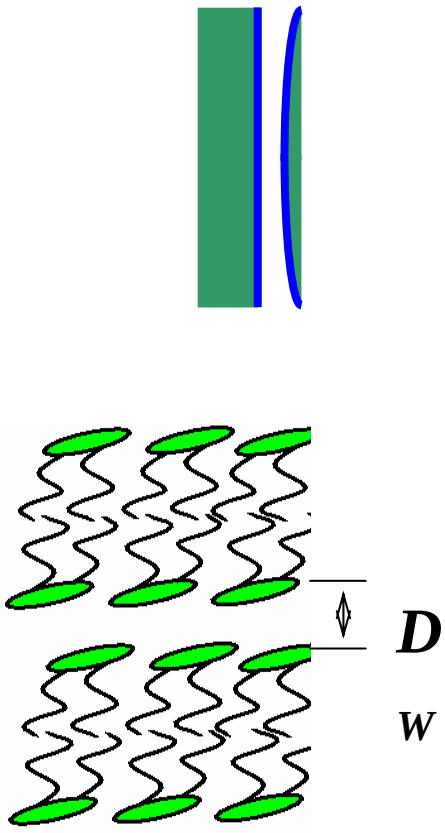


Suck on vesicles with pipettes

In practice, van der Waals forces appear mixed with lamellar motions as well as with repulsive hydration forces.

E. A. Evans, "Entropy-driven tension in vesicle membranes and unbinding of adherent vesicles" Langmuir, 7:1900-1908 (1991)

Between bilayers (Rand, Fuller, VAP, 1970's -90's) between bilayers on mica (Marra, Israelachvili)

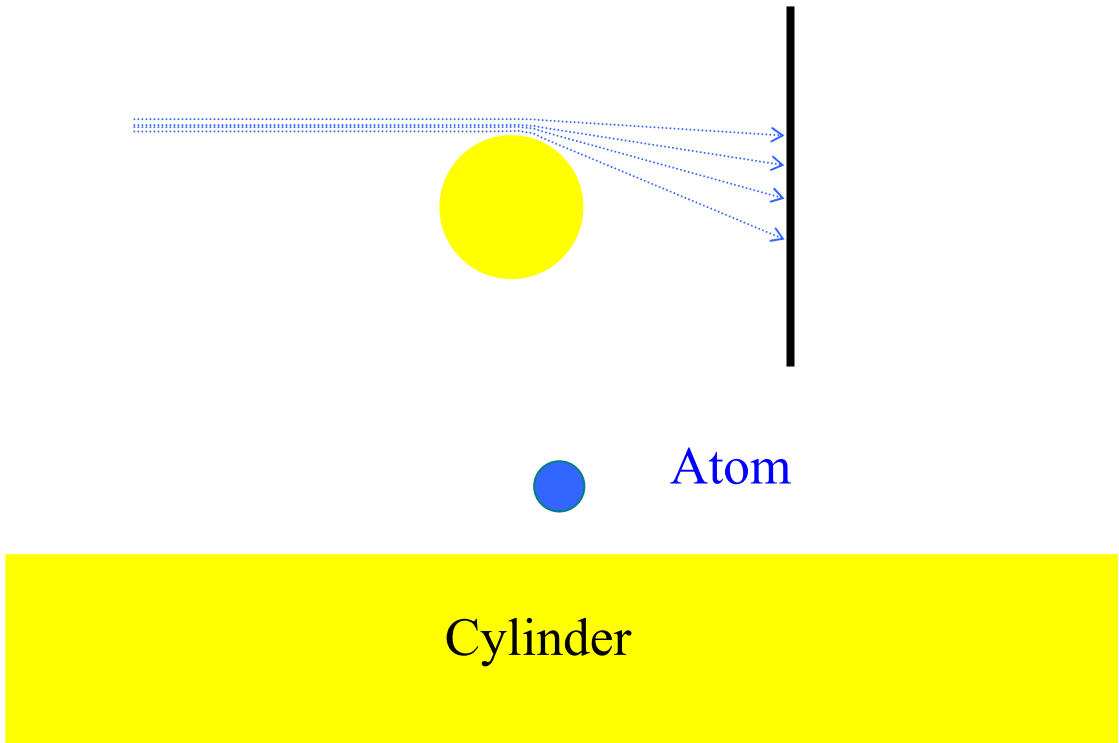


Between bilayers immobilized onto substrates
J. Marra & J. N. Israelachvili, "Direct measurements of forces between phosphatidylcholine and phosphatidylethanolamine bilayers in aqueous electrolyte solutions", Biochemistry, 24:4608-4618 (1985)

V. A. Parsegian, "Reconciliation of van der Waals force measurements between phosphatidylcholine bilayers in water and between bilayer-coated mica surfaces," Langmuir 9:3625-3628 (1993)

Deflection of an atomic beam $T = T_{room}$

Shih, Raskin, Kusch (Columbia, NBS 1970's)



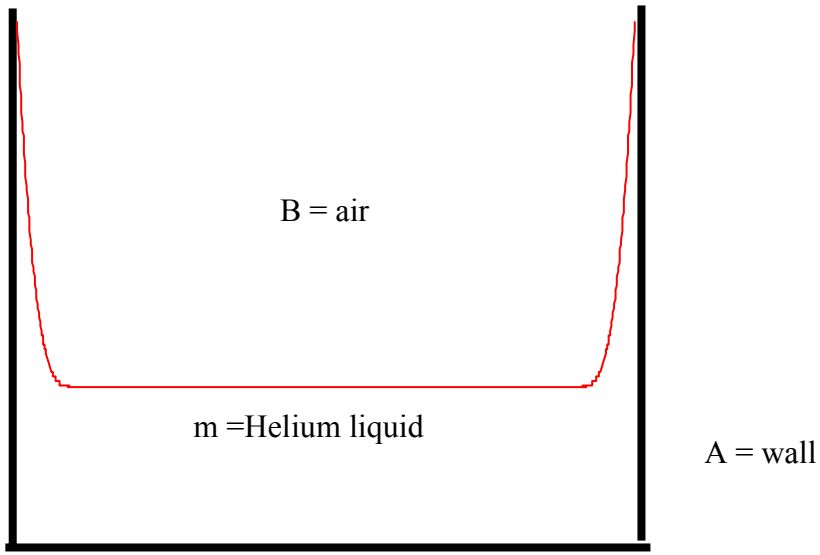
Arnold Shih & V. A. P., "Van der Waals forces between heavy alkali atoms and gold surfaces: comparison of measured and predicted values", Phys Rev A, 12(3):835 - 841 (1975)

Parsegian, V.A.: Formulae for the electrodynamic interaction of point particles with a substrate. Molecular Physics No. 6 27: 1503-1511 (1974)

Find a clean $1/d^3$ power law (non-retarded point-particle to surface)

Liquid helium crawling the walls

Sabisky & Anderson (1973)

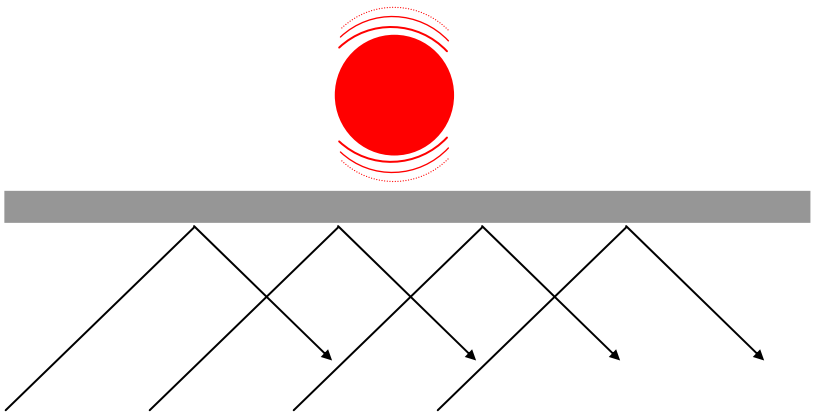


Put into a vessel, liquid helium will wet the walls, defying gravity with a layer of finite thickness

E. S. Sabisky and C. H. Anderson, "Verification of the Lifshitz Theory of the van der Waals Potential Using Liquid-Helium Films", Physical Review A, 7: 790-806, 1973

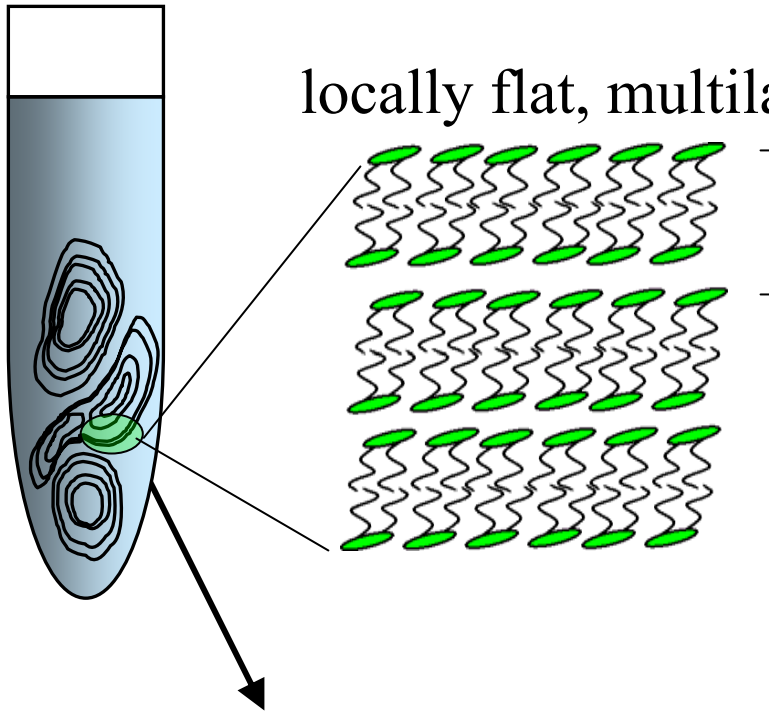
They measured the full spectrum of the substrate and used the full spectrum of the helium. This is one of the very few real (i.e., satisfactory) comparisons of measurement with theory!

Colloids
D. Prieve



The bounce of particles, observed via reflected light, gives the force between sphere and flat.
D. C. Prieve, "Measurement of colloidal forces with TIRM," Advances in Colloid and Interface Science 82:93-125 (1999)

Multilayers: Neutral lipid bilayers in salt water

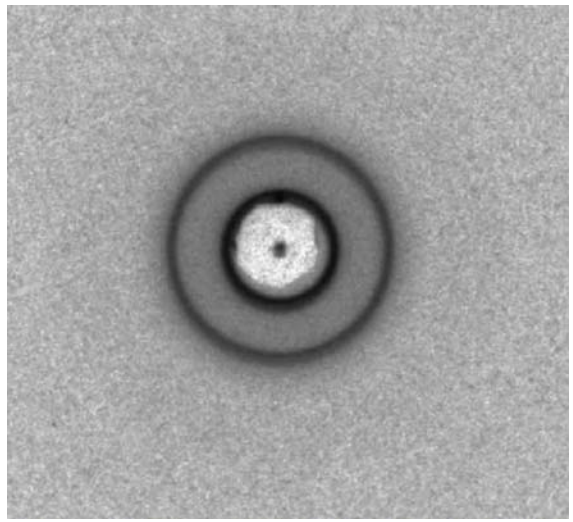


locally flat, multilayer stacks

D (repeat spacing, ~60 Ang)

Small-angle x-ray scattering

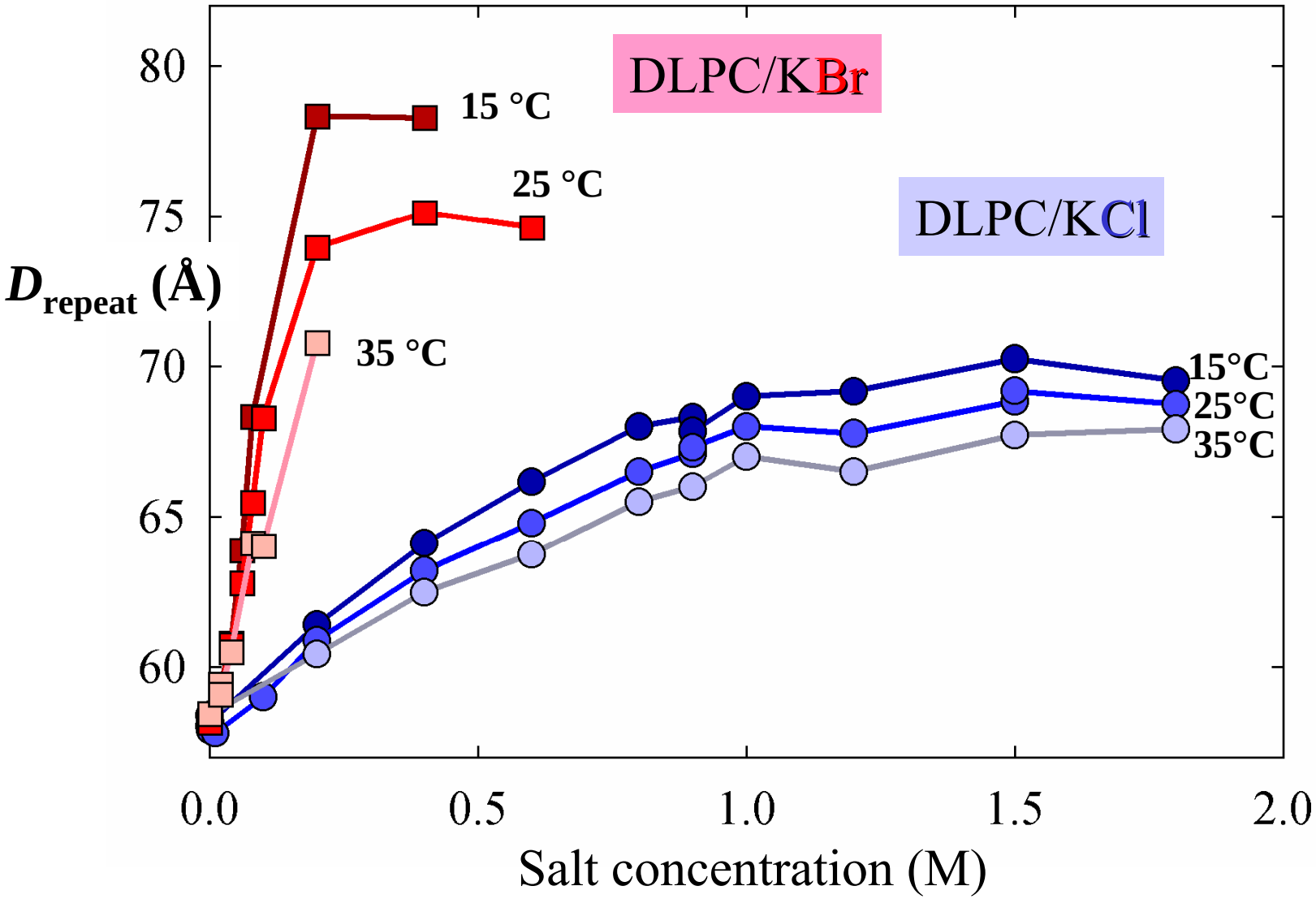
$D = 2\pi/q \sim 60$Å



H. Petrache, D. Harries, I. Kimche, J. Nagle, S. Tristram-Nagle, et al.

In excess solution, neutral lipids swell with added salt.

Horia Petrache et al (2006)



Salt screening/weakening of vdW forces: three new ideas

H. I. Petrache, S. Tristram-Nagle, D. Harries, N. Kucerka, J. F. Nagle, V. A. Parsegian, Swelling of phospholipids by monovalent salt J. Lipid Res. 47, 302-309 (2006)

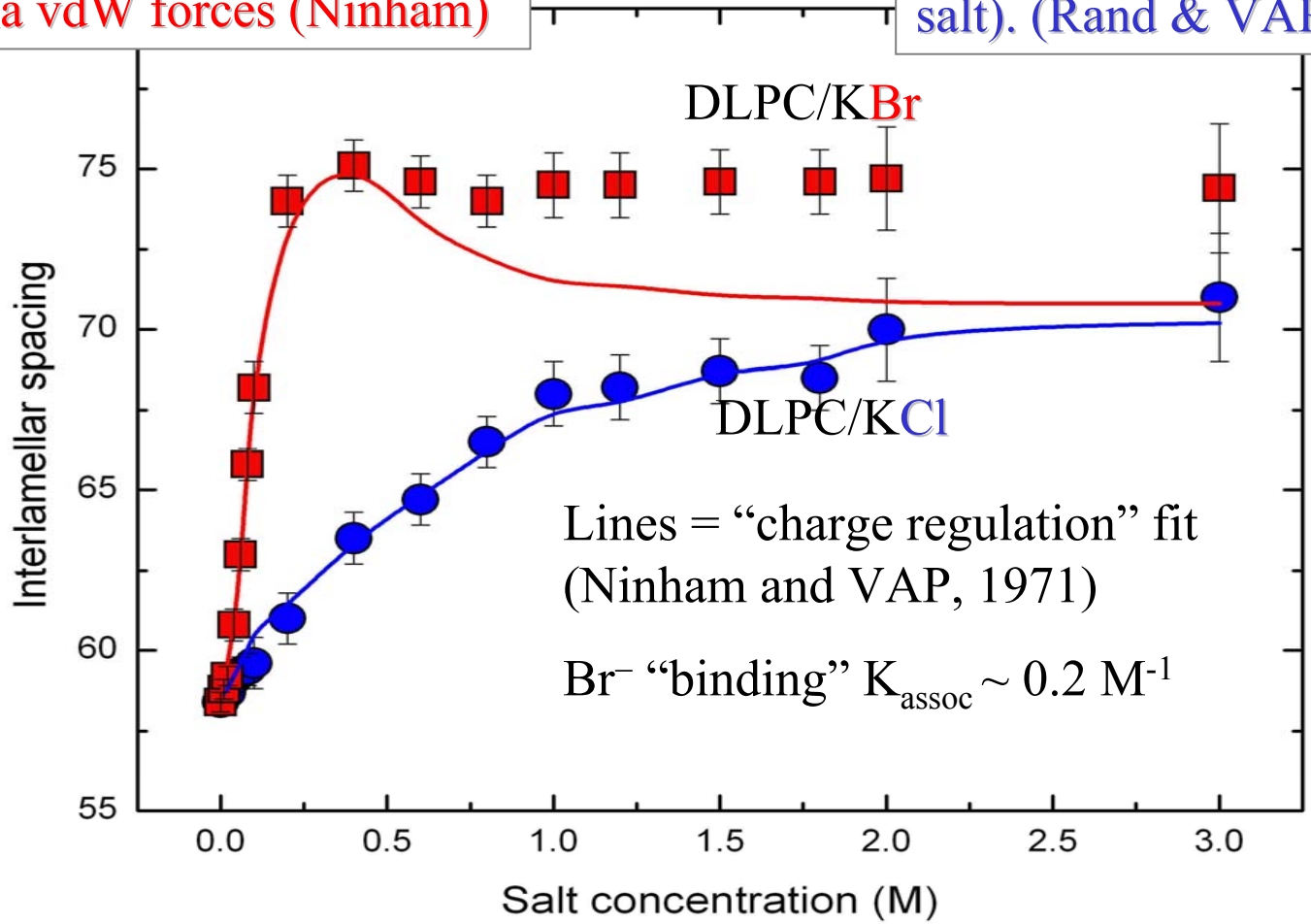
Low salt:

*screening of zero frequency vdW attraction (Ninham & VAP)

*electrostatic repulsion from Br binding via vdW forces (Ninham)

High salt:

* vdW weakening at optical frequencies (refractive index of salt solutions increases with salt). (Rand & VAP)



Kevin Cahill:

How about first-order interactions?”

distance; cf. §62, Problem 1, and §81, Problem.

‡ This, of course, does not imply that the mean value of the interaction energy of the atoms is precisely zero. It diminishes exponentially with distance, i.e. more rapidly than every finite power of $1/r$, and hence each term of the expansion vanishes. This occurs because the expansion of the interaction operator in terms of the multipole moments involves the assumption that the charges of the two atoms are at a large distance r apart, whereas in quantum mechanics the electron density distribution has finite (though exponentially small) values even at large distances.

Landau & Lifshitz, Quantum Mechanics, footnote page 341

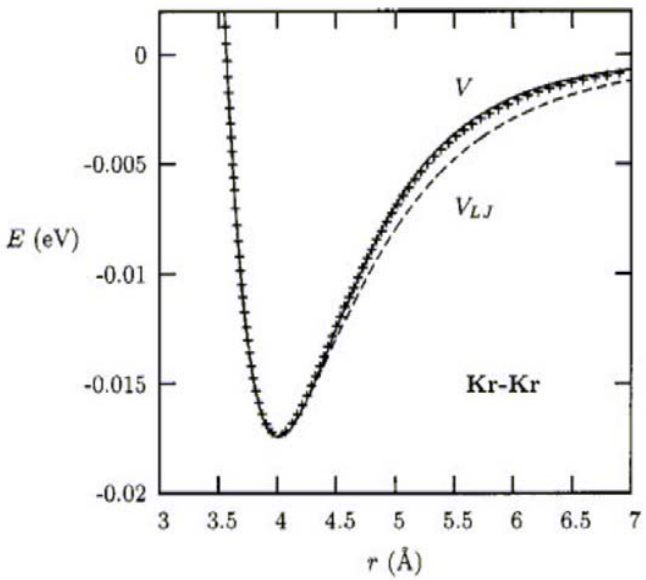
First-order van der Waals forces atom-atom attraction

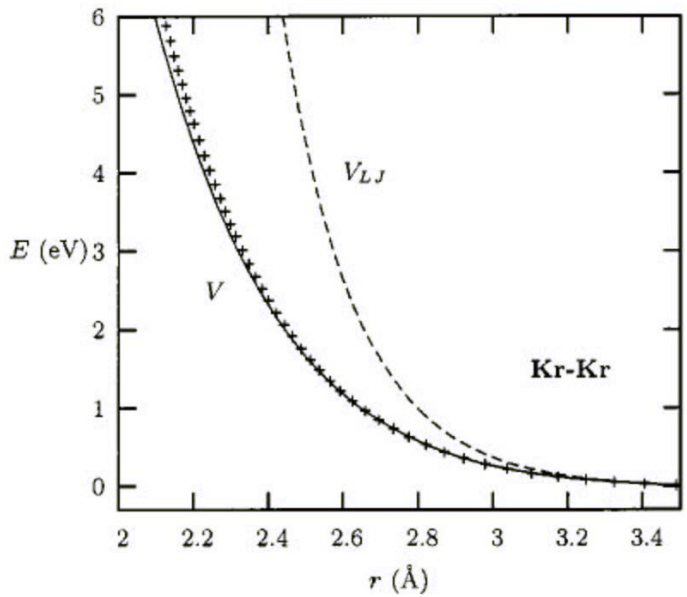
A Rydberg-like potential $V_{Rydberg}$,

better than Lennard-Jones V_{LJ} 6-12 potential generally used.

$$V_{Rydberg} = V(r) = ae^{-br}(1-cr) - \frac{d}{r^6 + er^{-6}} \qquad V_{LJ}(r) = |V(r_o)|\left[\left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_o}{r}\right)^{6}\right]$$

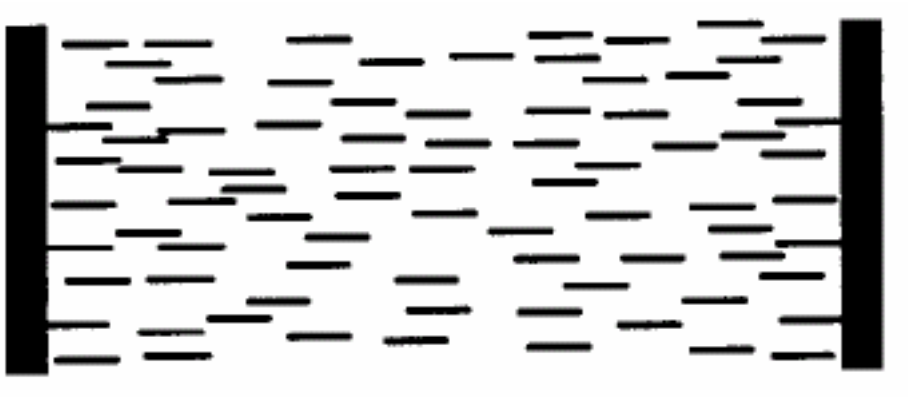
+ symbol "exact" numerical solution Meath and Aziz, Molec. Phys., 52, 225 (1984).

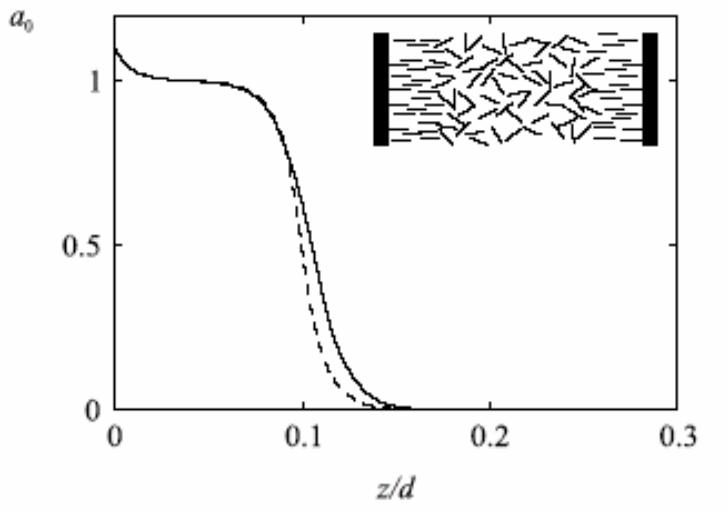




Kevin Cahill & VAP, J. Chem. Phys., 121:10839-42 (2004)

Pseudo Casimir effect for non-EM fields described with similar equations.





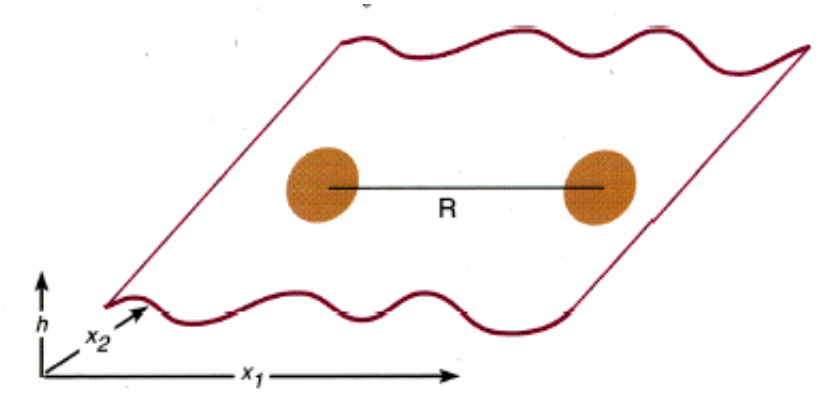
Nematic film with stiff boundaries
(Ajdari, Duplantier, Hone, Peliti, Prost, 1982; Mikheev, 1989).

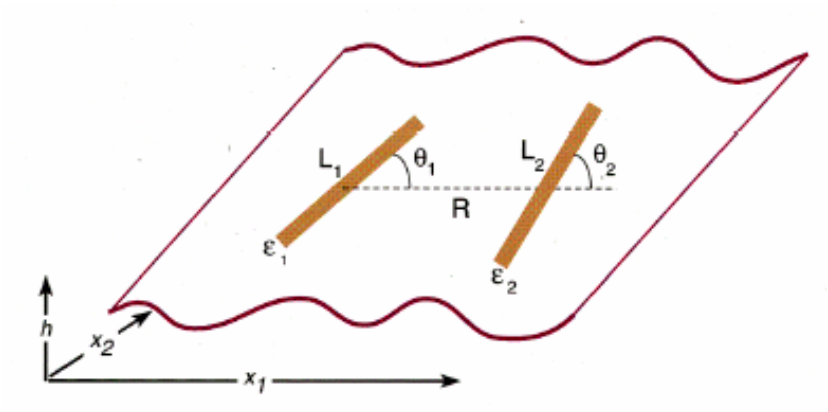
Nematic wetting (Ziherl, Podgornik and Zumer, 1998).

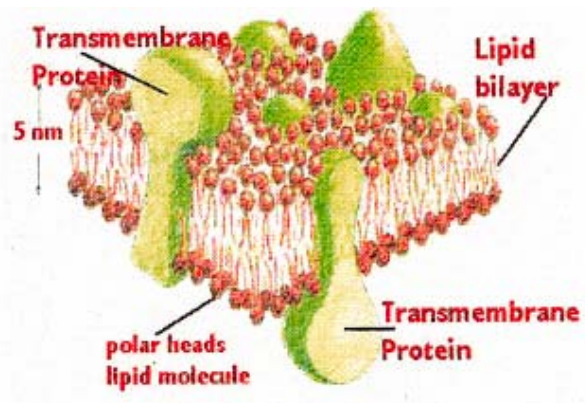
Smectic films (Li and Kardar, 1992).

Membrane inclusions

(Goulian, Bruinsma, Pincus 1993, Golestanian, Goulian and Kardar, 1996)







Interaction between (lipid) membrane inclusions such as proteins.

Important in understanding aggregation of membrane proteins.

Thanks

Lifshitz Theory and dielectric spectra of SWCNT

van der Waals - London Dispersion Interactions for Optically Anisotropic Cylinders:
Metallic and Semiconducting Single Wall Carbon Nanotubes

Rick Rajter††, Rudi Podgornik†⋆, V. Adrian Parsegian†, Roger H. French §, W.Y. Ching§†

Phys Rev B Sub'td

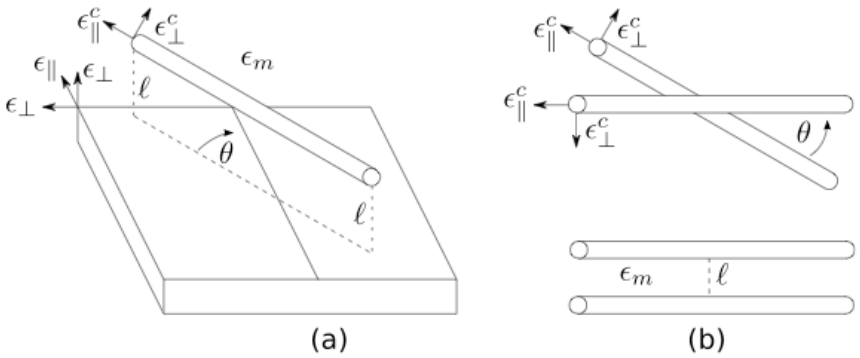
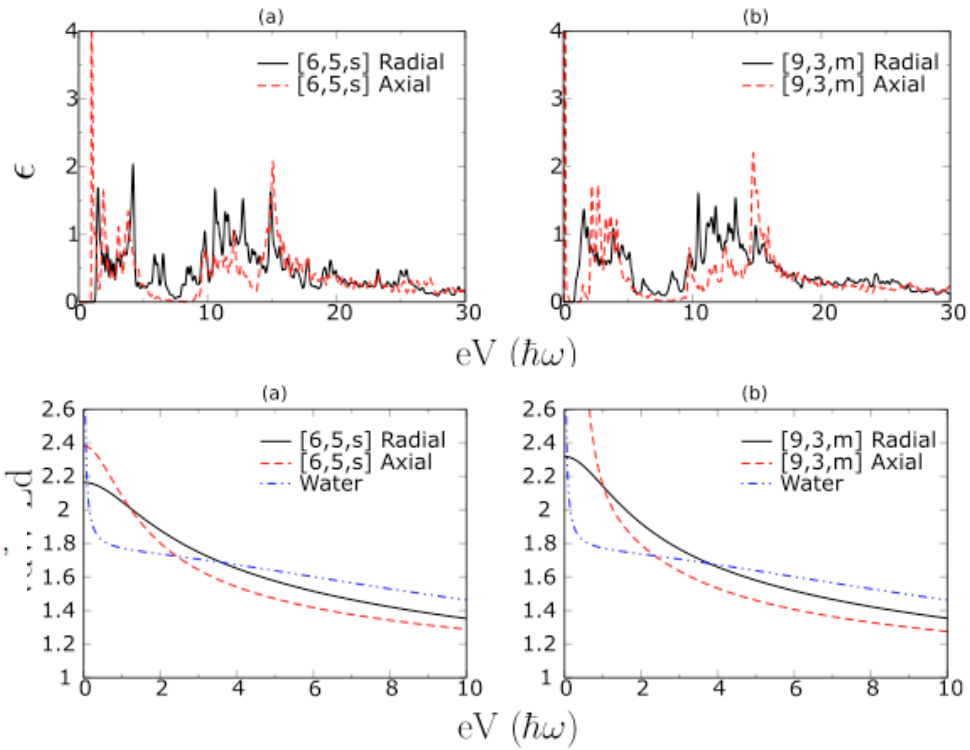


Figure 4: Schematic showing the geometry of the (a) anisotropic cylinder-anistropic planar substrate and (b) anisotropic cylinder-anisotropic cylinder systems.



$$g(\ell,\theta) = -\frac{k_B T\ (\pi a^2)}{4\pi\ \ell^3}\left(\mathcal{H}^{(0)} + \mathcal{H}^{(2)}\cos^2\theta\right).$$

$$\mathcal{H}^{(0)} + \mathcal{H}^{(2)} = \frac{1}{2\pi}\sum_{n=0}^{\infty\,\prime}\int_0^{2\pi} d\phi\ \Delta_{\mathcal{L}m}(\phi)\left(\Delta_\perp + \tfrac{1}{4}(\Delta_\parallel - 2\Delta_\perp)\cos^2\phi\right),$$

and for $\theta = \frac{\pi}{2}$,

$$\mathcal{H}^{(0)} = \frac{1}{2\pi}\sum_{n=0}^{\infty\,\prime}\int_0^{2\pi} d\phi\ \Delta_{\mathcal{L}m}(\phi)\left(\Delta_\perp + \tfrac{1}{4}(\Delta_\parallel - 2\Delta_\perp)\sin^2\phi\right).$$

$$\Delta_\perp = \frac{\varepsilon_\perp^c - \varepsilon_m}{\varepsilon_\perp^c + \varepsilon_m};\ \Delta_P = \frac{\varepsilon_P^c - \varepsilon_m}{2\varepsilon_m}$$

$$G_{AmB}(l) = -\frac{A_{Am/Bm}(l)}{12\pi l^2} \qquad A_{Am/Bm}(l) \approx \frac{3kT}{2}{\sum_{n=0}^{\infty}}' \bar{\Delta}_{Am}\bar{\Delta}_{Bm}\, R_n(l)$$

$$\bar{\Delta}_{Bm} = \frac{\varepsilon_B - \varepsilon_m}{\varepsilon_B + \varepsilon_m} \qquad \bar{\Delta}_{Am} = \frac{\varepsilon_A - \varepsilon_m}{\varepsilon_A + \varepsilon_m} \qquad \varepsilon_i = \varepsilon_i(i\xi_n)$$

$$h\xi_n \equiv 2\pi kTn \qquad \xi_n(T_{room}) = 2.41\times 10^{14}\, n$$

Finite temperature form

The first sampling frequency after $\xi_0 = 0$, corresponds to infra-red vibrations.

$\lambda_1 = 2\pi c/\xi_1 = 7.82 \times 10^{-4}$ cm $= 7.82$ μm $= 7.82 \times 10^4$ Angstroms.