Van der Waals forces

for geeks, geckos, and grad students

Adrian Parsegian

and many friends

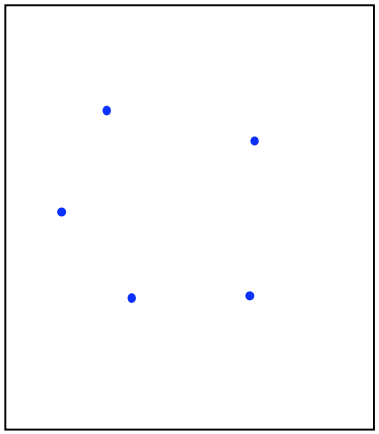
Barry Ninham, David Gingell, George Weiss,

Peter Rand, Rudi Podgornik, Horia Petrache,

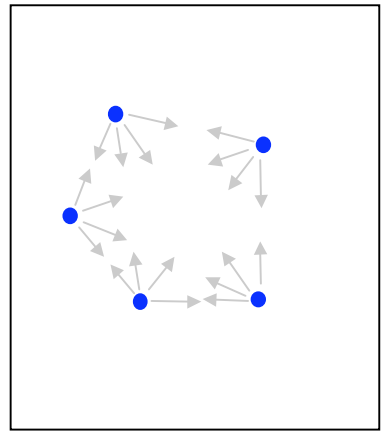
Roger French, Kevin Cahill, Vanik Mkrtchian,
Wayne Saslow et al. et al.

Laboratory of Physical and Structural Biology, National Institute of Child Health and Human Development, National Institutes of Health http://lpsb.nichd.nih.gov

Boyle and van der Waals gas equations



$$p_{\text{Boyle}} V = N\text{k}T$$



$$\left(p_{\text{vdW}} + \frac{\text{a}}{V^2} \right) (V - \text{b}) = N\text{k}T$$

1660 Boyle's Law, pV constant

N number of particles, k the Boltzmann constant,
T absolute temperature, p pressure, V volume of box

1873 van der Waals gas equation
Coefficient a ≥ 0, $p_{\text{vdW}} \leq p_{\text{Boyle}}$
because of attractive forces;
Total volume of particles, b ≥ 0

Thesis:
"Continuity of gas and liquid states"

Dipole-dipole interactions (1920's –30's)
van der Waals gasses

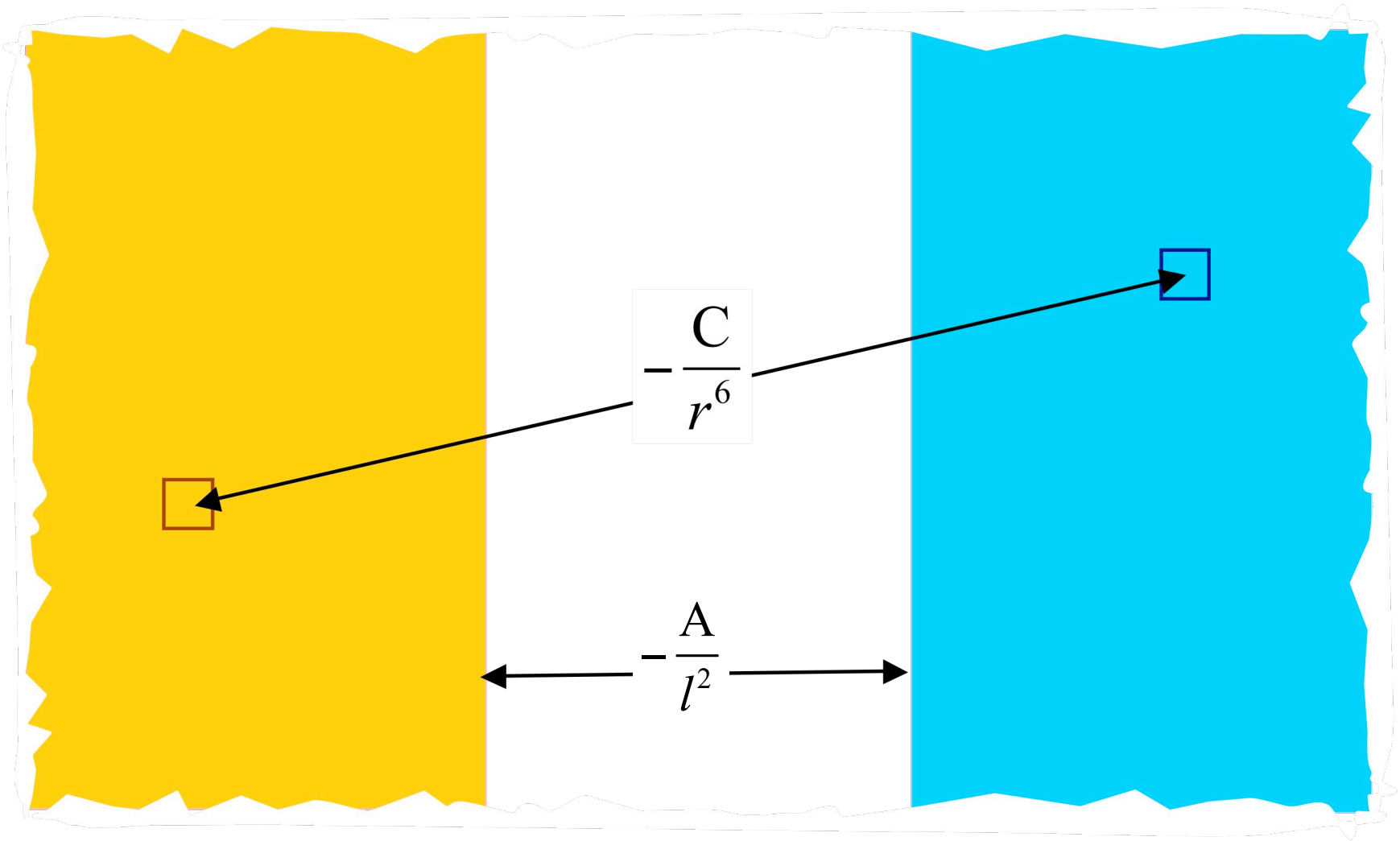
$$-\frac{C}{r^6}$$

<u>Keesom</u>:
permanent dipoles,
average attractive mutual orientation.

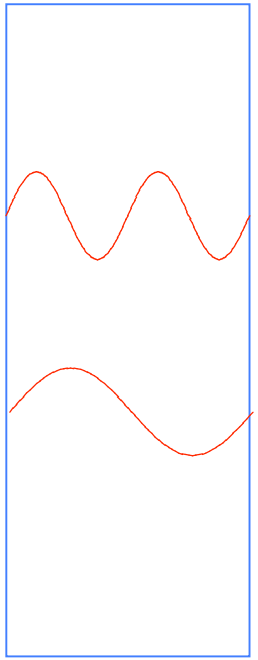
<u>Debye</u>:
permanent dipole induces a
dipole in another, non-polar,
molecule.

<u>London</u> dispersion:
transient dipoles on polarizable bodies.

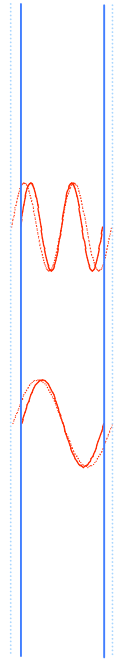
Extension to condensed media (two half-spaces: Pairwise summation of dipole interactions (Derjaguin, 1934, Hamaker, 1937)



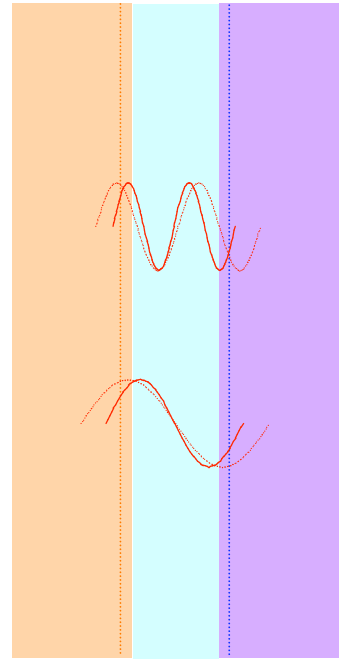
Modern, macroscopic point of view
Focus on electromagnetic waves



Planck (1890's):
Hollow "black" box

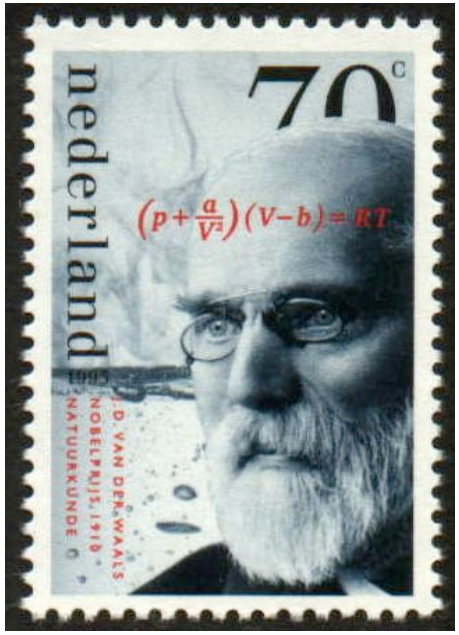


Casimir (1940's):
Parallel flat ideally conducting surfaces.



Lifshitz, Dzyaloshinskii & Pitaevski (1950's):
Any two flat surfaces of any materials

Dramatis personae



Johannes Diderik van der Waals
(1837–1923)

Hendrik Brugt Gerhard Casimir
(1909-2000)

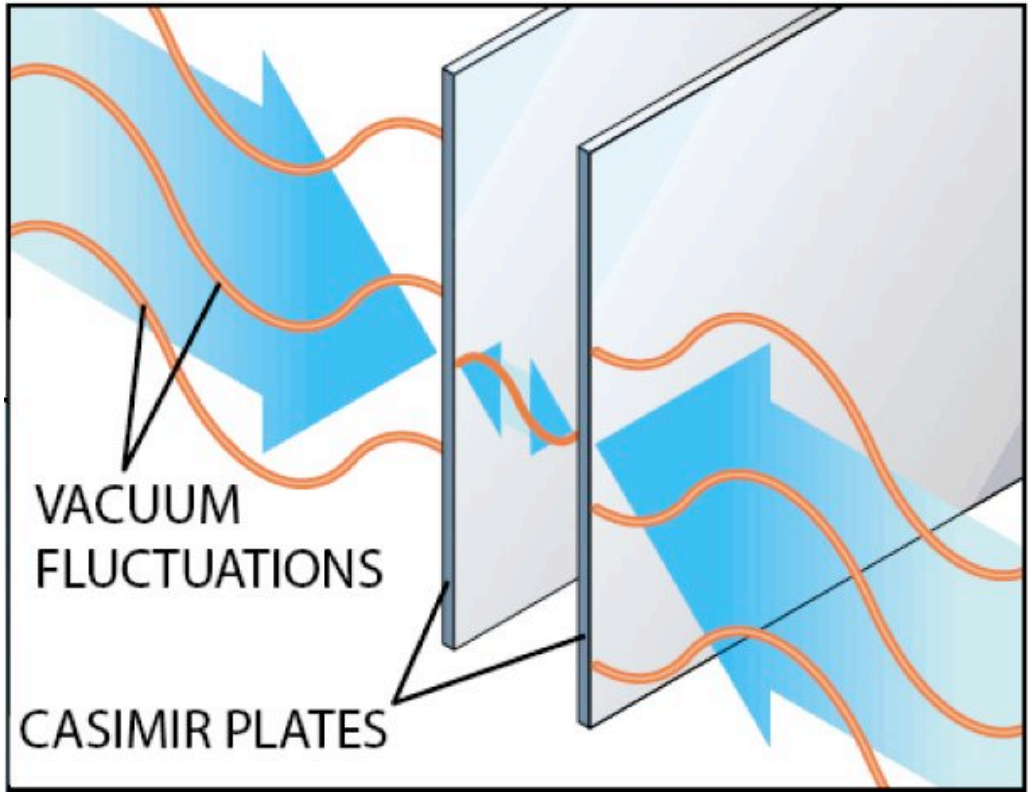
Evgeny Mikhailovich Lifshitz
(1915 – 1985)

His equation of state was so successful that it stopped the development of liquid state theory for a hundred years. (Lebowitz, 1985)

I mentioned my results to Niels Bohr, during a walk. “That is nice,” he said, “that is something new”... and he mumbled something about zero-point energy. That was all, but in retrospect I have to admit that I owe much to this remark. (Casimir, 1992)

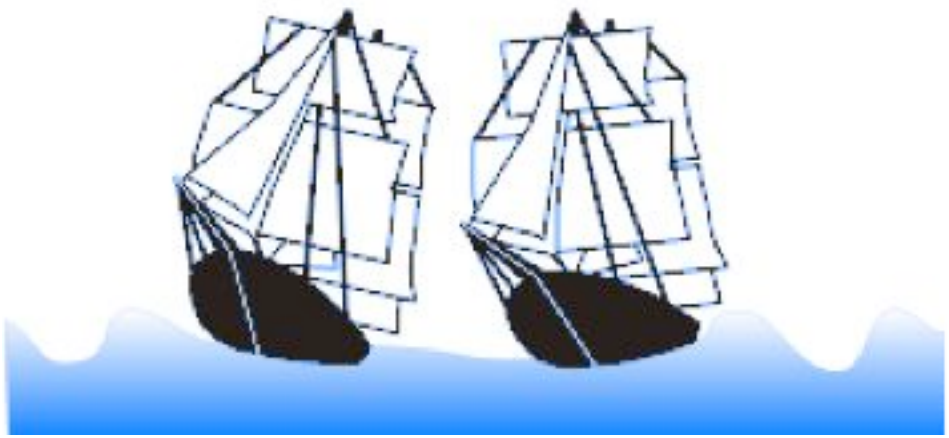
His [Lifschitz’] calculations were so cumbersome that they were not even reproduced in the relevant Landau and Lifshitz volume, where, as a rule, all important calculations are given. (Ginzburg, 1979)

Casimir force – metal plates in the storm of the quantum vacuum



Scientific American December 1997

“Une force certaine d’attraction“
(P.C. Causee: The mariners’ album 19th C)



NY Times
quantum
foam

Science Times

The New York Times

TUESDAY, JANUARY 21, 1997

Physicists Confirm Power of Nothing, Measuring Force of Quantum 'Foam'

Fluctuations in the vacuum are the universal pulse of existence.

By MALCOLM W. BROWNE

FOR a half century, physicists have known that there is no such thing as absolute nothingness, and that the vacuum of empty space, devoid of even a single atom of matter, seethes with subtle activity. Now, with the help of a pair of metal plates and a fine wire, a scientist has directly measured the force exerted by fleeting fluctuations in the vacuum that pace the universal pulse of existence.

The sensitive experiment performed at the University of Washington in Seattle by Dr. Steve K. Lamoreaux, an atomic physicist who is now at Los Alamos National Laboratory, was described in a recent issue of the journal Physical Review Letters. Dr. Lamoreaux's results almost perfectly matched theoretical predictions based on quantum electrodynamics, a theory that touches on many of the riddles of existence and on the origin and fate of the universe.

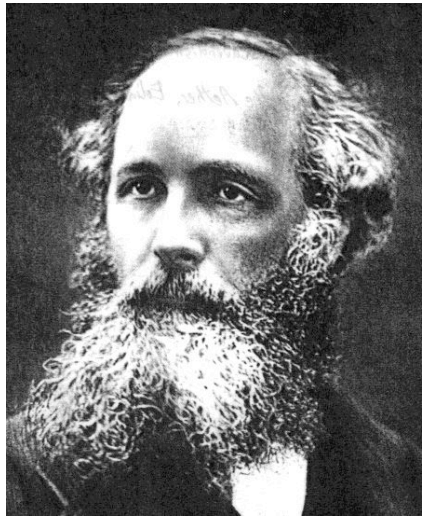
The theory has been wonderfully accurate in predicting the results of subatomic particle experiments, and it has also been the basis of speculations verging on science fiction. One of the wilder ones is the possibility that the universal vacuum — the ubiquitous empty space of the universe — might actually be a false vacuum.

If that were so, something might cause the present-day universal vacuum to collapse to a different vacuum of a lower energy. The effect, propagating at the speed of light, would be the annihilation of all matter in the universe. There would be no warning for humankind; the earth and its inhabitants would simply cease to exist at

Continued on Page C6

1864 and 1873 J. C. Maxwell

1888 H. Hertz



Ph.D. thesis of P.N. Lebedev (1894):

Hidden in Hertz's research, in the interpretation of light oscillations as electromagnetic processes, is still another as yet undealt with question, that of the source of light emission of the processes which take place in the molecular vibrator at the time when it give up light energy to the surrounding space; such a problem leads us [...] to one of the most complicated problems of modern physics -- the study of molecular forces.

[...] Adopting the point of view of the electromagnetic theory of light, we must state that between two radiating molecules, just as between two vibrators in which electromagnetic oscillations are excited, there exist ponderomotive forces: They are due to the electromagnetic interaction between the alternating electric current in the molecules [...] ; we must therefore state that there exist between the molecules in such a case molecular forces whose cause is inseparably linked with the radiation processes.

Of greatest interest and of greatest difficulty is the case of a physical body in which many molecules act simultaneously on one another, the vibrations of the latter not being independent owing to their close proximity.

Simplest form of Lifshitz interaction energy: half-spaces A and B across medium m

$$\text{Interaction} = -\frac{\mathrm{A}(l)}{12\pi l^2} \qquad \mathrm{A}(l) = \frac{3\mathrm{k}T}{2} \sum_{\substack{\text{Matsubara sampling} \\ \text{frequencies } \xi_n}} \left(\frac{\varepsilon_\mathrm{A} - \varepsilon_\mathrm{m}}{\varepsilon_\mathrm{A} + \varepsilon_\mathrm{m}}\right)\left(\frac{\varepsilon_\mathrm{B} - \varepsilon_\mathrm{m}}{\varepsilon_\mathrm{B} + \varepsilon_\mathrm{m}}\right) \times Rel(l)$$

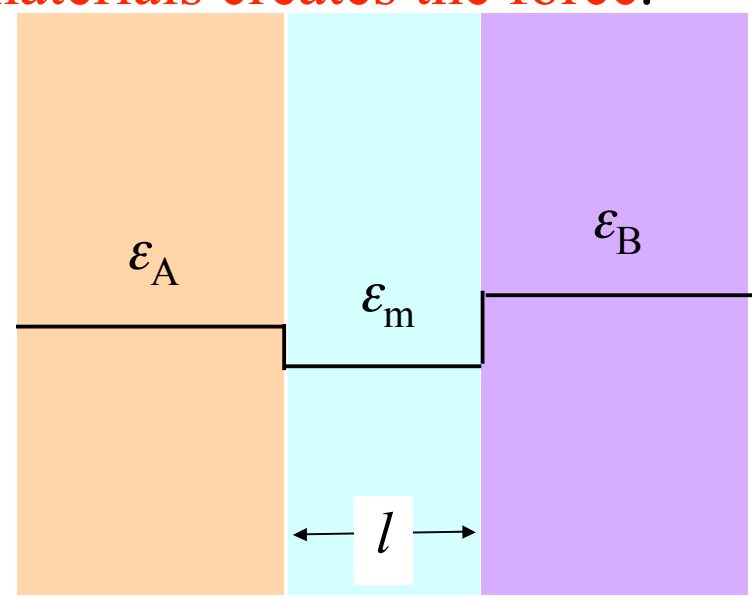
Sum over entire frequency spectrum!

Inverse square dependence of the energy per unit area.

Difference in the responses of materials creates the force.

The usual way to think about interaction is as though bodies have sharp boundaries.

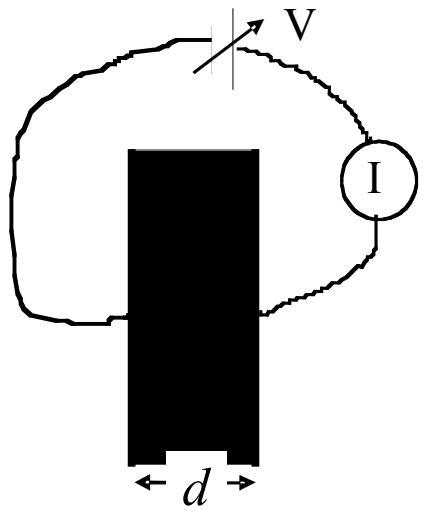
The divergence upon contact is a fiction of these sharp interfaces



Epsilons ε_A, ε_B, ε_m, for interaction come from noise!

$$\left(I^2\right)_\omega = \frac{4kT}{R}$$ (traditional, Nyquist, Johnson)

$$\left(I^2\right)_\omega = \frac{\hbar\omega}{2\pi}\coth\left(\frac{\hbar\omega}{2kT}\right)\frac{\omega\varepsilon''(\omega)}{4\pi d}$$ (modern)



Recall the dissipation term $\varepsilon''(\omega)$ in

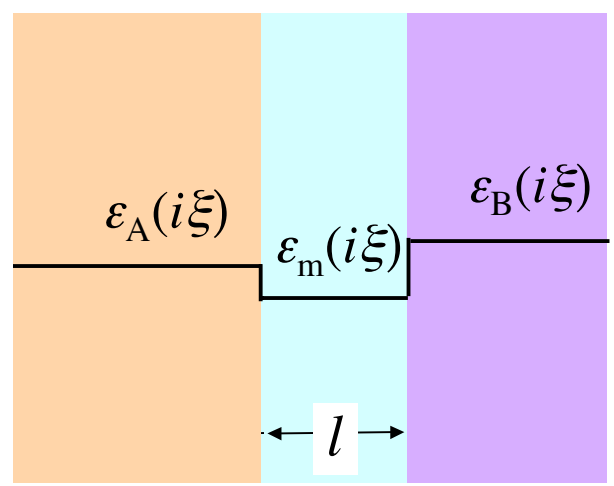
$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega).$$

Use the Kramers-Kronig transform

For "imaginary frequency"

$$\varepsilon(i\xi) \equiv 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\,\varepsilon''(\omega)}{\omega^2 + \xi^2}d\omega$$

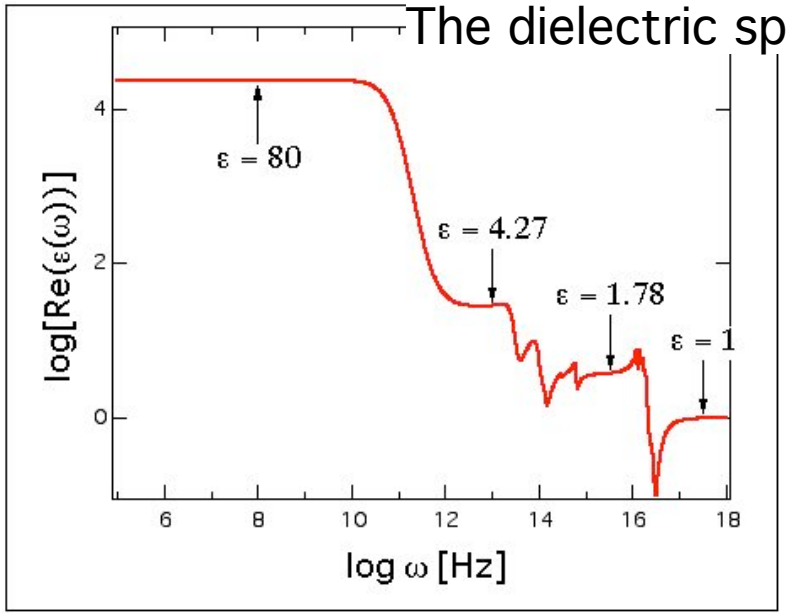
$$\xi = \xi_n \equiv \frac{2\pi kT}{\hbar}n,\ n = 0,1,2,..\infty$$

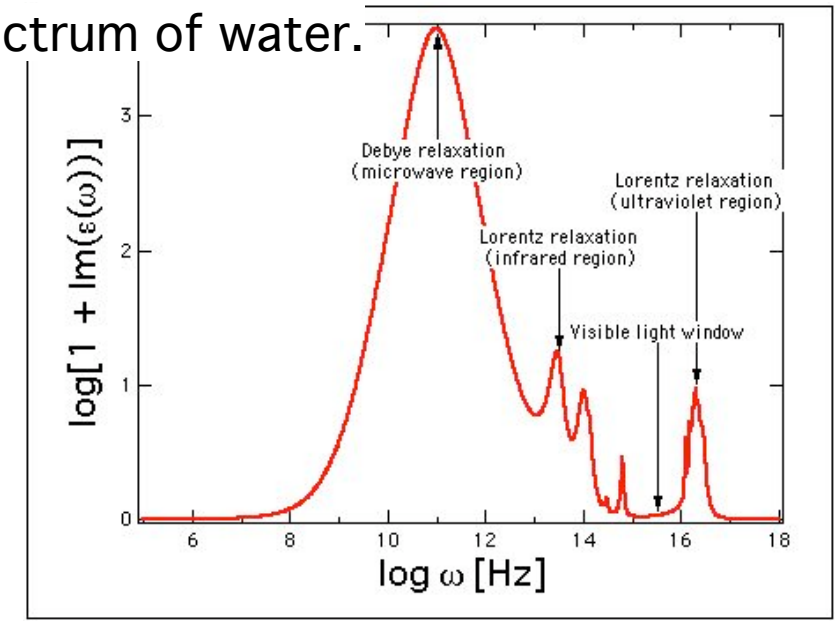


Barry Ninham, David Gingell &
VAP, 1970-80

Connecting van der Waals forces with spectra

The dielectric spectrum of water.





$A_{Am/Am}(l=0)$, Symmetric systems, retardation screening neglected	
Interaction	Hamaker coefficient (kT_{room} units)
hydrocarbon across water	0.95 kT_{room}
mica across hydrocarbon	2.1 kT_{room}
mica across water	3.9 kT_{room}
gold across water	28.9 kT_{room}
water across vacuum	9.4 kT_{room}
hydrocarbon across vacuum	11.6 kT_{room}
mica across vacuum	21.8 kT_{room}
gold across vacuum	48.6 kT_{room}

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Inverse square dependence of the energy per unit area.

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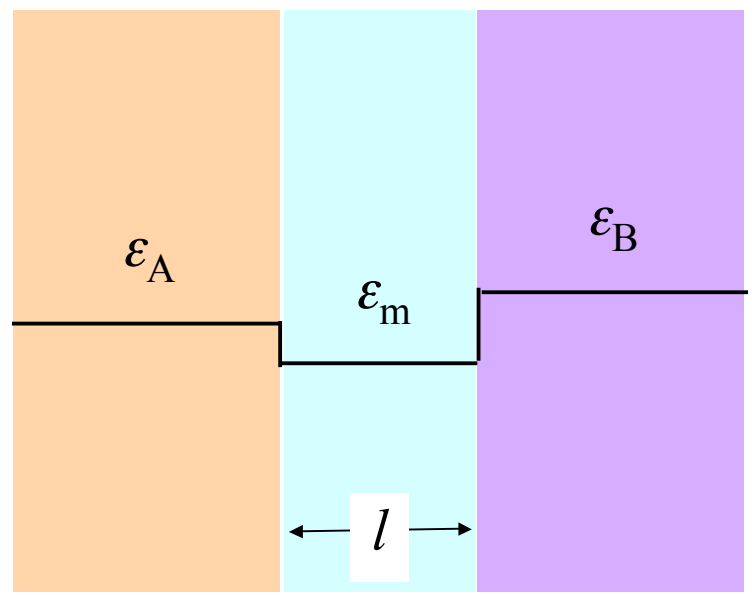
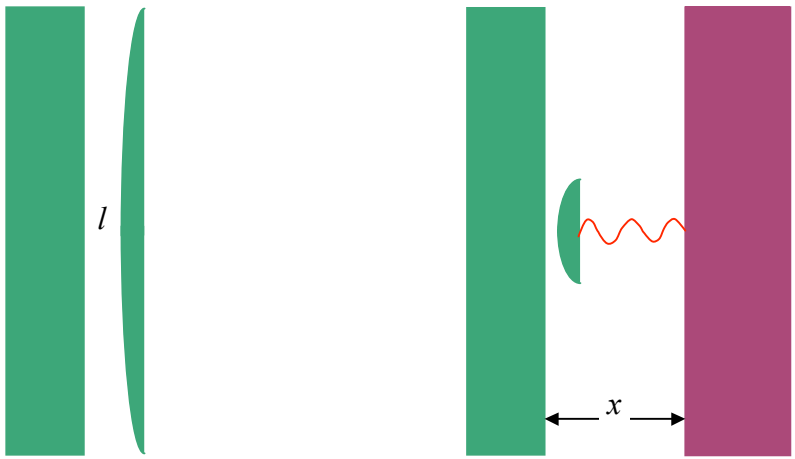


By now, many experimental verifications!

Force balances

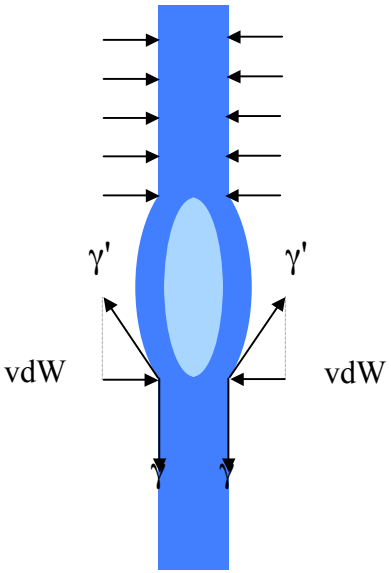
Glass (Derjaguin, Lifshitz, Abrikosova, 1950's)
Mica (Tabor, Winterton, Israelachvili, 1970's)



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)

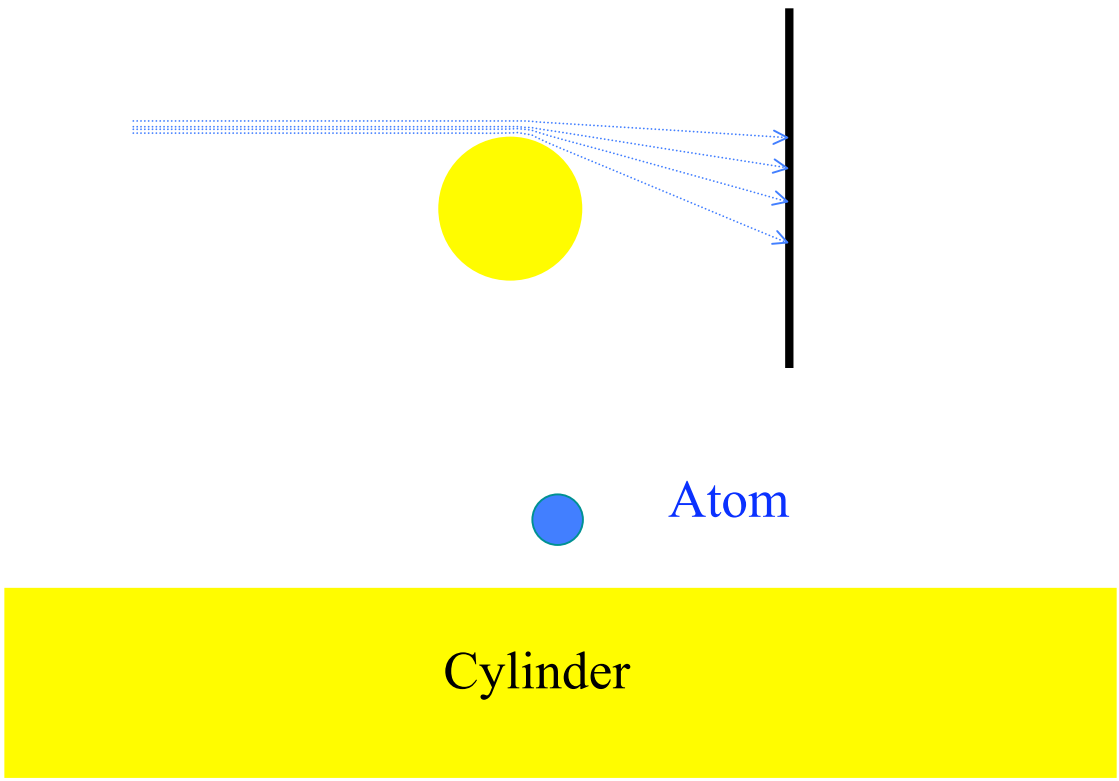


By the strength with which they flatten against each other, two juxtaposed bilayers create a measurable contact angle.

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)

Deflection of an atomic beam

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

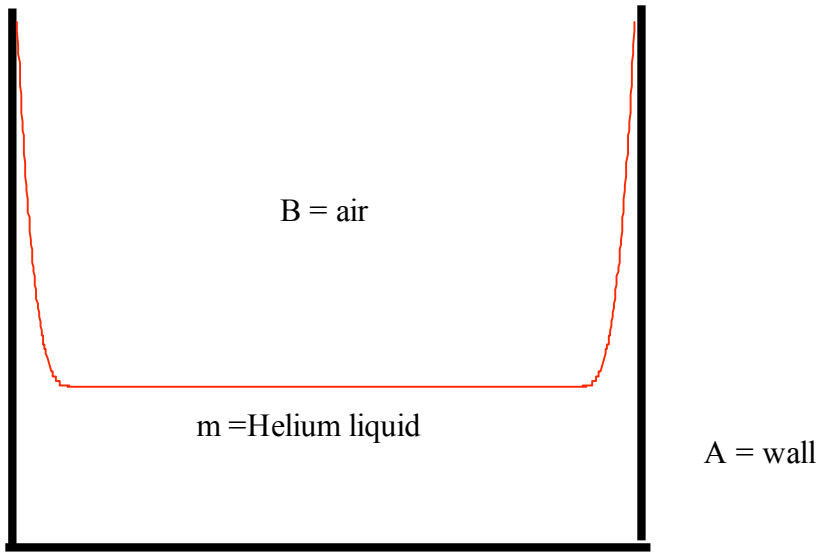


Arnold Shih & V. A. P., "Van der Waals forces between heavy alkali atoms and gold surfaces: comparison of measured and predicted values",

Phys Rev A, 12(3):835 - 841 (1975)

Liquid helium crawling the walls

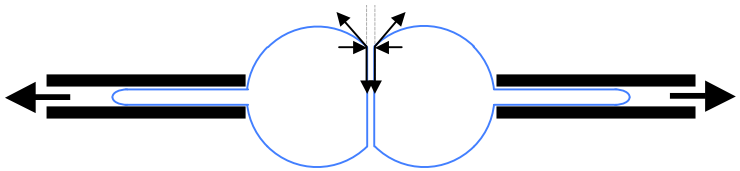
Sabisky & Anderson (1973)



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

Forces between bilayers (Evans, Rand, VAP)



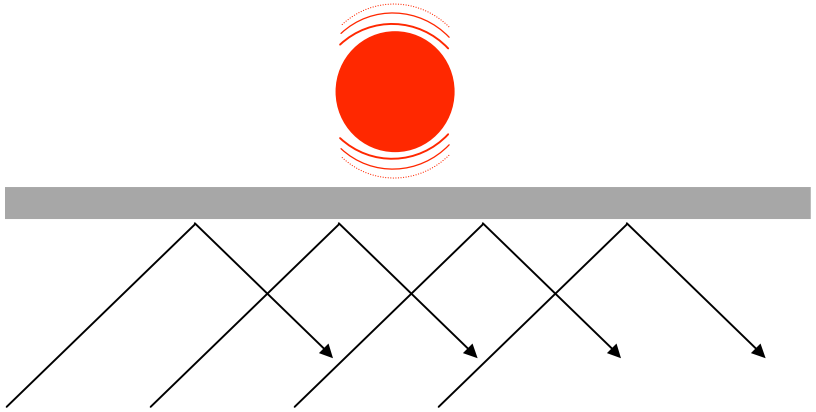
In practice, Van der Waals forces appear mixed with lamellar motions as well as with repulsive hydration forces. E. A. Evans, "Entropy-driven tension in vesicle membranes and unbinding of adherent vesicles" Langmuir, 7:1900-1908 (1991)

Between bilayers (Rand, VAP, 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)

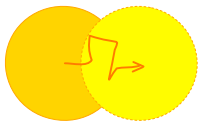
V. A. Parsegian, "Reconciliation of van der Waals force measurements between phosphatidylcholine bilayer in water and between bilayer-coated mica surfaces," Langmuir 9:3625-3628 (1993)

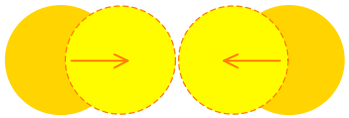
Colloids
D. Prieve



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)

Aerosols (Marlow et al.)

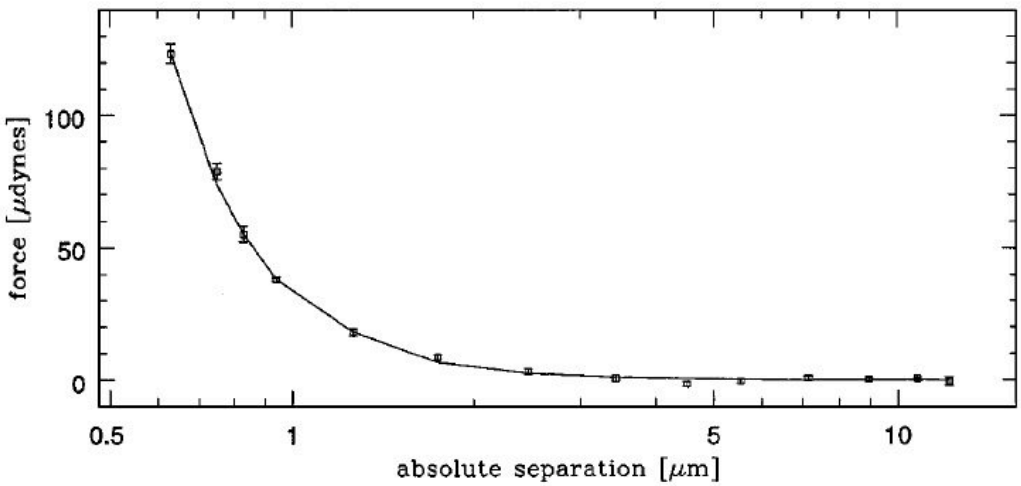


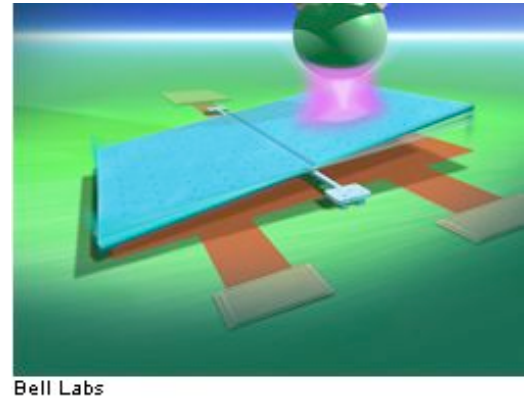


V. Arunachalam, R. R. Lucchese, & W. H. Marlow
"Development of a picture of the van der Waals interaction energy between clusters of nanometer-range particles," Phys. Rev. E 58:3451-347 (1998)
"Simulations of aerosol aggregation including long-range interactions," Phys. Rev. E, 60:2051-2064 (1999)

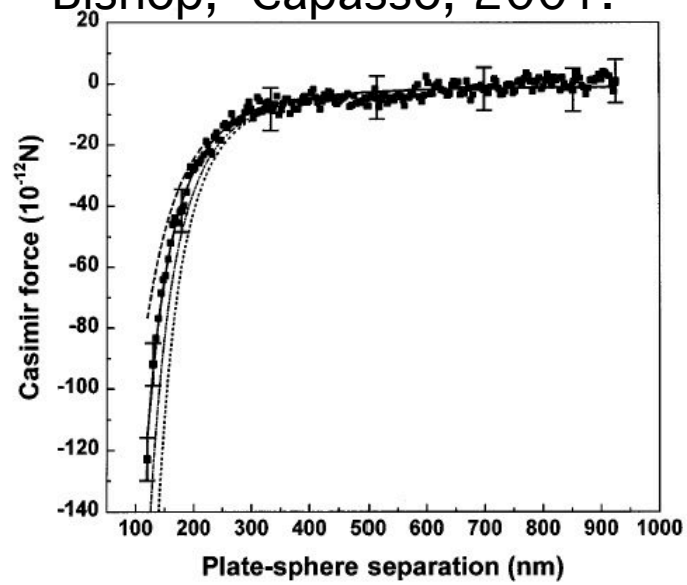
Casimir “effect” (metals)

Lamoreaux, 1997.

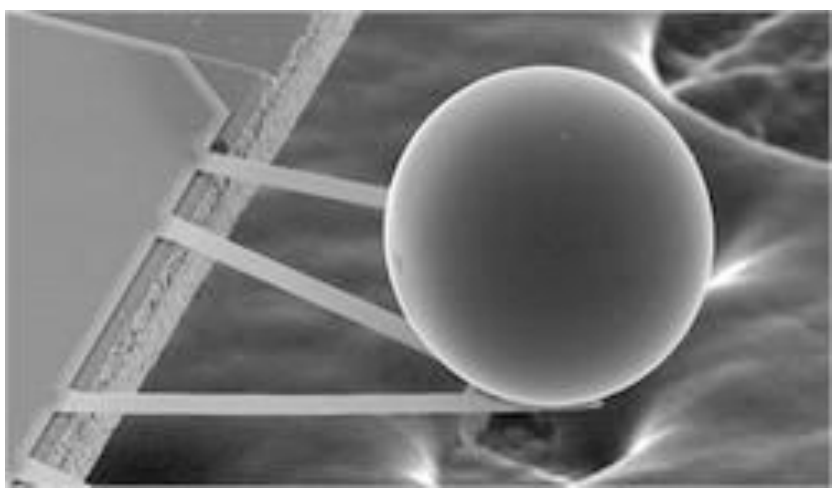




Chan, Aksyuk, Kleiman, Bishop, Capasso, 2001.



Mohideen and Roy, 1998.



Sensitive sphere. This 200-μm-diameter sphere mounted on a cantilever was brought to within 100 nm of a flat surface (not shown) to detect the Casimir force.

Get a grip

Story by Carl Zimmer ~ Illustration by Sally J. Bensusen

Get a Grip

The gecko owes its superior climbing skills to atomic power.

Racing up a tree at three feet per second, a gecko seems to defy physics. This lizard can generate enough sticking power with one toe to support its entire weight, yet it uses no detectable force when pulling away from the tree to take its next step. The secret to this climbing prowess, according to a group of researchers who call themselves the Gecko Team, is a special sort of stickiness. Geckos, the team has found, do obey physical laws, but it's the subatomic realm that makes the rules governing their ascension.

Led by environmental physiologist Kellar Autumn, of Lewis and Clark College in Portland, Oregon, and bioengineer Robert Full, of the University of California, Berkeley, and supported by IS Robotics (ISR) in Massachusetts, the Gecko Team studies on a microscopic scale how geckos climb. Thin leaves of tissue, arranged like pages in a book, cover the animal's toes. Each leaf is covered with hundreds of thousands of tiny hairlike growths called setae; a single gecko may have 2 million of them on its feet. These setae, in turn, branch into hundreds of spatula-shaped tips, each only 200 nanometers in diameter (smaller than a bacterium).

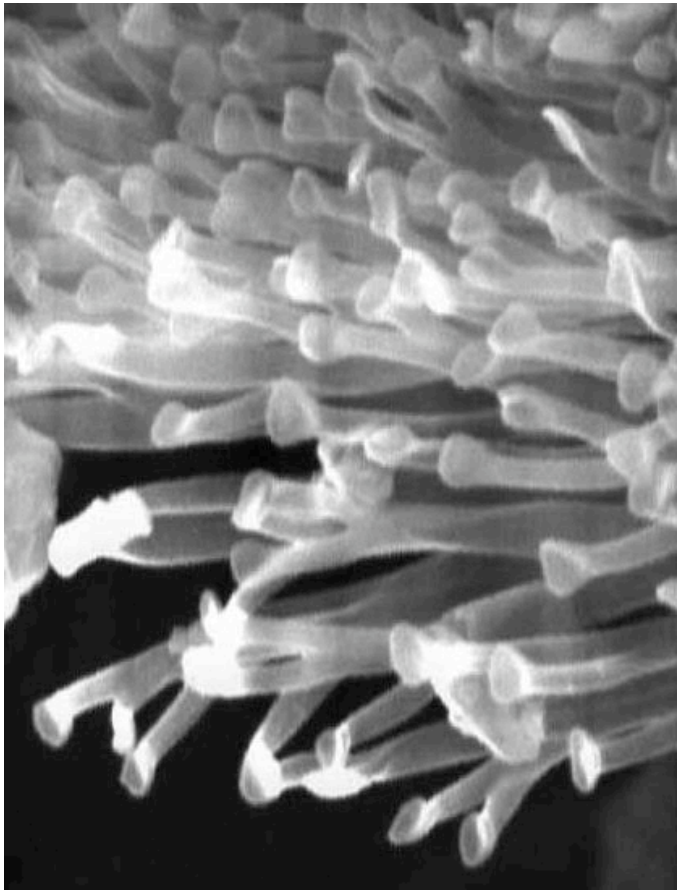
In the laboratories of Tom Kenny, at Stanford University, and Ron Fearing, at UC Berkeley, team members isolated individual setae and used a microscopic sensor to measure adhesive force. Simulating the movements of a gecko's foot, the researchers first pressed the seta against the sensor and then pulled it away. They discovered that a single seta could resist their efforts with surprising force—enough, in fact, to support the weight of an ant.

According to the Gecko Team, this reptile owes its sticking power to a faint interplay between the atoms on the seta's spatula-shaped tips and the atoms on the surface of whatever the animal is climbing. This interplay stems from a phenomenon known in quantum physics as van der Waals forces.

An atom is composed of a positively charged nucleus surrounded by a cloud of negatively charged electrons. If the positive charge of the nucleus equals the negative charge of the electrons, the atom as a whole carries no charge. But electrons flit unpredictably around the nucleus. Sometimes a number of them will pile up—just for an instant—on one side of the atom. When that happens, the atom temporarily has a

K. Autumn et al. "Evidence for van der Waals adhesion in gecko setai," PNAS, 192252799

Gecko's grip grasped



K. Autumn, W.-P. Chang, R. Fearing, T. Hsieh, T. Kenny, L. Liang, W. Zesch, R.J. Full. Nature 2000.
Adhesive force of a single gecko foot-hair.

How does Gecko manage to walk on vertical smooth walls?

Suction? (Salamander). Capillary adhesion? (Small frogs). Interlocking? (Cockroach)

It's van der Waals interactions!

Two measurements in detail to show consequences of

1. Spatially continuous dielectric response

2. Added solutes changing dielectric properties of solution.

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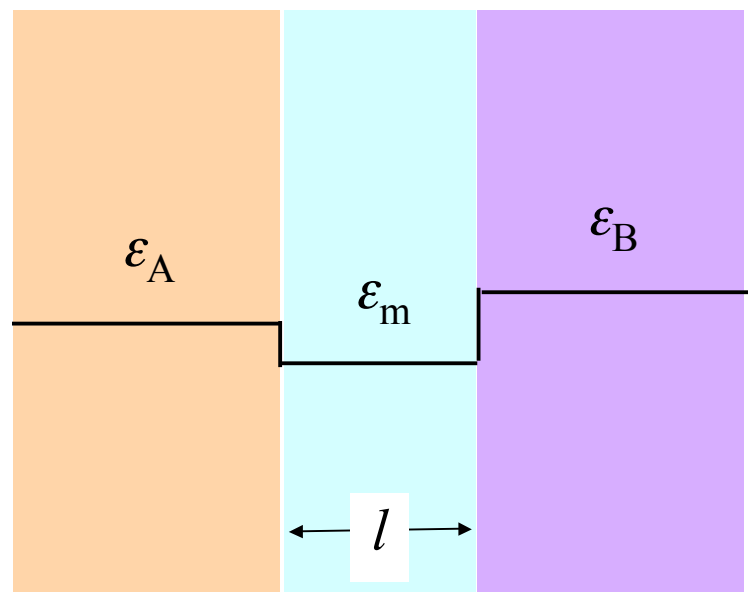
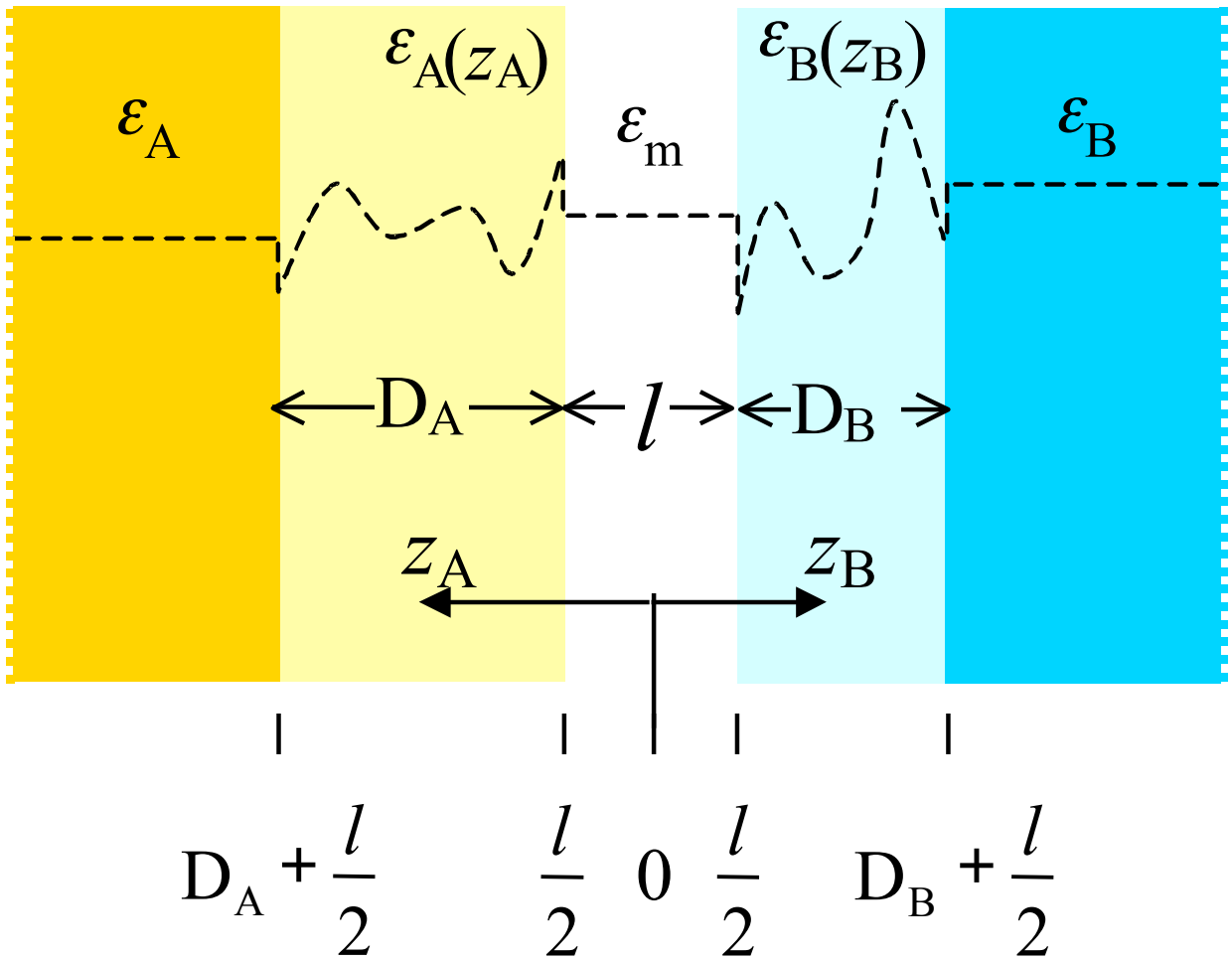


Generalization for spatially varying polarizability $\varepsilon(z)$

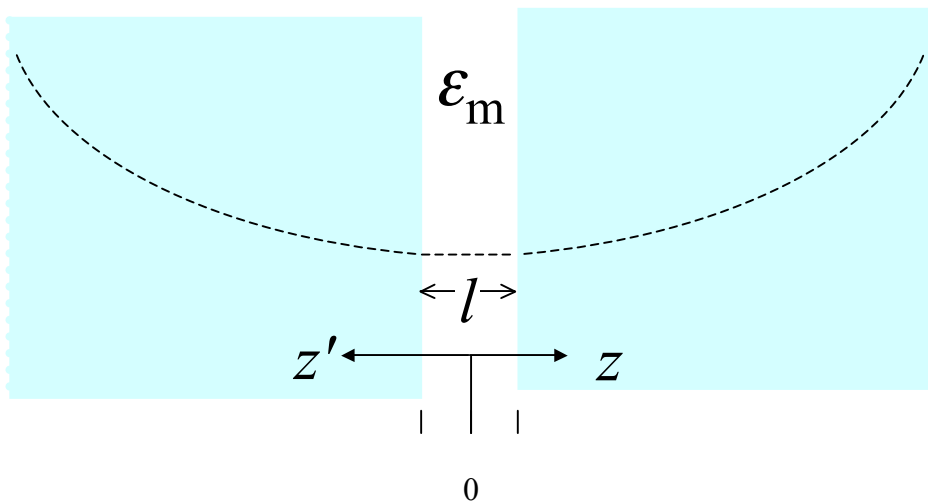


Rudi Podgornik & VAP 2001-04

E.g., Exponential variation of response in an infinitely thick layer

$$\varepsilon_{a'}(z') = \varepsilon_m e^{-\gamma_e (z' - l/2)}$$

$$\varepsilon_a(z) = \varepsilon_m e^{-\gamma_e (z - l/2)}$$

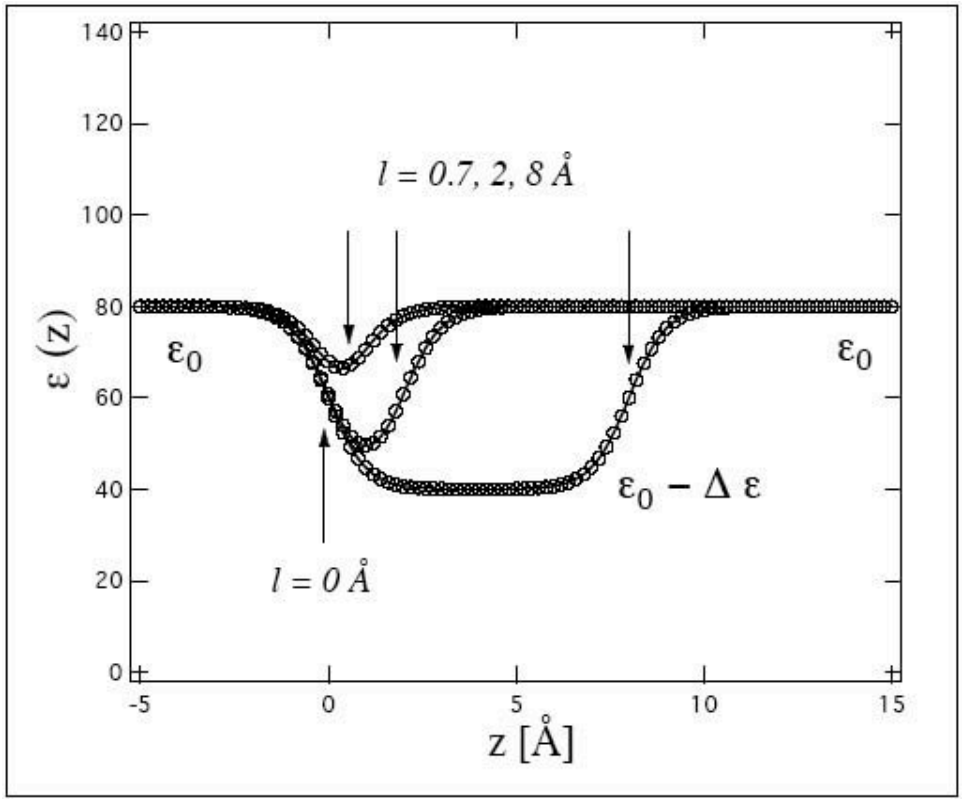


Small $\gamma_e l$ limit

$$G(\gamma_e l \to 0) \sim \frac{kT\gamma_e^2}{32\pi} \sum_{n=0}^{\infty}{}' \gamma_e^2 \ln(\gamma_e l)$$

George Weiss & VAP 1970's

Now relax even the assumption of a constant medium.



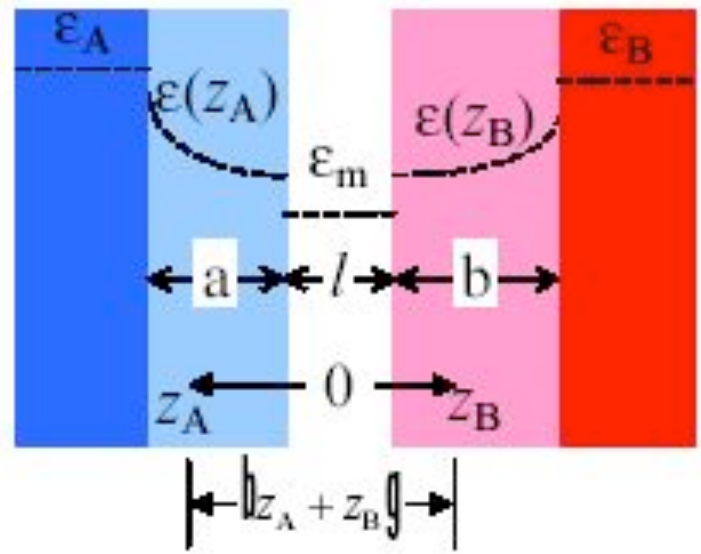
Rudi Podgornik & VAP J Chem. Phys. 2005

Example 1. Computer chip design

Graded Layer Hamaker Constants

Finite steps in ε at $z_A = \frac{l}{2} + a, \frac{l}{2}, z_B = \frac{l}{2} + b, \frac{l}{2}$ create attractions as they do in cases where ε is constant across planar regions

Parsegian & Weiss, J. Colloid & Interf. Sci, 1971



- Inhomogeneous Graded Layers
  - Variations in epsilon in layer

$$\varepsilon_A(z_A) = \varepsilon_m + \frac{(\varepsilon_A - \varepsilon_m)}{a^2}\left(z_A - l/2\right)^2, \quad \varepsilon_B(z_B) = \varepsilon_m + \frac{(\varepsilon_B - \varepsilon_m)}{b^2}\left(z_B - l/2\right)^2.$$

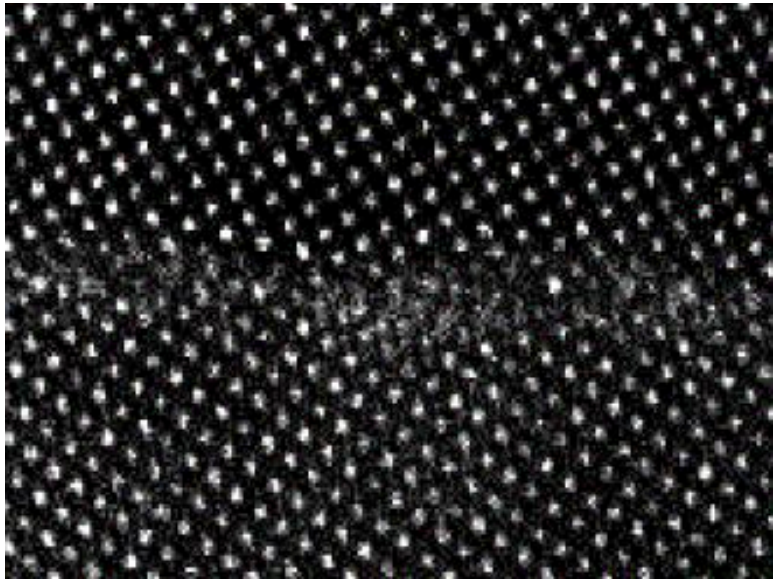
- Assume Quadratic Grading In Layer
  - Use Effective Medium Approx.

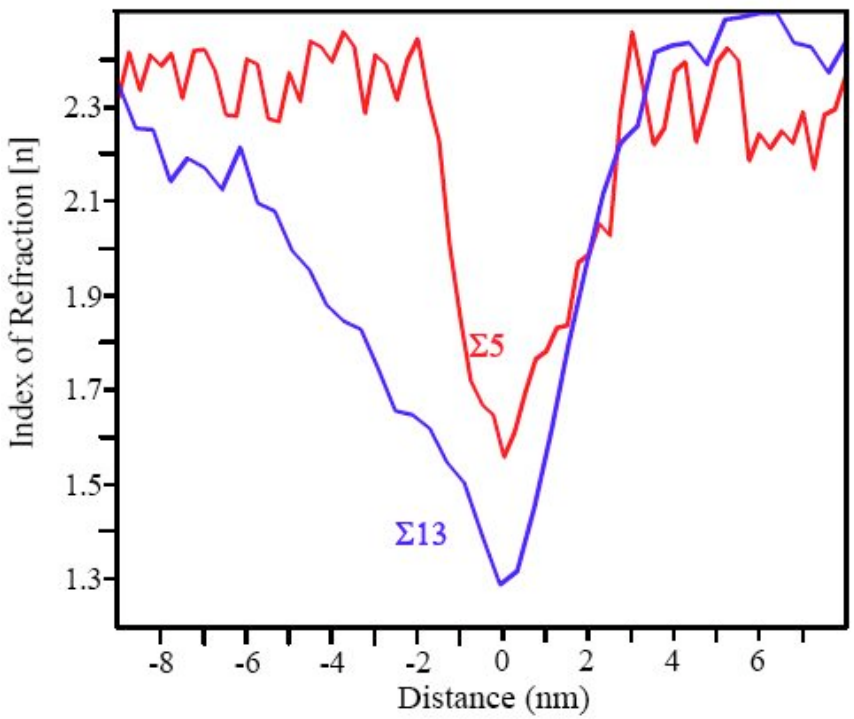
Roger French et al. 2000, Dupont Labs

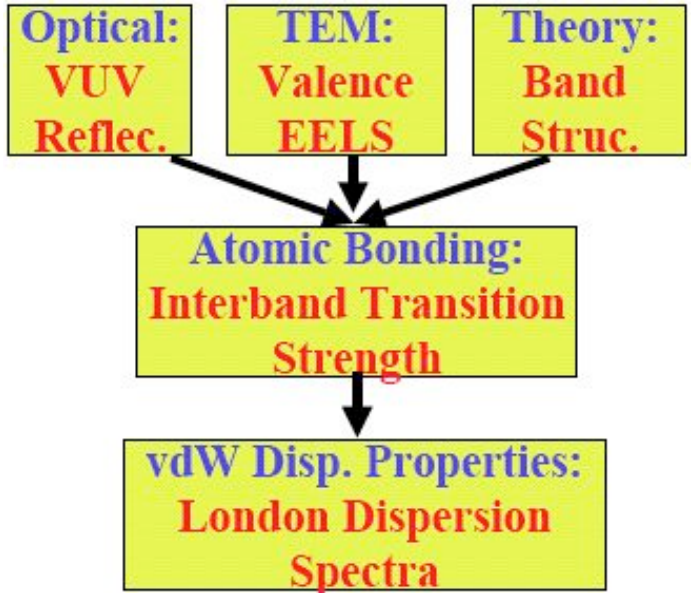
Measure $\varepsilon(z)$!

SrTiO3 vdW interaction across grain boundaries.

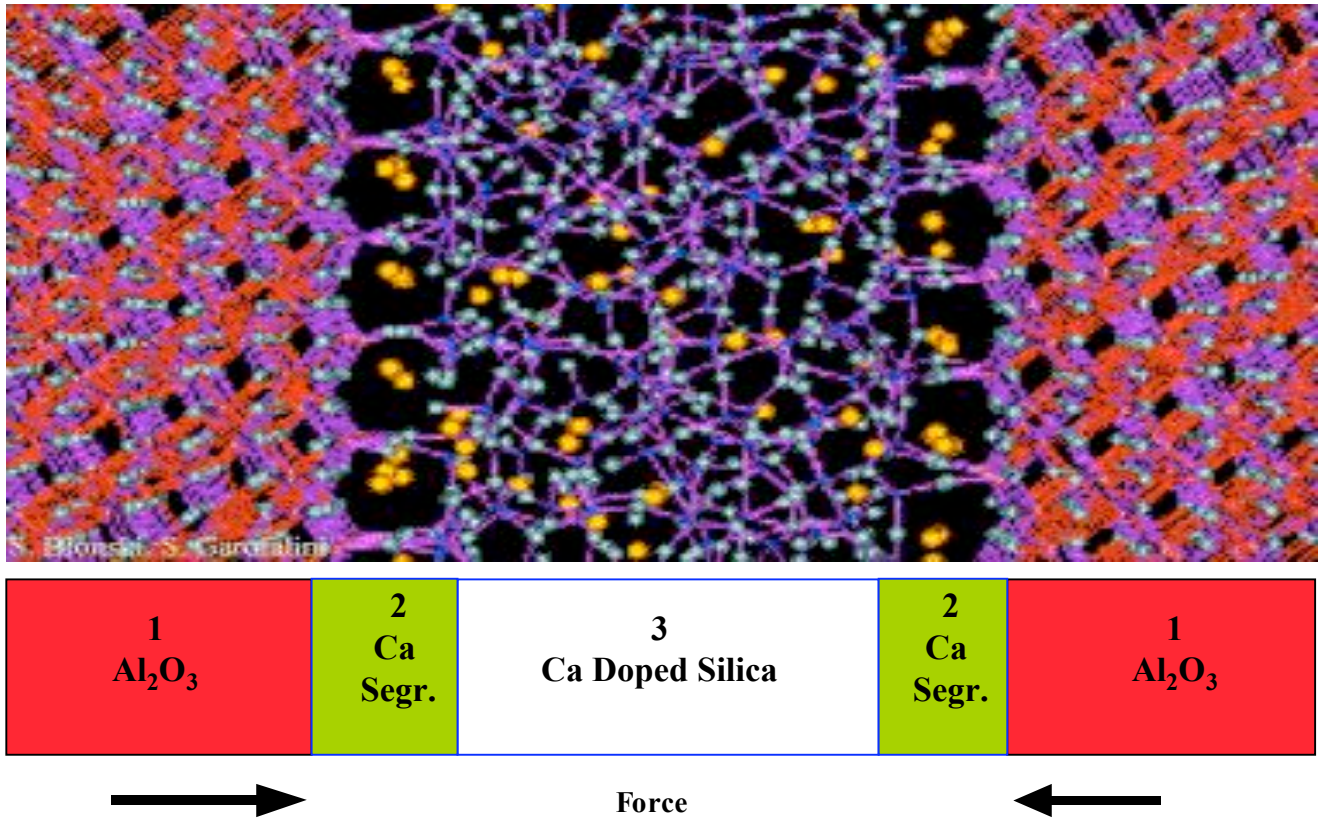
Roger French, Klaus van Benthem, Lin Desnoyers et al.







Interfacial Adsorption, Segregation, Diffuse Layers



Ca Doped Silica IGF in Alumina

Calcium Segregation To Interface (Garofalini – Rutgers)

As A Function of Ca Conc.

Extra Shielding Layer For Dispersion Interaction

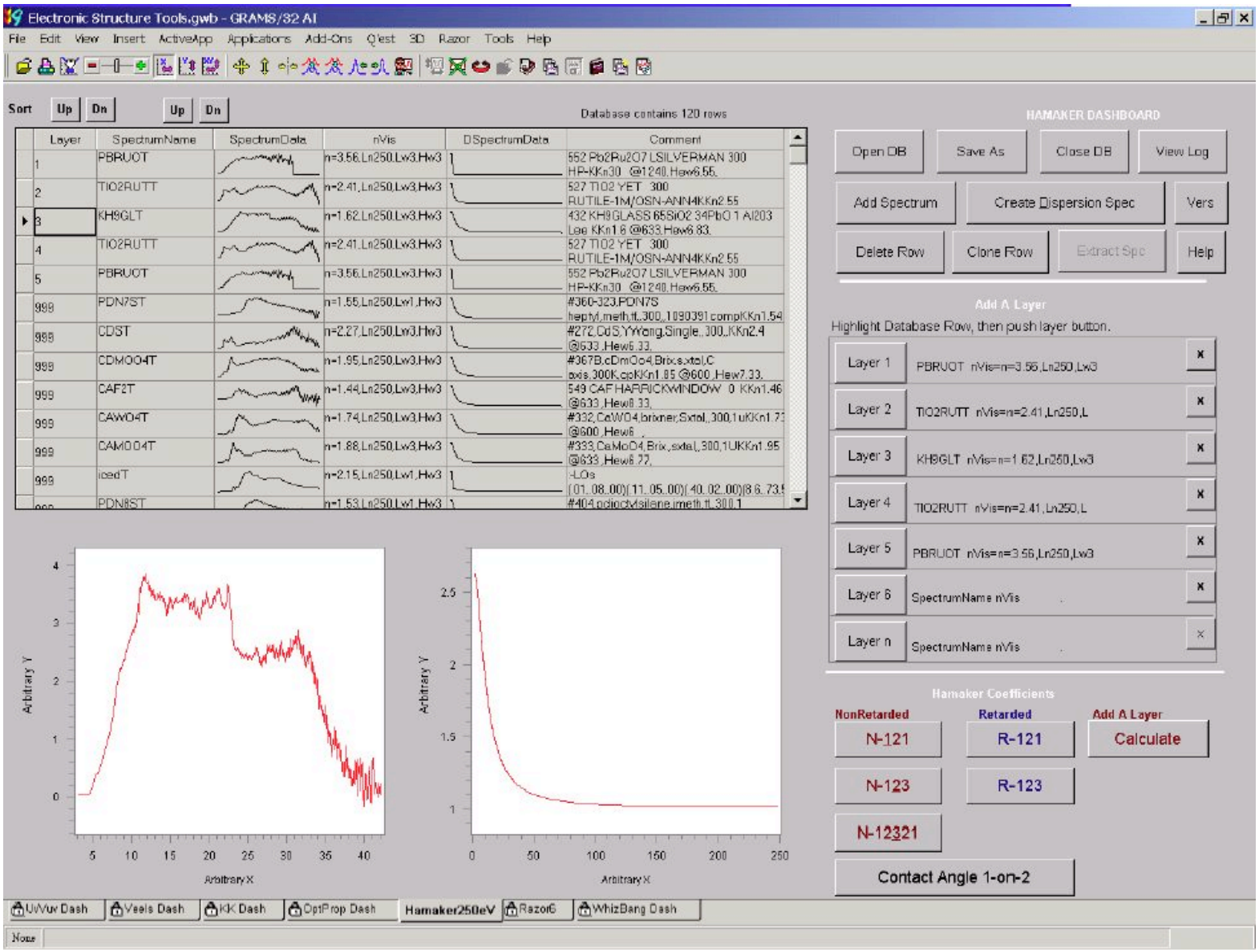
(from Roger French 2004)

Practical, profitable, instructive

- Production of thin film resistors
- ~ 300 in every desk/laptop computer
- Spectroscopy

  to stimulate theory and

  to examine new systems

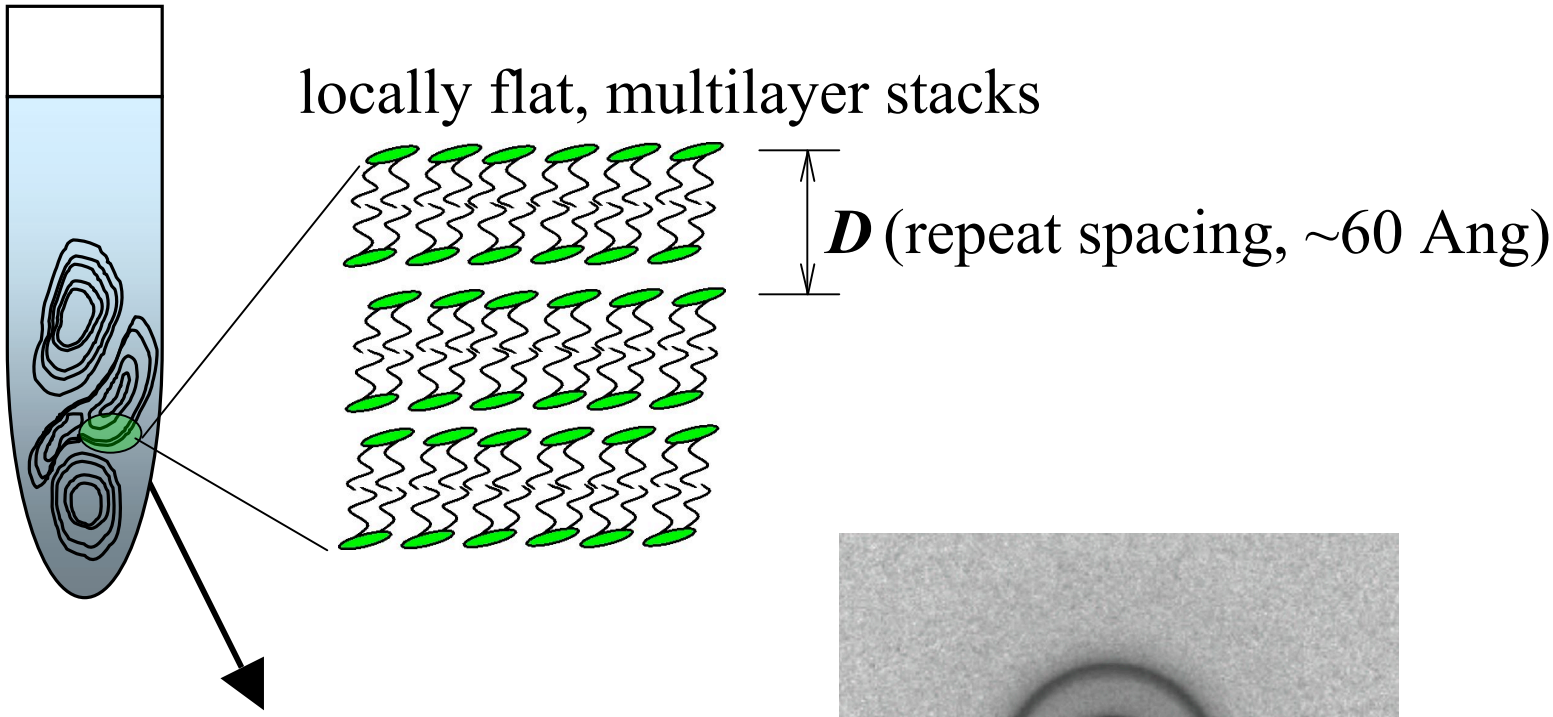


Online program

R. French, L. DeNoyer (2003) Gecko Hamaker program, available for education and research at http://sourceforge.net/projects/geckoproj/

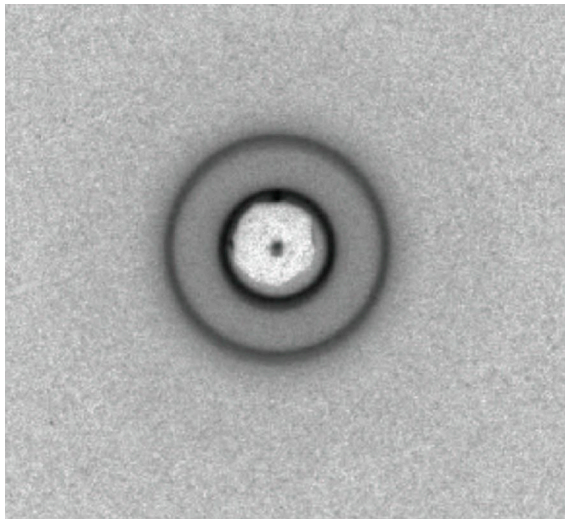
Example 2. Lipid bilayers, solutes control spectra

Multilayers: Neutral lipid bilayers in salt water



Small-angle x-ray scattering

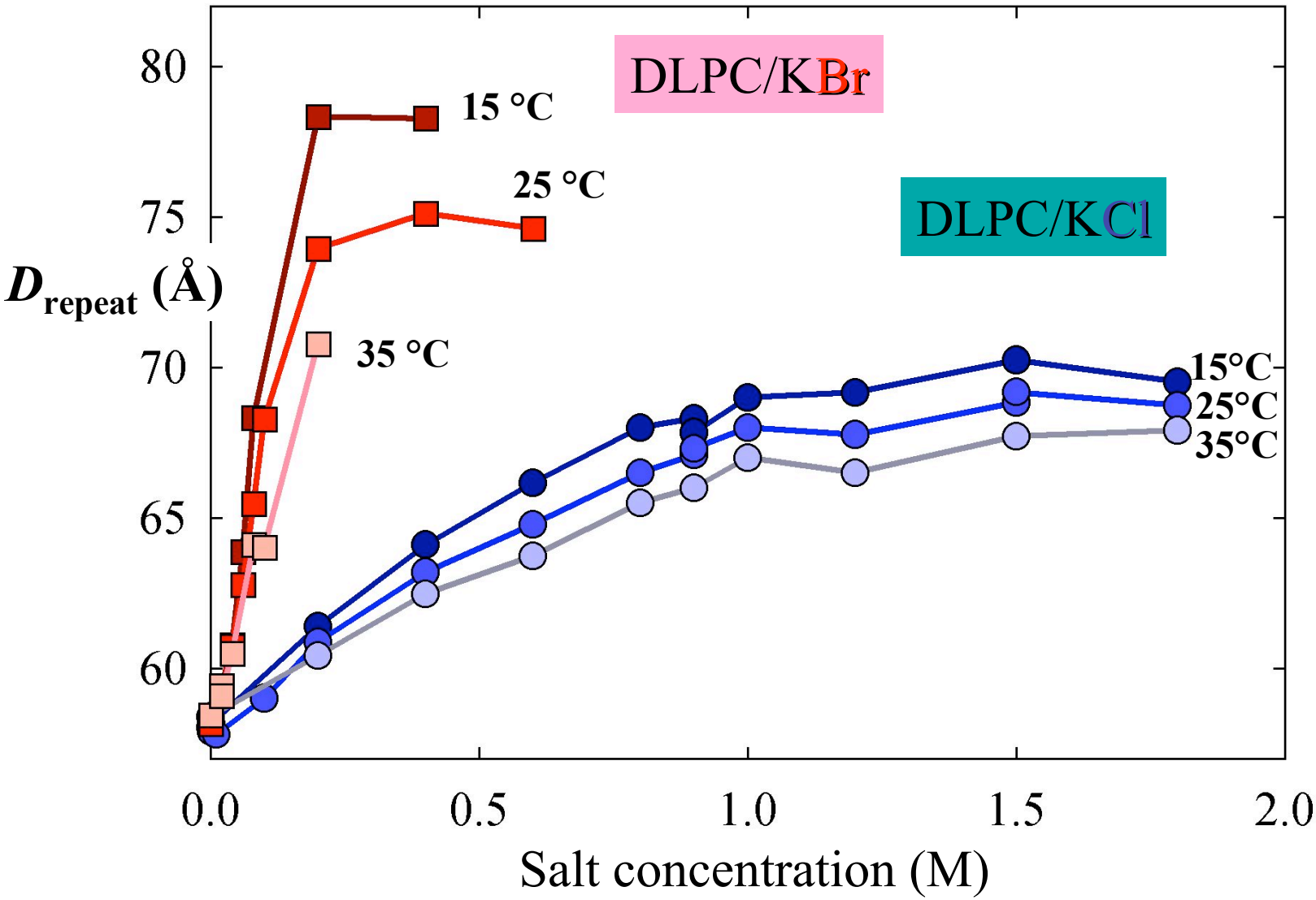
$D = 2\pi/q \sim 60$Å



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

In excess solution, neutral lipids swell with added salt.

Horia Petrache (2004)

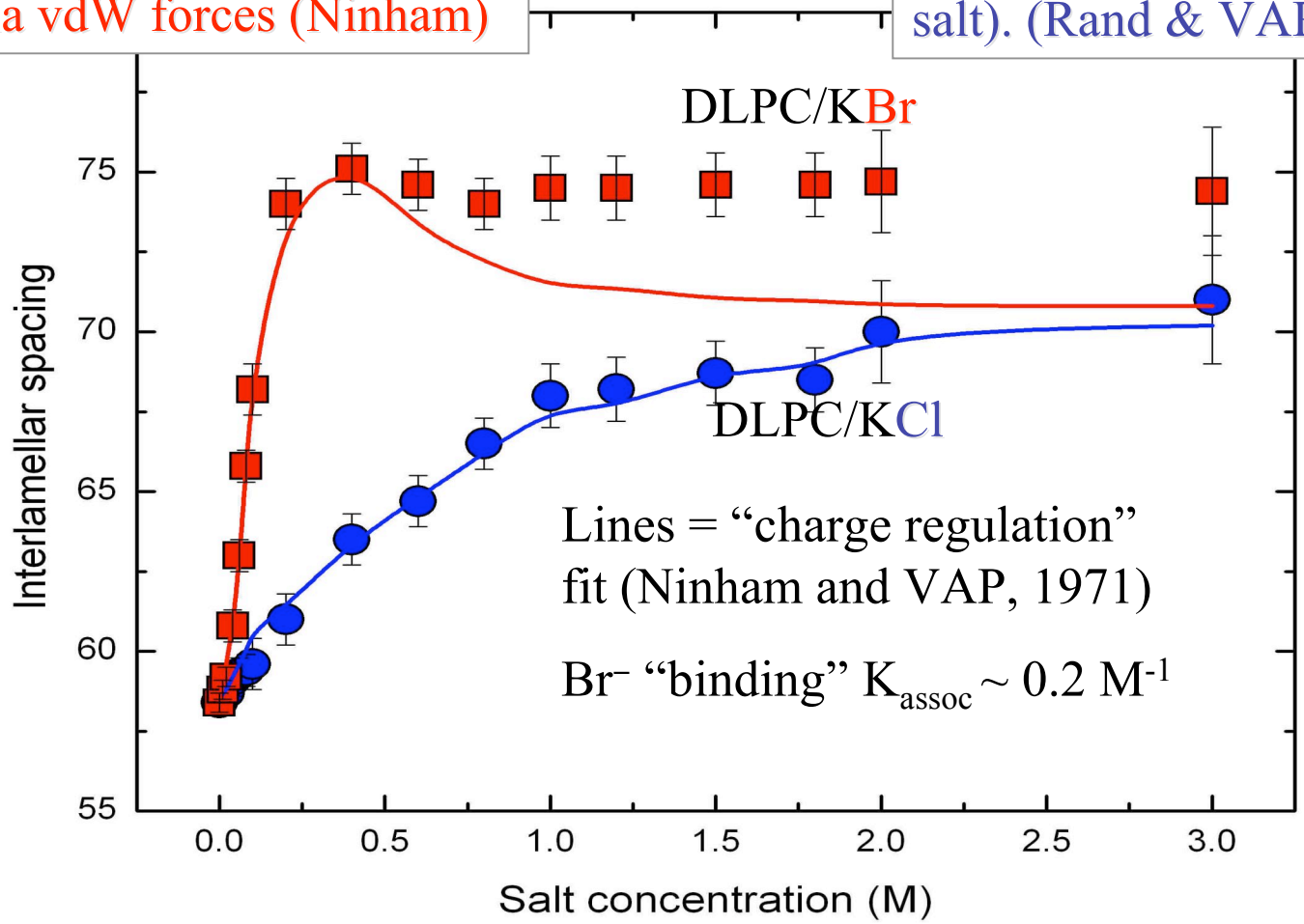


Salt screening/weakening of vdW forces: three new ideas

Horia Petrache, Itamar Kimche, Daniel Harries, VAP 2005

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)



Example 3.
Kevin Cahill:
"Only Keesom, Debye, London power law?
How about first-order interactions?"

distance; cf. §62, Problem 1, and §61, 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

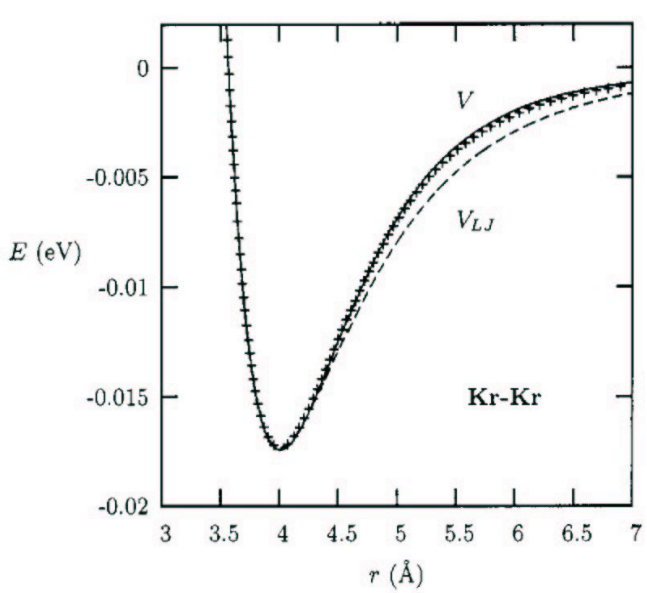
A Rydberg-like potential $V_{Rydberg}$,

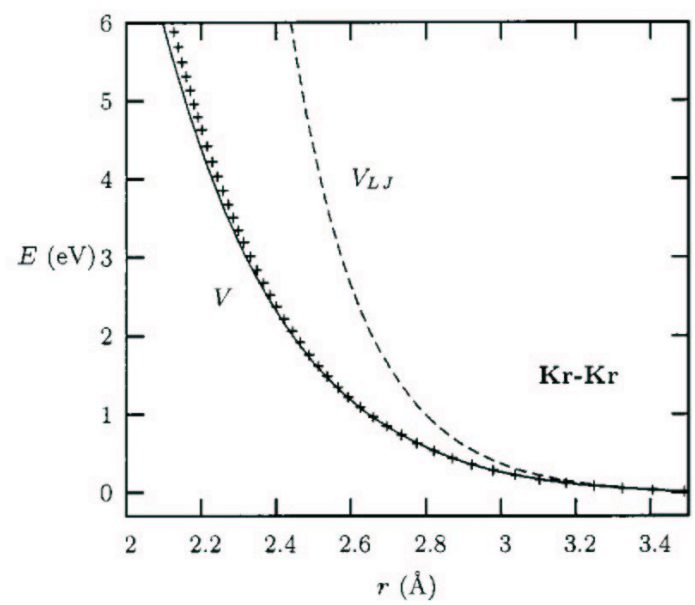
better than Lennard-Jones V_{LJ} 6-12 potential generally used.

$$V_{Rydberg} = V(r) = ae^{-br}(1 - cr) - \frac{d}{r^6 + er^{-6}}$$

$$V_{LJ}(r) = |V(r_o)|\left[\left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_o}{r}\right)^{6}\right]$$

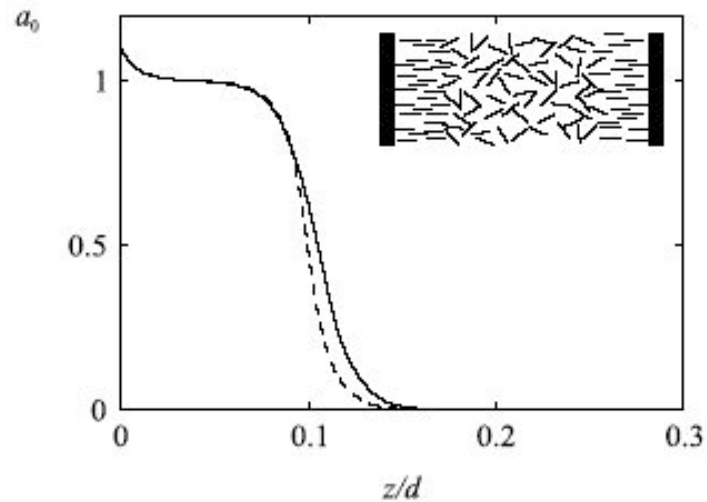
+ symbol "exact" numerical solution Meath and Aziz, Molec. Phys., 52, 225 (1984).





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

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



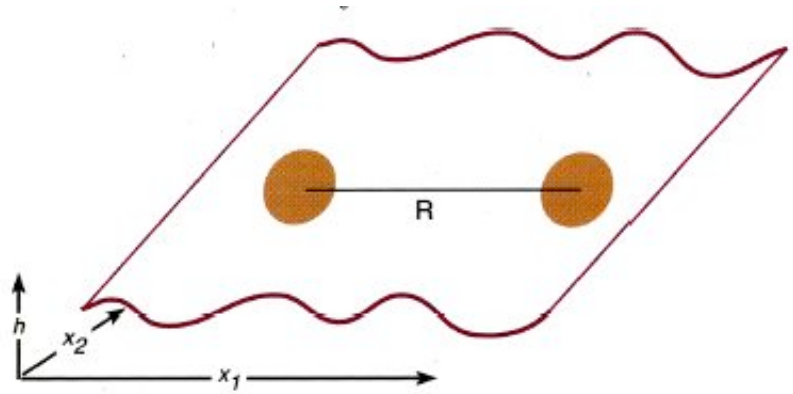
Nematic film with stiff boundaries
(Ajdari, Duplantier, Hone, Peliti, Prost, 1982; Mikheev, 1989).

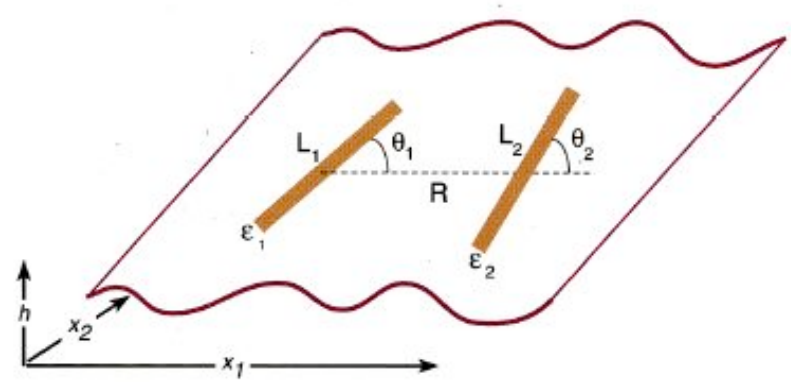
Nematic wetting (Ziherl, Podgornik and Zumer, 1998).

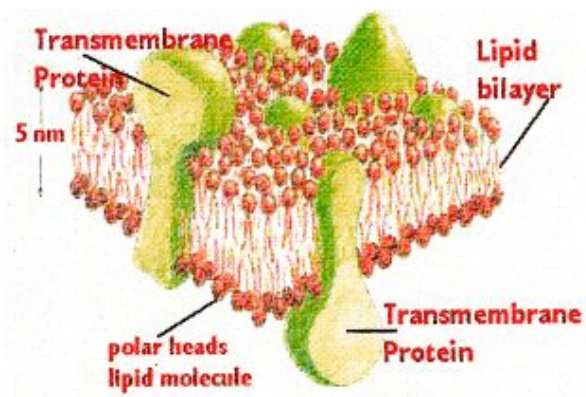
Smectic films (Li and Kardar, 1992).

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

Back to the boats!







Interaction between (lipid) membrane inclusions such as proteins.

Important in understanding aggregation of membrane proteins.

“Universal thermal radiation drag on neutral objects”

Vanik Mkrtchian, VAP,
Rudi Podgornik,
Wayne Saslow`

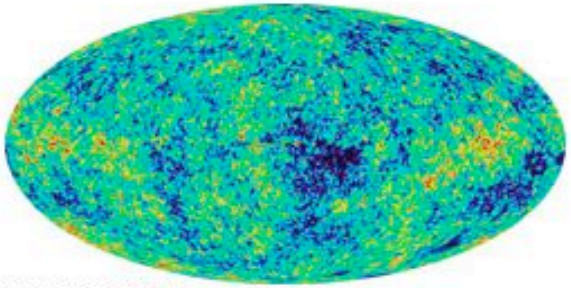
Physical Review Focus

Phys. Rev. Lett. **91**, 220801
(issue of 28 November 2003)
Title and Authors

5 December 2003

Photons Are a Drag

There's no escape from friction. Objects moving through a vacuum or even interstellar space feel a universal drag from the photons that are everywhere, according to the 28 November *PRL*. Although the drag is tiny, the researchers believe it may alter cosmologists' estimates of the time it took for atoms to coalesce after the big bang. But some cosmologists say the effect, although real, is not relevant to cosmology.



NASA/WMAP Science Team

Glowing cosmos. Any object in motion should feel a tiny slowing force from the sea of light emitted by its surroundings. The glow from the big bang (full-sky image above) might have slowed hot debris and affected the early evolution of the Universe. (Click picture for larger image.)

Bring two pieces of metal close enough together, and they will almost always attract or repel one another, even in a vacuum, thanks to the Casimir effect. This minute force comes from virtual photons--particles of light--that continually flit in and out of existence. The effect leads to friction as one chunk of metal moves past another. Rudi Podgornik, of the University of Ljubljana, Slovenia, and his colleagues imagined taking away the second chunk, and wondered what the remaining piece of metal would experience simply moving through space.