

# 50 years of the Lifshitz theory of van der Waals forces

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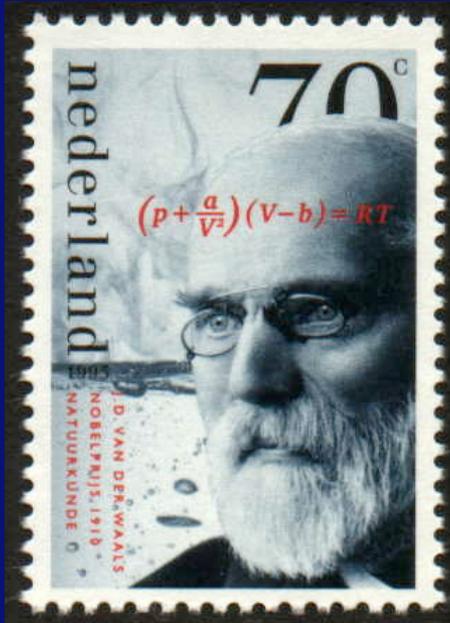
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VACUUM  
FLUCTUATIONS

CASIMIR PLATES

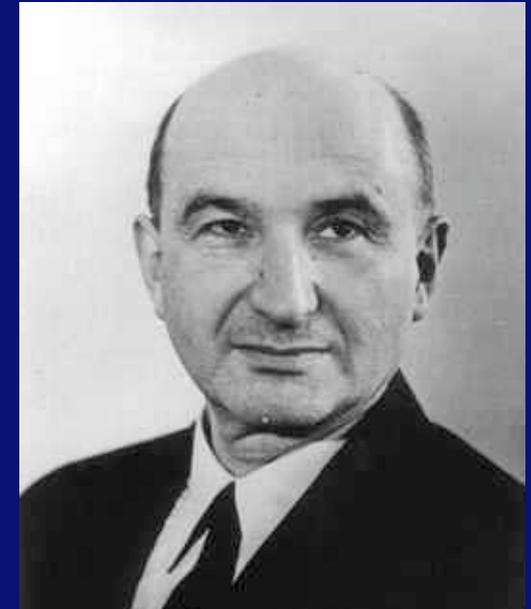
# Dramatis personae



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.  
(Casimir, 1992)

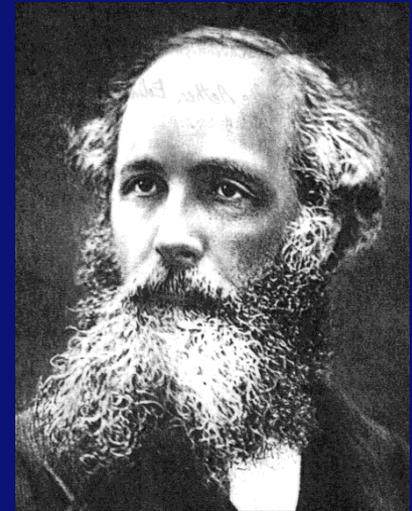
His calculations were so cumbersome that they were not even reproduced in the relevant Landau and Lifshitz volume, where, as a rule, all important calculations are given.  
(Ginzburg, 1979)

# Maxwell, Hertz and Lebedev



1864 and 1873 J. C. Maxwell

1888 H. Hertz



PhD thesis of P.N. Lebedev (1894):

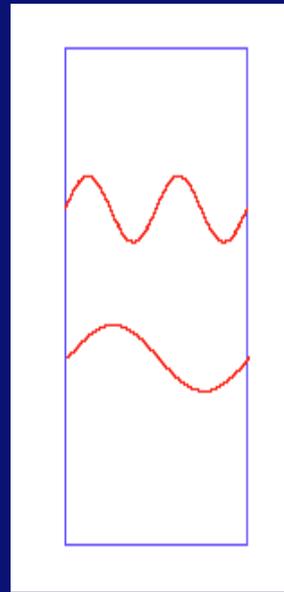
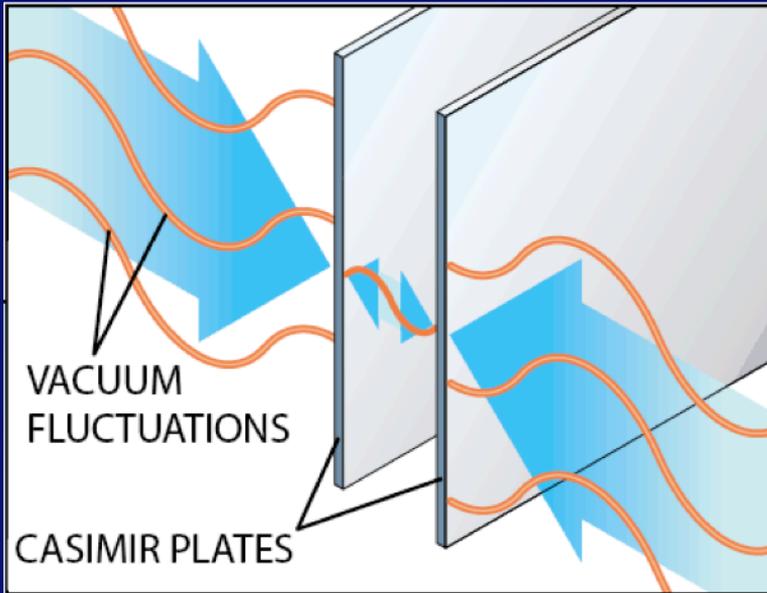
Hidden in Hertz's research, in the interpretation of light oscillations as electromagnetic processes, is still another as yet undealt with question, that of the source of light emission of the processes which take place in the molecular vibrator at the time when it give up light energy to the surrounding 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.**



# H. B. G. Casimir (1948).



Schematic representation of the geometry of the problem. We are solving the Maxwell's equations between the two bounding surfaces.

In empty space they are reduced to wave equations. Ideally polarizable (metal) interfaces.

EM field wave equation in empty space between the two conducting plates:

$$\nabla^2 \mathbf{E}(\mathbf{r}) + \frac{\epsilon\mu\omega^2}{c^2} \mathbf{E}(\mathbf{r}) = 0, \quad \nabla \cdot \mathbf{E}(\mathbf{r}) = 0, \quad \nabla^2 \mathbf{H}(\mathbf{r}) + \frac{\epsilon\mu\omega^2}{c^2} \mathbf{H}(\mathbf{r}) = 0, \quad \nabla \cdot \mathbf{H}(\mathbf{r}) = 0,$$

Eigenfrequencies of the EM field :

$$\omega_{\ell km}(D) = \pi c \sqrt{\left(\frac{\ell^2}{L^2} + \frac{k^2}{L^2} + \frac{m^2}{D^2}\right)} \longrightarrow \pi c \sqrt{\left(Q^2 + \frac{m^2}{D^2}\right)}$$

Quantum zero point energy :

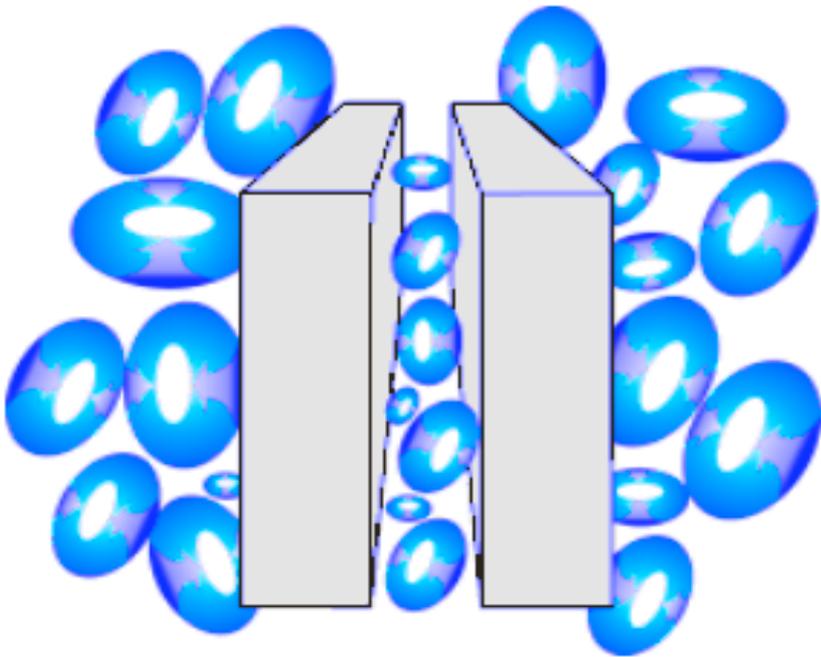
$$E(D) = 2 \sum'_{\ell, k, m} \frac{1}{2} \hbar \omega_{\ell km} \longrightarrow E(D) = -\frac{\pi^2 \hbar c}{720 D^3} L^2$$

# Casimir force as the EM depletion force

Evaluating the integrals and the sums via the Poisson summation formula (plus taking into account the physical considerations about the response of any body at large frequencies) one obtains Casimir's result:

$$U(d) = \left( \frac{\pi^2 \hbar c}{4d^3} \right) L^2 \left( \frac{-4}{720} \right) = - \left( \frac{\pi^2 \hbar c}{720d^3} \right) L^2$$

What is the physical meaning of this result? The Casimir force is the EM field depletion force!



Not all EM modes fit between the two ideally polarizable interfaces! Only those fit, with the appropriate wavelength.

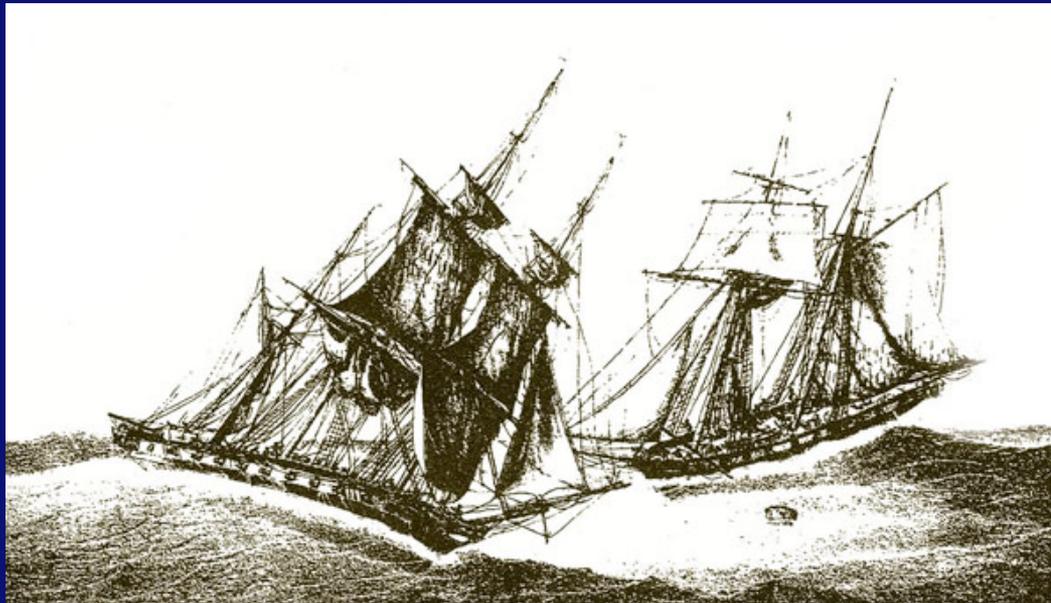
There are more modes outside than inside and each mode exerts Maxwell's pressure on the boundary thus  
– presto –  
the Casimir effect is there!

1 cm<sup>2</sup> areas 1 μm apart attract with 10<sup>-7</sup> N – weight of water droplet 0.5 mm in diameter. At 10 nm the Casimir force is equivalent to 1 atm pressure.

# “Une force certaine d’attraction”

In 1996 by Dutch scientist Sipko Boersma (A maritime analogy of the Casimir effect Am.J.Phys. 64. 539–541 (1996)) dug up the French nautical writer P. C. Caussée and his 1836 book **The Album of the Mariner** that two ships should not be moored too close together because they are attracted one towards the other by a **certain force of attraction**. Boersma suggested that this early observation could be described by a phenomenon analogous to the Casimir effect.

P.C. Causee: L'Album du Marin, (Mantes, Charpentier, 1836)



In the age of great sailboats it was noted that at certain conditions of the sea the ships attract misteriously, leading often to major damage.

G. Nolan: I had first hand experience of this in 1998, while waiting for our start in the sailing regatta for the New South Wales Hood championships on Sydney Harbour. We had ... a lot of waves caused by everything from power boat and ferry wakes to waves made by arriving and departing float planes. I made the prediction that, because of the conditions and the Casimir effect, the waiting boats would drift together. Within minutes that's exactly what had happened ...r

# The story is however more complicated. The original figure captions from P.C. Causee: The mariners' album

## Calme avec grosse houle.

À la suite d'un très-mauvais temps il arrive quelquefois que le vent calme tout-à-coup; mais il n'en est pas de même de la mer, qui reste grosse long-temps encore, et tourmente le bâtiment par des mouvements d'autant plus violents qu'il n'est plus appuyé par la résistance du vent sur les voiles.

Dans cette position, la mâture est compromise, si on ne prend pas promptement les mesures nécessaires pour la soutenir, en ridant les gal-

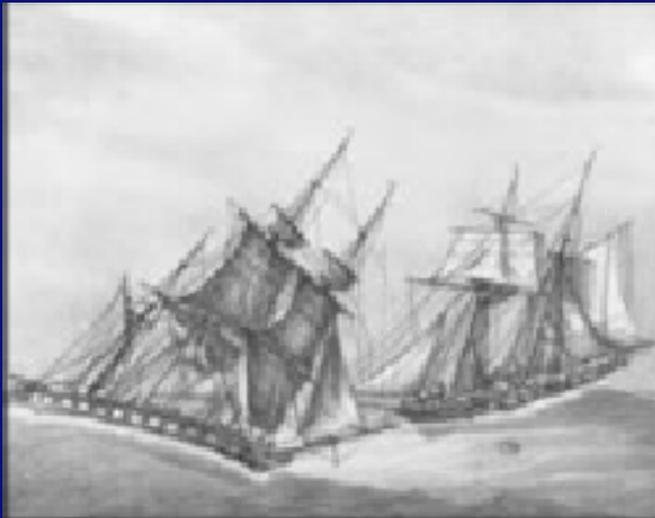
haubans des deux bords et bridant les bas-haubans s'ils ont pris trop de mou.

Lorsque plusieurs bâtiments se trouvent réunis, on ne doit pas négliger de manœuvrer pour saisir le plus petit souffle de vent, afin de s'écarter et d'éviter les abordages, qui seraient extrêmement dangereux. Lorsqu'on se trouve assez éloigné du bâtiment le plus voisin, on peut amener et carguer les voiles pour les ménager.

## Le Calme plat.

LORSQUE deux bâtiments sont en calme, ils tendent toujours à se rapprocher et finissent par s'aborder, étant attirés l'un vers l'autre par une certaine force attractive: dans ce cas, on se sert des canots pour s'éloi-

gner, et on y parvient plus promptement en faisant remorquer l'un des bâtiments par les canots des deux. Les petits bâtiments ont de plus la ressource de leurs avirons de galère.



Calme avec grosse houle  
(Calm with big swell)



Le calme plat  
(Flat calm)

Two figures presented  
by Causee in his book.  
What do they actually  
show?  
Is this really the  
Casimir effect?

# “Une force certaine de confusion“

Fabrizio Pinto thinks that the whole tale is symptomatic of physicists' approach to the history of their subject. "Physicists love lore about their own science," he says.

"There are other stories that are unfounded historically." (Nature, 4 may 2006).

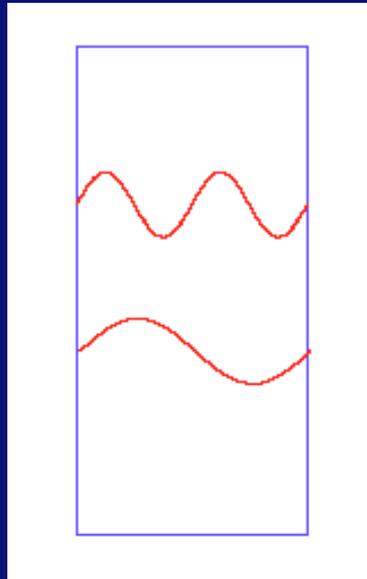
You may read about this in Nature blog.

[http://blogs.nature.com/news/blog/2006/05/  
popular\\_physics\\_myth\\_is\\_all\\_at.html](http://blogs.nature.com/news/blog/2006/05/popular_physics_myth_is_all_at.html)

The ships are free floating, not moored. I was told that the effect was also reported in the world literature: Herman Melville's "Moby Dick" and Philip Roth's "Rites of passage". It is not a myth, the original paper Am.J.Phys. 64. 539–541 (1996) gives the quantitative theory to calculate the attractive force, given Ships rolling amplitude, weight, metacentric height, "Q" oscillator quality factor and wave period. An example for two 700 ton clipper ships gives 2000 Newton, quite reasonable. The theory gives also another effect: Repulsion. **An atom is attracted to a conducting plate but a ship in a wave field is repelled from a steep cliff.** This is due to a difference in boundary conditions between Electromagnetic waves and Seawaves. This repulsion was already known to the Cape Horn sailors of the Cape Horn Society, Hoorn Holland. Caussé's error: Caussé put his ships in a "Flat Calm" without any waves. That won't work. However, already a small swell suffices if its period matches the natural period of the ships and we have resonance magnification. A long light swell can easily have been overlooked by the mariners on board. The second possibility is that Caussé should have put his ships In "Calm with Big Swell" which after all to me seems less likely.

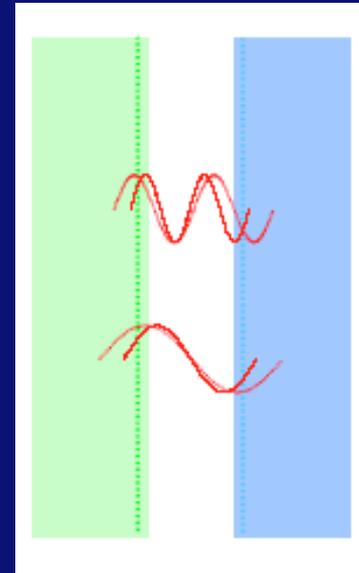
S.L. Boersma Delft The Netherlands

# Enter Lifshitz (1954).

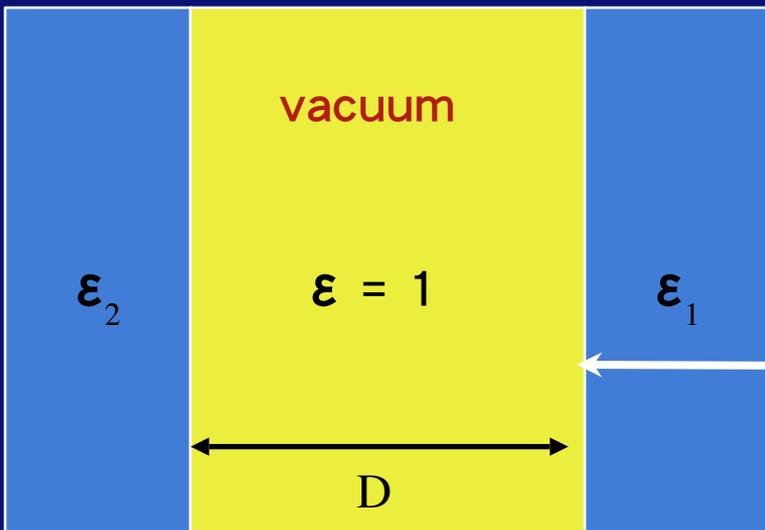


Real dielectric as opposed to Casimir's idealized interfaces.  
 Casimir vs. Lifshitz  
 Hard boundary vs. soft boundary

$$\begin{aligned}
 B_{1n} &= B_{2n} & D_{1n} &= D_{2n} \\
 E_{1t} &= E_{2t} & H_{1t} &= H_{2t}
 \end{aligned}$$



$$\epsilon = \epsilon(\omega)$$



Maxwell stress tensor **in vacuo**:

$$p_{ik} = \epsilon_0 E_i E_k - \frac{1}{2} \epsilon_0 E^2 \delta_{ik} + \frac{1}{\mu_0} B_i B_k - \frac{1}{2\mu_0} B^2 \delta_{ik},$$

$$\langle p_{zz}(D) \rangle$$

Thermodynamic average of the stress tensor at the boundary.

Lifshitz in 1954 got the most prestigious soviet science prize for this theory.

# Main ingredients of the Lifshitz calculation ...

His 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)

Theoretical constituents for a **finite temperature, real dielectric interfaces in planar geometry.**

FD theorem:

$$\langle A_i(\omega, \mathbf{r}) A_k(\omega, \mathbf{r}') \rangle = \text{ctanh} \frac{\hbar\omega}{2k_B T} \text{im} \mathcal{D}_{ik}(\omega, \mathbf{r}, \mathbf{r}')$$

Maxwell equations:

$$\begin{aligned} \nabla \cdot \mathbf{D} &= 0 & \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} & \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \end{aligned}$$

$$\begin{aligned} B_{1n} &= B_{2n} & D_{1n} &= D_{2n} \\ E_{1t} &= E_{2t} & H_{1t} &= H_{2t} \end{aligned}$$

Constitutive relations  
and BC:

$$\begin{aligned} \mathbf{D} &= \epsilon \epsilon_0 \mathbf{E} & \epsilon &= \epsilon(\omega) \\ \mathbf{B} &= \mu \mu_0 \mathbf{H} & \mu &= \mu(\omega) \end{aligned}$$

The average of the stress tensor again on the vacuum side:

$$\langle p_{zz} \rangle = \epsilon_0 \langle E_z^2 \rangle - \frac{1}{2} \epsilon_0 \langle E^2 \rangle + \frac{1}{\mu_0} \langle B_z^2 \rangle - \frac{1}{2\mu_0} \langle B^2 \rangle$$

# Lifshitz result:

$$\langle p_{zz}(D) \rangle = \frac{k_B T}{\pi c^3} \sum_{n=0}^{\infty} \omega_n^3 \int_1^{\infty} p^2 \left( \left[ \frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} e^{-\frac{2p\omega_n D}{c}} - 1 \right]^{-1} + \left[ \frac{(s_1 + p\epsilon_1)(s_2 + p\epsilon_2)}{(s_1 - p\epsilon_1)(s_2 - p\epsilon_2)} e^{-\frac{2p\omega_n D}{c}} - 1 \right]^{-1} \right) dp$$

$$s_i = \sqrt{\epsilon_i - 1 + p^2} \quad \omega_n = \frac{2\pi n k_B T}{\hbar}$$

$10^{15}$  n Hz

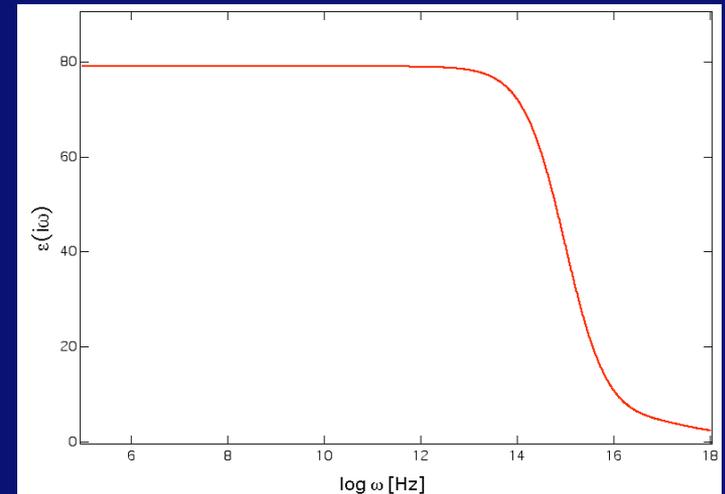
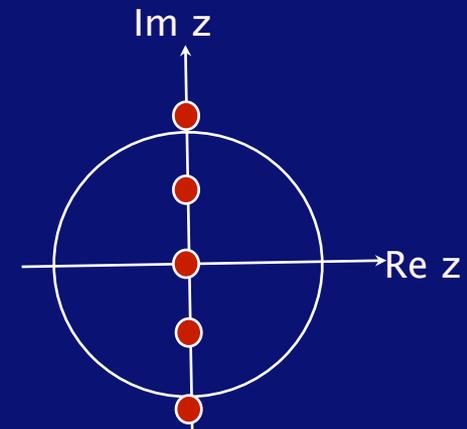
All the frequency dependence is reduced to discrete sum over Matsubara frequencies:

$$\epsilon_i = \epsilon_i(i\omega_n)$$

Discrete frequencies are due to the poles of the coth function in the FT theorem in the complex plane.

$$\epsilon_i(i\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\zeta \operatorname{Im} \epsilon(\zeta) d\zeta}{\omega^2 + \zeta^2}$$

Kramers-Kronig relations for the epsilons of imaginary frequencies – real and decaying!



# Limiting forms:

The influence of temperature usually (but not always!!!) not very important.  
Summation over  $n$  turned into an integral.

## Small separations

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{\hbar}{16\pi^2 D^3} \int_0^\infty \int_0^\infty x^2 \left[ \frac{(\epsilon_1(i\zeta) + 1)(\epsilon_2(i\zeta) + 1)}{(\epsilon_1(i\zeta) - 1)(\epsilon_2(i\zeta) - 1)} e^x - 1 \right]^{-1} dx d\zeta$$

At small separations corresponds to the Hamaker formula:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{A}{6\pi D^3}$$

## Large separations

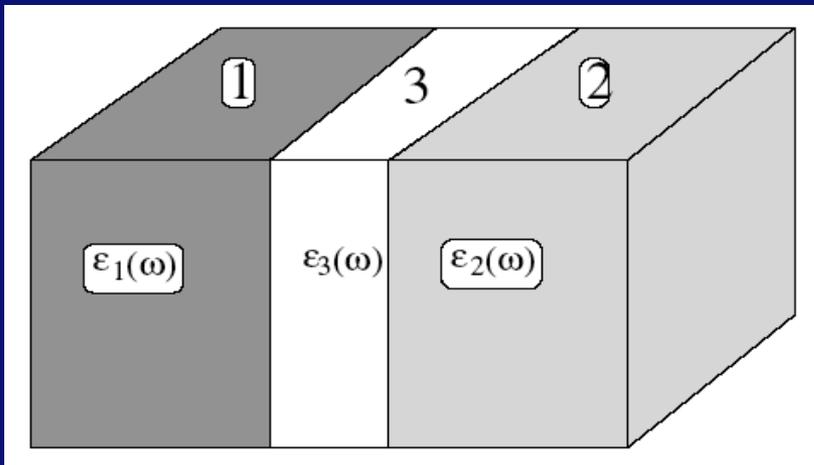
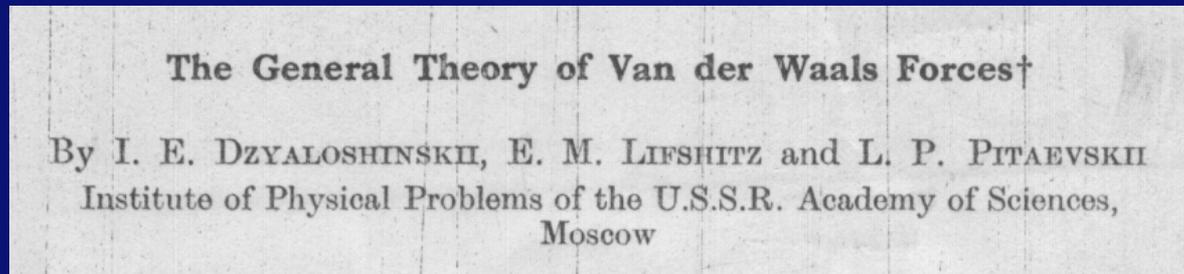
$$\langle p_{zz}(D \rightarrow \infty) \rangle = \frac{\hbar c}{16\pi^2 D^3} \int_0^\infty \int_1^\infty \frac{x^3 dx d\zeta}{\zeta^2 \left( \frac{(\epsilon_1(0)+1)(\epsilon_2(0)+1)}{(\epsilon_1(0)-1)(\epsilon_2(0)-1)} e^x - 1 \right)} \rightarrow -\frac{\pi^2 \hbar c}{240 D^4}$$

For ideal metals  $\epsilon(0) \rightarrow \infty$ , obviously reduces to the Casimir result!

$$E(D) = 2 \sum'_{\ell, k, m} \frac{1}{2} \hbar \omega_{\ell k m} \rightarrow E(D) = -\frac{\pi^2 \hbar c}{720 D^3} L^2$$

Lifshitz result is a straightforward generalization of the Casimir result and **contains it as a limit**.  
An incredible tour de force!

# Dzyaloshinskii, Lifshitz, Pitaevskii (1961).



$$\epsilon_2 > \epsilon_3 > \epsilon_1$$
$$\epsilon_2 > \epsilon_3 < \epsilon_1$$

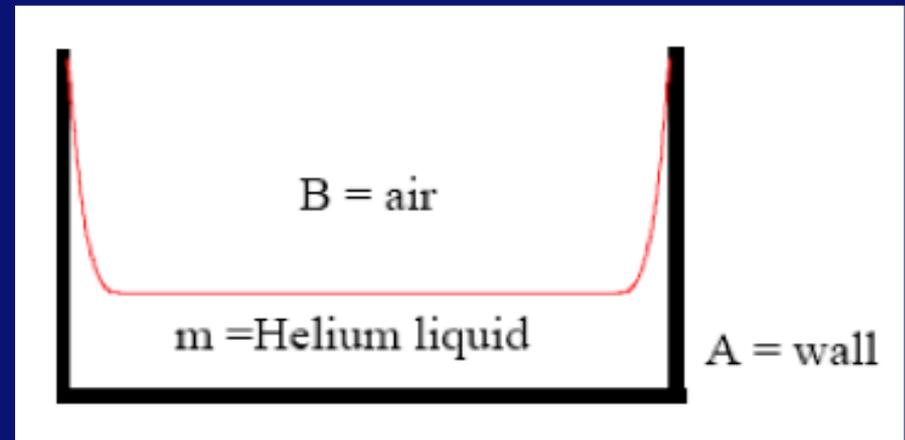
Complicated separation dependence because  $\epsilon = \epsilon(\omega)$

QED calculation.

Pressure is not necessarily monotonic!

$$\langle p_{zz}(D) \rangle \lesssim 0.$$

Thickness from 10 Å to 250 Å.  $\epsilon \sim 1.057$   
Sabisky and Anderson, 1970.



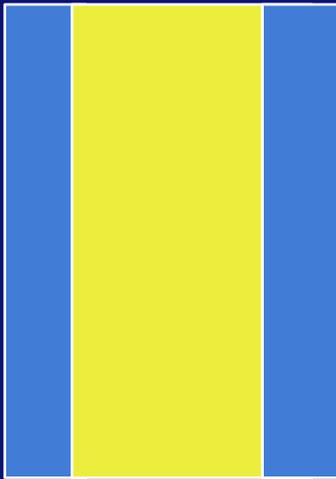
# The heuristic theory of vdW interactions

Nice, but too difficult to use for anything!

The theory just too complex to apply to any new problems, thus:

Van Kampen, Nijboer, Schramm (1968) – Parsegian, Ninham, Weiss (1972) – Barash, Ginzburg (1975).  
Based on the concept of EM mode eigenfrequencies and secular determinants.

In some respects a return to the original Casimir formulation! Take the eigenfrequencies of the EM field and get the corresponding free energy from quantum harmonic oscillators (which are not really harmonic oscillators):



Eigenmodes for a particular geometry

van Kampen et al.  $T = 0$

$$E(T = 0) = \frac{1}{2} \sum_i \hbar \omega_i$$

.... and Parsegian et al.  $T \neq 0$ .

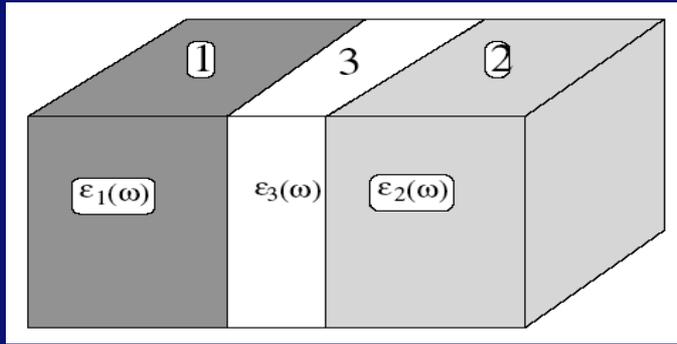
$$\mathcal{F}(T \neq 0) = k_B T \sum_i \ln 2 \sinh \frac{\hbar \omega_i}{2k_B T}$$

Use the argument principle to do the summation over the modes:

$$\frac{1}{2\pi i} \oint_C g(z) \frac{d}{dz} f(z) dz = \sum_i g(z_i) |_{f(z_i)=0} - \sum_i g(z_i) |_{f(z_i)=\infty}$$

# EM modes and vdW interactions

The brilliant idea of Niko van Kampen. Modes and energies.



$$\rho_{A,B}^2 = Q^2 - \frac{\epsilon_{A,B}\omega^2}{c^2}$$

$$D_{TM}^R(\omega) = 1 + \bar{\Delta}_{12}^R(\omega)\bar{\Delta}_{23}^R(\omega)e^{-2\rho_2(\omega)d} = 0,$$

$$D_{TE}^R(\omega) = 1 + \Delta_{12}^R(\omega)\Delta_{23}^R(\omega)e^{-2\rho_2(\omega)d} = 0,$$

$$\bar{\Delta}_{ij}^R(\omega) = \frac{\epsilon_i(\omega)\bar{\rho}_j(\omega) - \epsilon_j(\omega)\bar{\rho}_i(\omega)}{\epsilon_i(\omega)\bar{\rho}_j(\omega) + \epsilon_j(\omega)\bar{\rho}_i(\omega)},$$

$$\Delta_{ij}^R(\omega) = \frac{\rho_i(\omega) - \rho_j(\omega)}{\rho_i(\omega) + \rho_j(\omega)}.$$

Secular determinant of the modes. It gives eigenfrequencies as a function of the separation.  
Much easier to calculate than Green functions!

$$\mathcal{D}(i\xi_N, Q) = \mathcal{D}_E(i\xi_N, Q)\mathcal{D}_H(i\xi_N, Q) = 0.$$

$$\xi_N = N\frac{kT}{\hbar}$$

And then the interaction free energy comes from the application of the argument principle:

$$\mathcal{F} = kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}(i\xi_N, Q) = kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}_E(i\xi_N, Q) + kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}_H(i\xi_N, Q).$$

# Final result for the T-dependent vdW interactions

$$G_{LmR}(l) = \frac{kT}{(2\pi)} \sum_{n=0}^{\infty} \int_{\frac{\xi_n}{c}}^{\infty} \rho_m \ln \left[ \left(1 - \bar{\Delta}_{Lm} \bar{\Delta}_{Rm} e^{-2\rho_m l}\right) \left(1 - \Delta_{Lm} \Delta_{Rm} e^{-2\rho_m l}\right) \right] d\rho_m$$

This is the interaction free energy between two planar dielectric interfaces. The following definitions have been used:

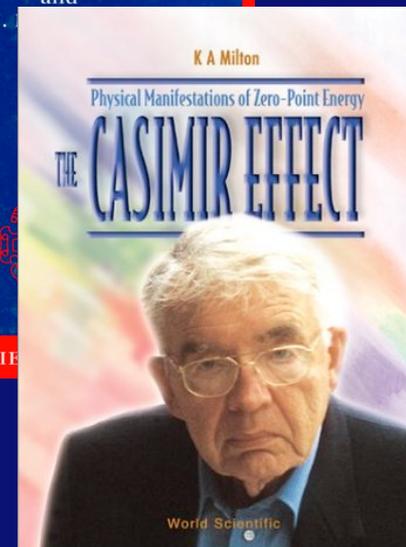
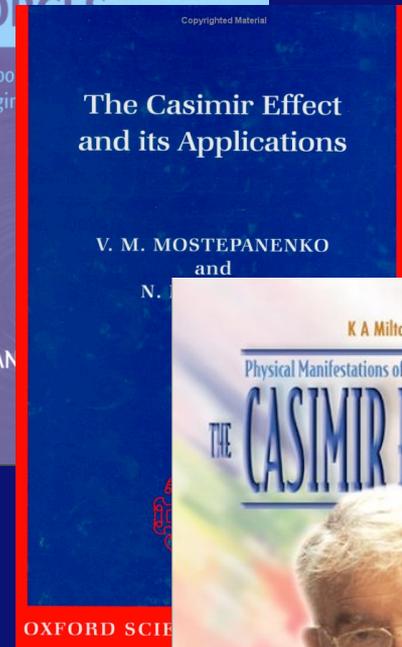
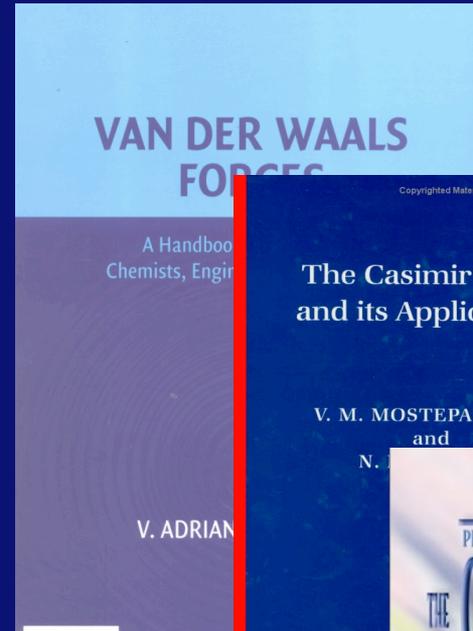
$$\bar{\Delta}_{ji} = \frac{\rho_i \epsilon_j - \rho_j \epsilon_i}{\rho_i \epsilon_j + \rho_j \epsilon_i}, \quad \Delta_{ji} = \frac{\rho_i \mu_j - \rho_j \mu_i}{\rho_i \mu_j + \rho_j \mu_i}, \quad \rho_i^2 = \rho_m^2 + \frac{\xi_n^2}{c^2} (\epsilon_i \mu_i - \epsilon_m \mu_m).$$

$$\rho_L^2 = \rho^2 + \frac{\epsilon_L \mu_L \xi_n^2}{c^2}, \quad \rho_m^2 = \rho^2 + \frac{\epsilon_m \mu_m \xi_n^2}{c^2}, \quad \rho_R^2 = \rho^2 + \frac{\epsilon_R \mu_R \xi_n^2}{c^2}.$$

$$\xi_N = N \frac{kT}{\hbar}$$

Still looks complicated but can be cast into a variety of simplified forms and can be easily generalized.

A lively subject to this day!



# Experimental confirmation of the Lifshitz theory?

Deryagin and Abrikosova (1953), Spaarnay, 1958. 100% error!  
 "did not contradict Casimir's theoretical prediction"

Shih and Parsegian, 1975.

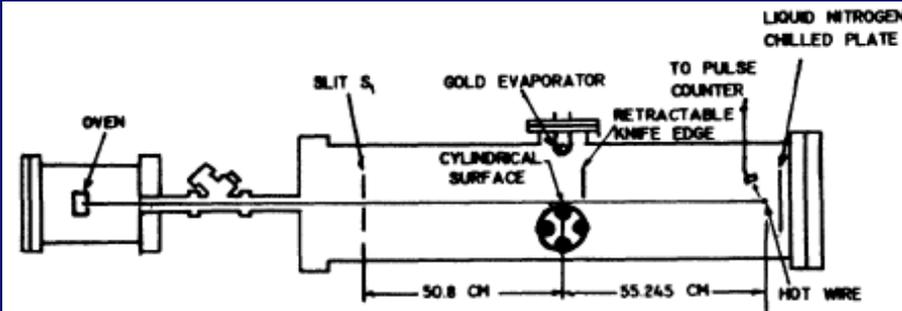


FIG. 1. Atomic beam apparatus.

Atomic beam of alkali metals above gold.

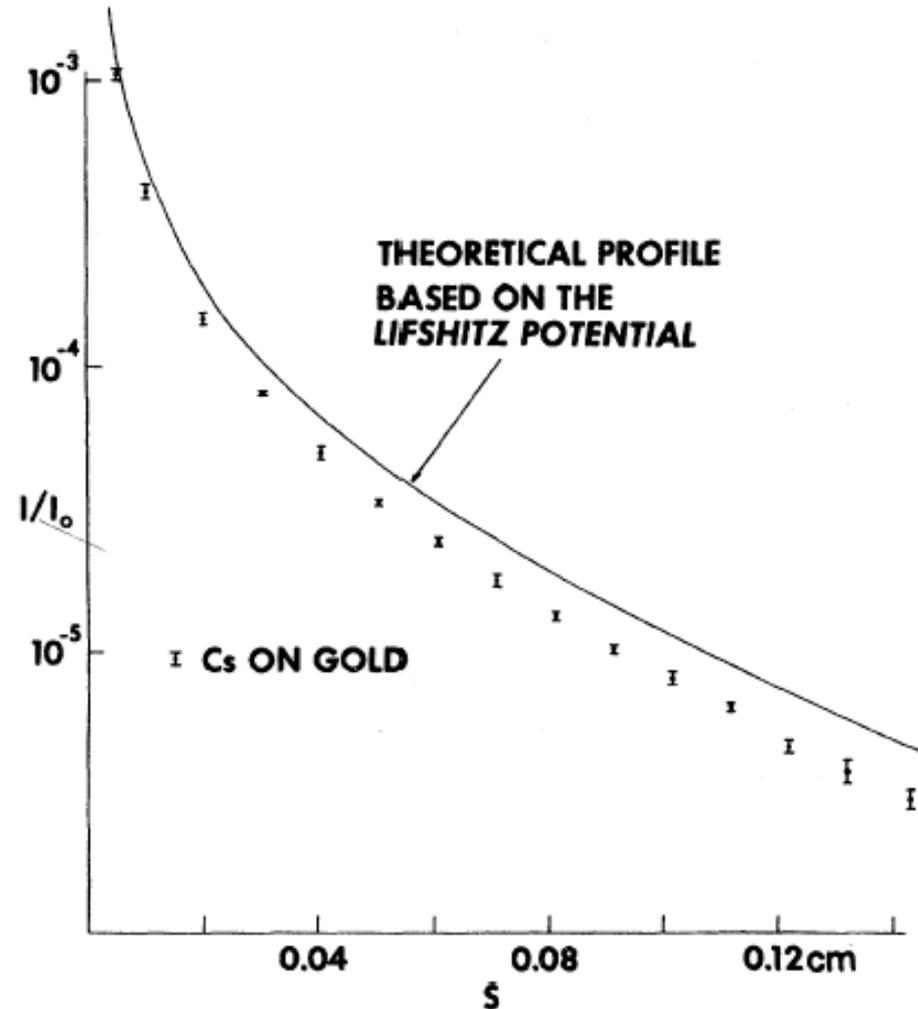
$$V(R) = -k_L/R^3,$$

where

$$k_L = \frac{\kappa T}{2} \sum_{n=0}^{\infty} \alpha(i\xi_n) \frac{\epsilon(i\xi_n) - 1}{\epsilon(i\xi_n) + 1} \left(1 + r_n + \frac{1}{4} r_n^2\right) e^{-r_n}$$

$$r(n) = 2 \xi(n) R/c$$

Computation based upon Lifshitz theory.

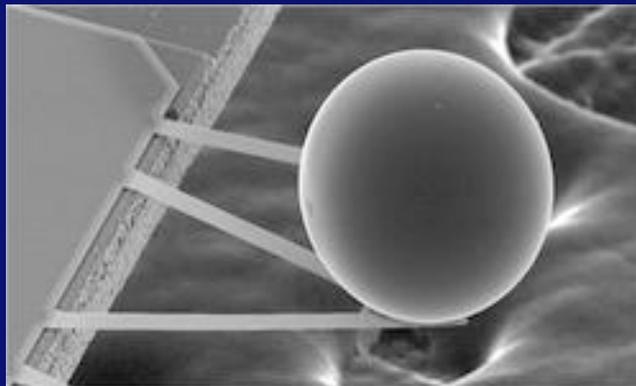
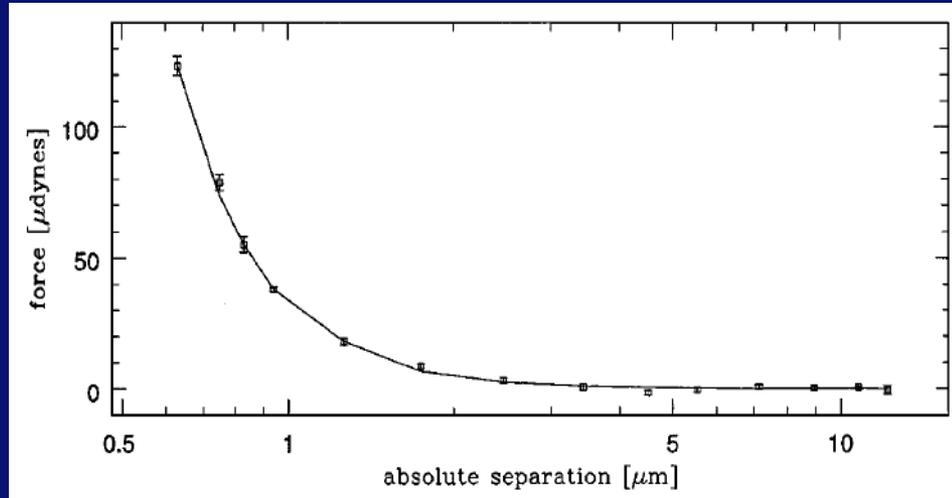


Almost quantitative correspondence ...

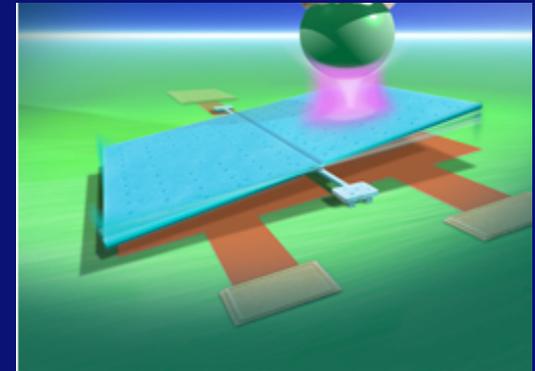
# Experimental confirmation of the Casimir theory!

Modern developments show that also the Casimir effect proper can be exactly measured even though it is small.

Lamoreaux, 1997.

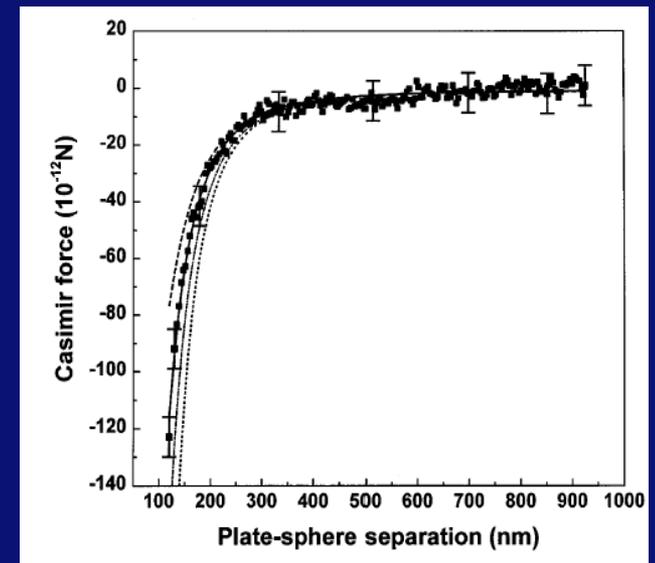


Sensitive sphere. This 200- $\mu\text{m}$ -diameter sphere mounted on a cantilever was brought to within 100 nm of a flat surface (not shown) to detect the elusive Casimir force.



Bell Labs

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



Mohideen and Roy, 1998.

# 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

**F**OR 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.

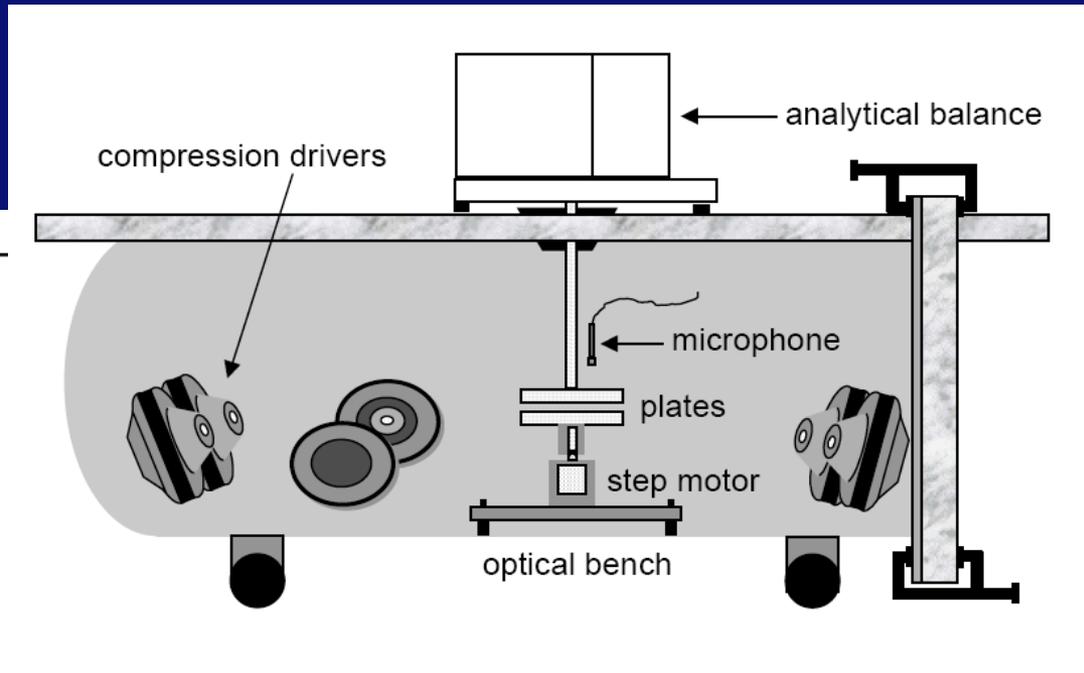
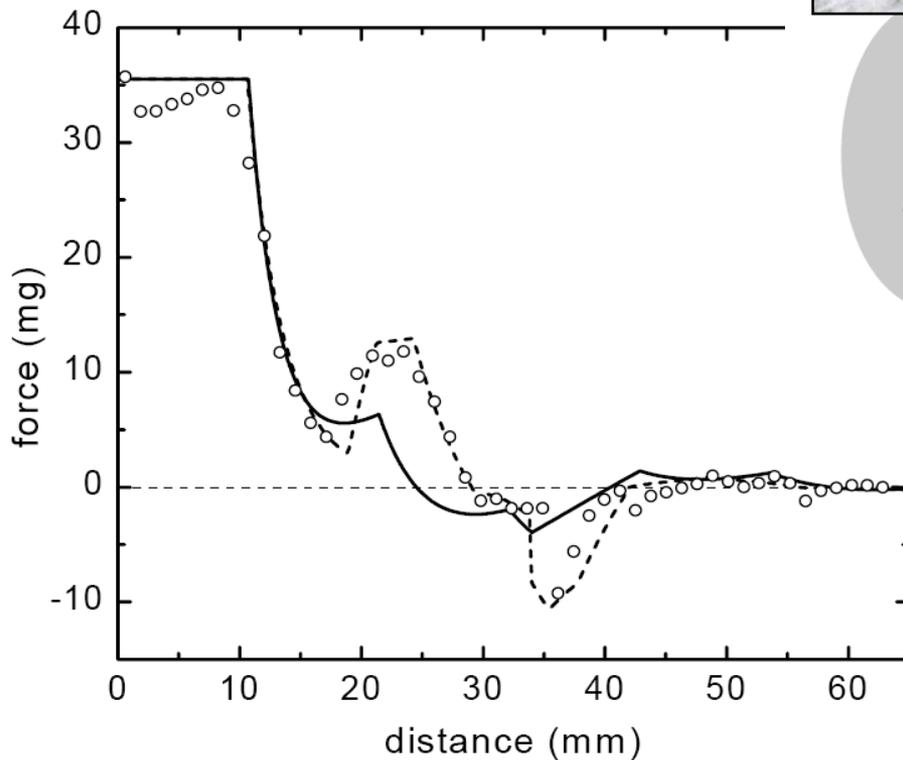
If that were so, something might cause the present-day universal vacuum to collapse to a different vacuum of a lower energy. The effect, propagating at the speed of light, would be the annihilation of all matter in the universe. There would be no warning for humankind; the earth and its inhabitants would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

*Continued on Page C6*

# Interesting variations: acoustic Casimir effect

This variant of the “Casimir effect” is not driven by thermal fluctuations!  
It is driven by the **artificially generated acoustic noise**.

Not a thermal acoustic noise.  
Results depend on the nature of  
the noise spectrum.



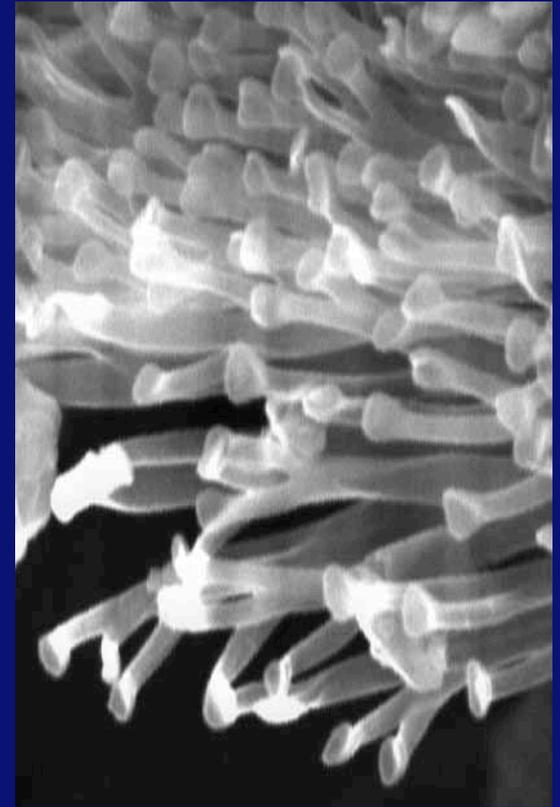
Flat white-noise spectrum vs.  
frequency dependent spectrum.

Non-monotonic interactions!

A. Larraza and B. Denardo 1998.

Hydrodynamic Casimir effect invoked in a **cryptic remark** at the end of the Dzyaloshinskii et al. 1961.

## Casimir effect *in vivo*

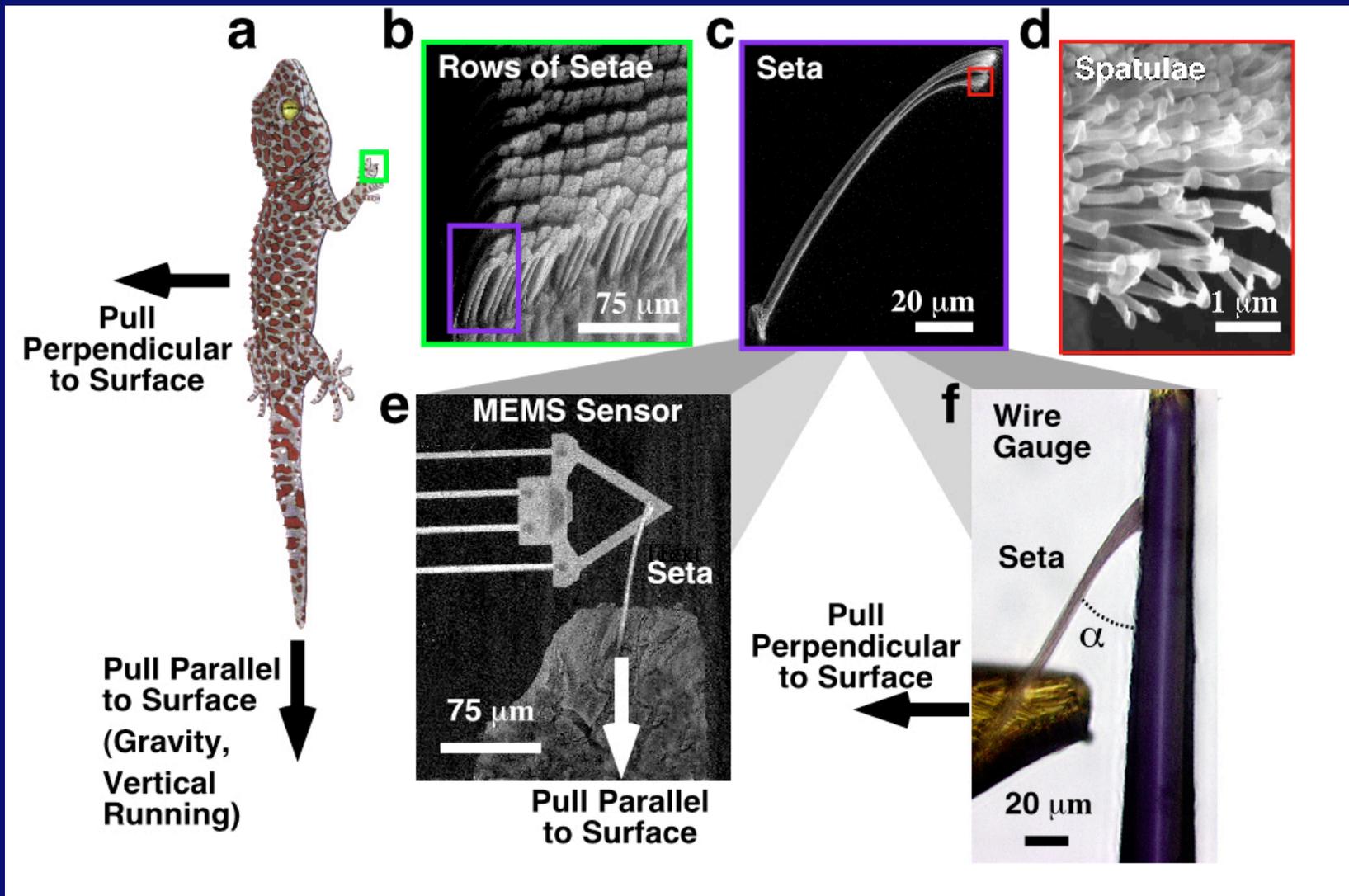


K. Autumn, W.-P. Chang, R. Fearing, T. Hsieh, T. Kenny, L. Liang, W. Zesch, R.J. Full. Nature 2000.  
Adhesive force of a single gecko foot-hair.

How does Gecko manage to walk on vertical smooth walls?

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

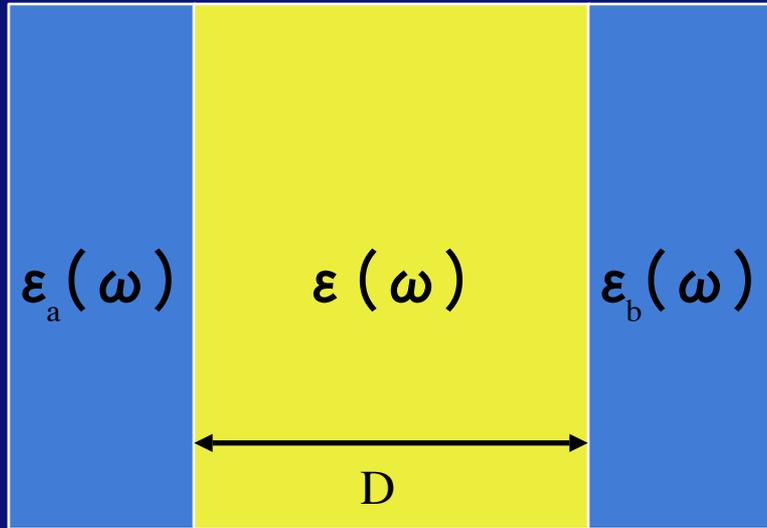
It's van der Waals interactions!



A single seta can lift the weight of an ant  $200 \mu\text{N} = 20 \text{ mg}$ . A million setae (1 square cm) could lift the weight of a child (20kg, 45lbs). Maximum potential force of 2,000,000 setae on 4 feet of a gecko =  $2,000,000 \times 200 \text{ micronewton} = 400 \text{ newton} = 40788 \text{ grams force}$ , or about 90 lbs! Weight of a Tokay gecko is approx. 50 to 150 grams.

# Pair interactions and the Pitaevskii *ansatz*

How does one derive the interactions between isolated atoms (molecules)?  
L.P. Pitaevskii, 1959.



$$\epsilon_{a,b}(\omega) \simeq \epsilon(\omega) + n_{a,b}\alpha_{a,b}(\omega)$$

The Pitaevskii equation (1959):

$$\frac{\partial^3 \mathcal{F}_{a,b}(D)}{\partial D^3} = -2\pi D n_a n_b f_{a,b}(D)$$

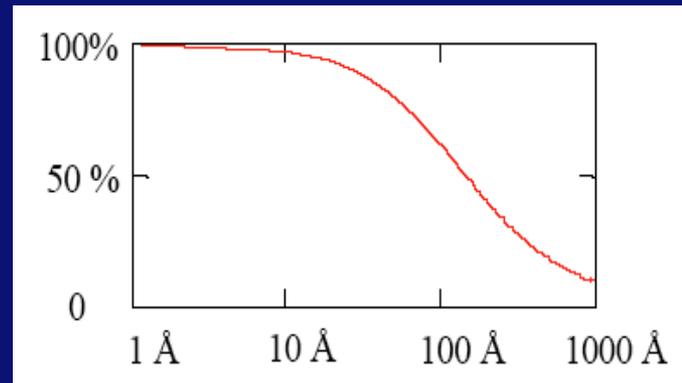
For rarefied dispersive media.

$$f_{a,b}(D) = -\frac{3k_B T}{8\pi^2 D^6} \sum_{n=0}^{\infty} \frac{\alpha_a(i\omega_n)\alpha_b(i\omega_n)}{\epsilon^2(i\omega_n)} \mathcal{R}(r_n)$$

$$r_n = \frac{2\sqrt{\epsilon(i\omega_n)\mu(i\omega_n)} \omega_n}{c} D$$

Retardation effects. Finite velocity of light!

$n=0$  terms is classical!



# London-van der Waals dispersion interaction

Back to the beginning of the story.

$$f_{a,b}(D \rightarrow 0) \cong -\frac{3\hbar}{16\pi^3 D^6} \int_0^\infty d\omega \frac{\alpha_a(i\omega)\alpha_b(i\omega)}{\epsilon^2(i\omega)}$$

London interaction, 1930.  
Debye-Keesom-London interaction

$$f_{a,b}(D \rightarrow \infty) \cong -\frac{23\hbar c}{64\pi^3 D^7} \frac{\alpha_a(0)\alpha_b(0)}{\epsilon^{5/2}(0)}$$

Casimir - Polder interaction, 1948.

**Non-pairwise additive:** Axilrod-Teller potential

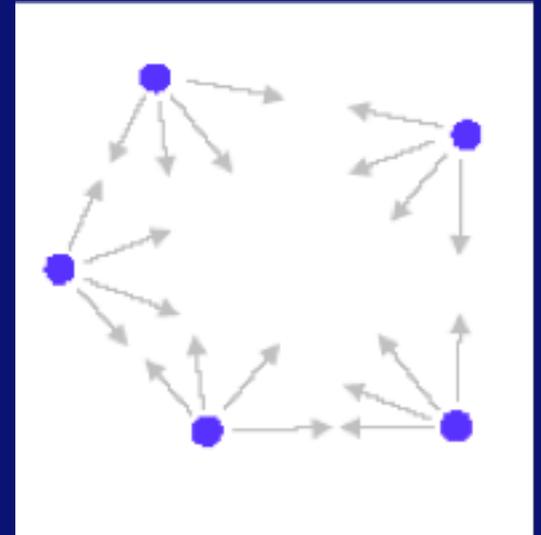
$$E_{AT}(i, j, k) = \frac{\gamma(1 + 3\cos\theta_{ij}\cos\theta_{jk}\cos\theta_{ki})}{R_{ij}^3 R_{jk}^3 R_{ki}^3}$$

Historically a reversed course via **Hamaker - de Boer summation**, 1937.

$$\mathcal{F}(D) = n_1 n_2 \int_{V_1} \int_{V_2} f(|\mathbf{r}_1 - \mathbf{r}_2|) dV_1 dV_2$$

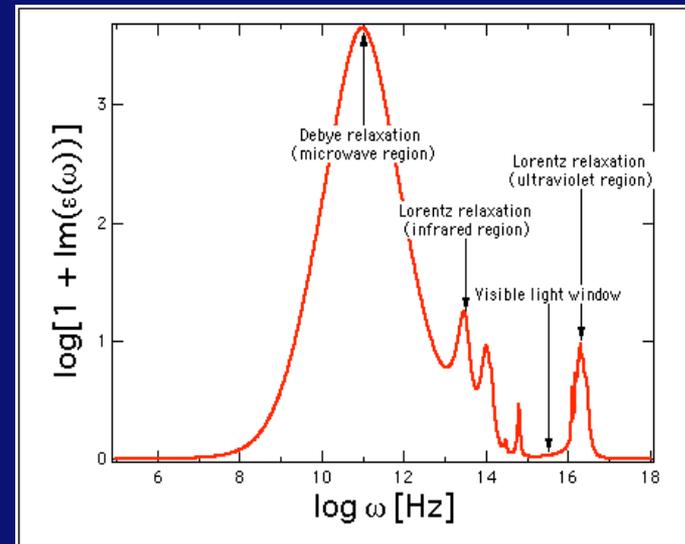
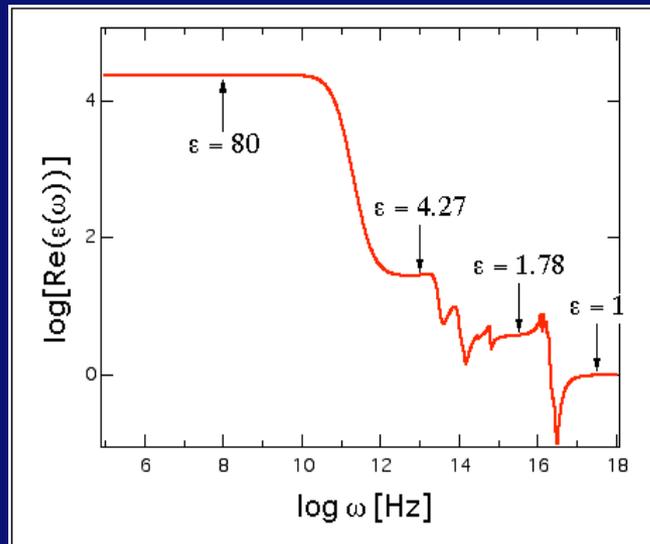
van der Waals equation of state, 1873.

$$(p + (a/V^2))(V - b) = NkT .$$



# Calculating vdW interactions - Lebedev's dream fulfilled

Connecting the strength of van der Waals interaction with spectra. Lebedev's dream fulfilled.  
Parsegian - Ninham calculations, 1970-80.



The dielectric spectrum of water.

Let us investigate the limit of small separations:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{\hbar}{16\pi^2 D^3} \int_0^\infty \int_0^\infty x^2 \left[ \frac{(\epsilon_1(i\zeta) + 1)(\epsilon_2(i\zeta) + 1)}{(\epsilon_1(i\zeta) - 1)(\epsilon_2(i\zeta) - 1)} e^x - 1 \right]^{-1} dx d\zeta$$

At small separations corresponds to the Hamaker (pairwise summation) formula:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{A}{6\pi D^3}$$

# The Hamaker coefficient

The Hamaker coefficient quantifies the magnitude of the vdW interaction.  
Different cultures within the physics community.

$A_{Am/Am} (l = 0)$ , 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 $kT_{room}$

SOFT

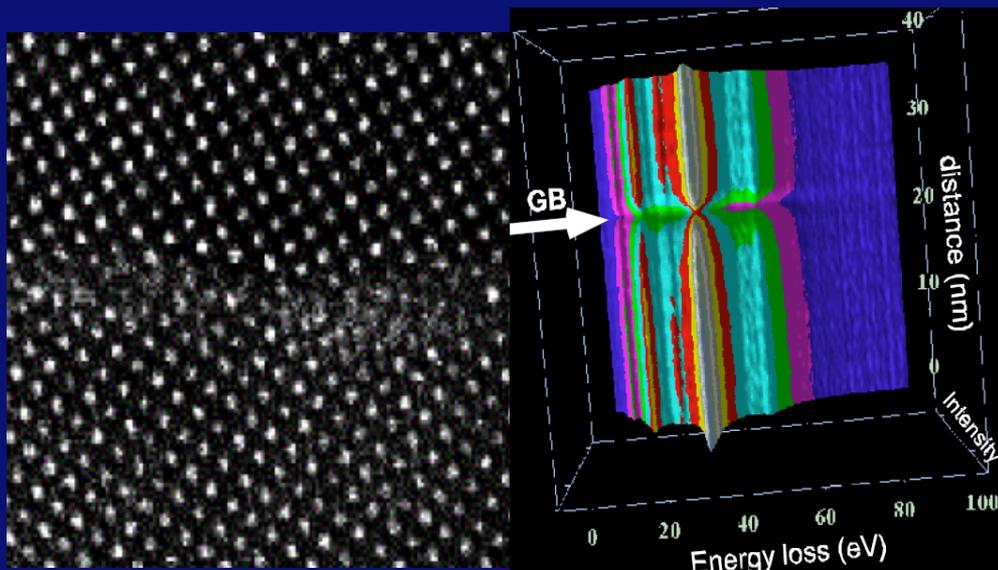
In order to evaluate the Hamaker coefficient one needs the dielectric spectrum  $\epsilon(i\omega)$ .  
This spectrum can be sometimes measured directly or can be calculated from models.

$A_{AlN/water/AlN} = 102.2zJ$	$A_{AlN/vac/AlN} = 228.5zJ$
$A_{Al_2O_3/water/Al_2O_3} = 58.9 zJ (27.5 zJ^{108})$	$A_{Al_2O_3/vac/Al_2O_3} = 168.7zJ (145 zJ^{108})$
$A_{MgO/water/MgO} = 26.9zJ$	$A_{MgO/vac/MgO} = 114.5zJ$
$A_{SiO_2/water/SiO_2} = 6.0zJ (1.6 zJ^{108})$	$A_{SiO_2/vac/SiO_2} = 66.6zJ (66 zJ^{108})$
$A_{Si/water/Si} = 112.5zJ$	$A_{Si/vac/Si} = 212.6zJ$

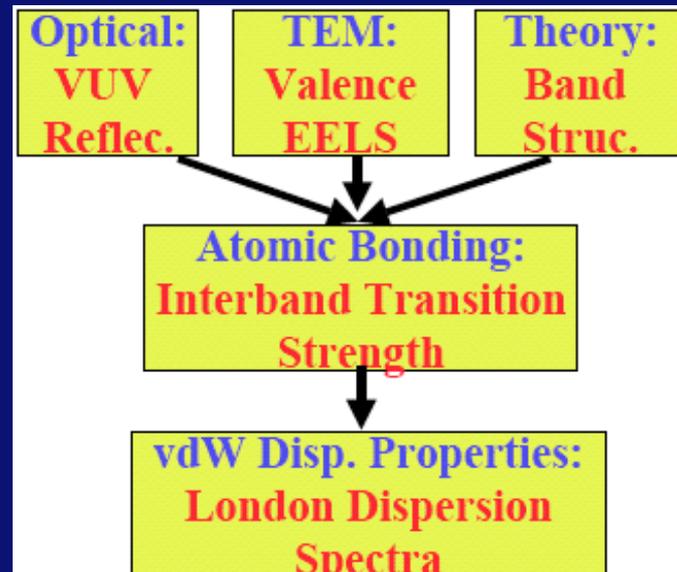
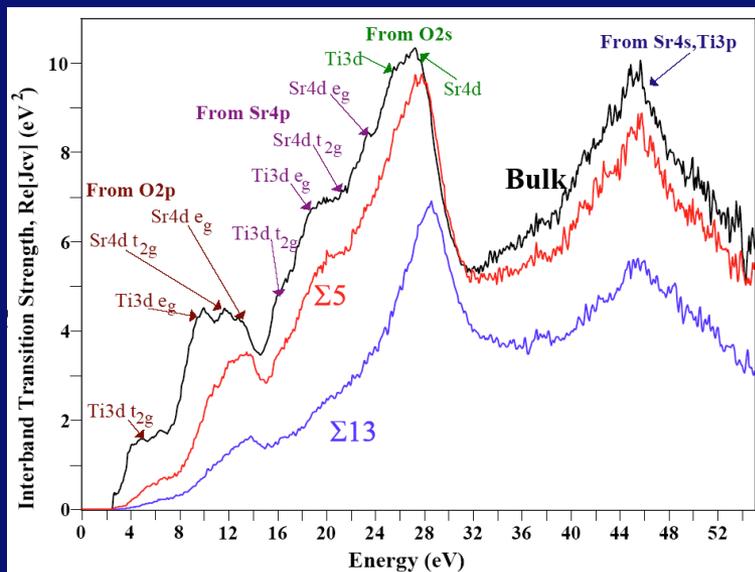
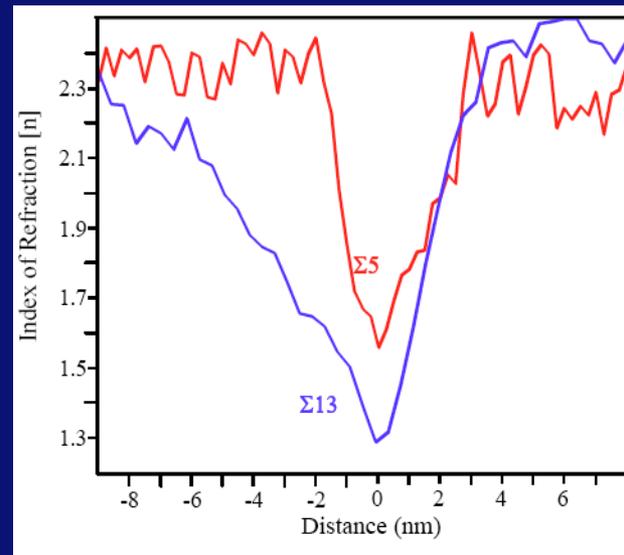
HARD

# Current approach

SrTiO<sub>3</sub> vdW interaction across grain boundaries. R. French, 2003.



Kienzle, 1999.



# The Hamaker coefficient - directly from experiment

Calculated Hamaker coefficients from measured dielectric spectra:

- ◆ Using Lifshitz Theory, QED

- ◆ Acquire Exp. Spectra
- ◆ Calc. London Disp. Spectrum
  - Kramers Kronig Transform

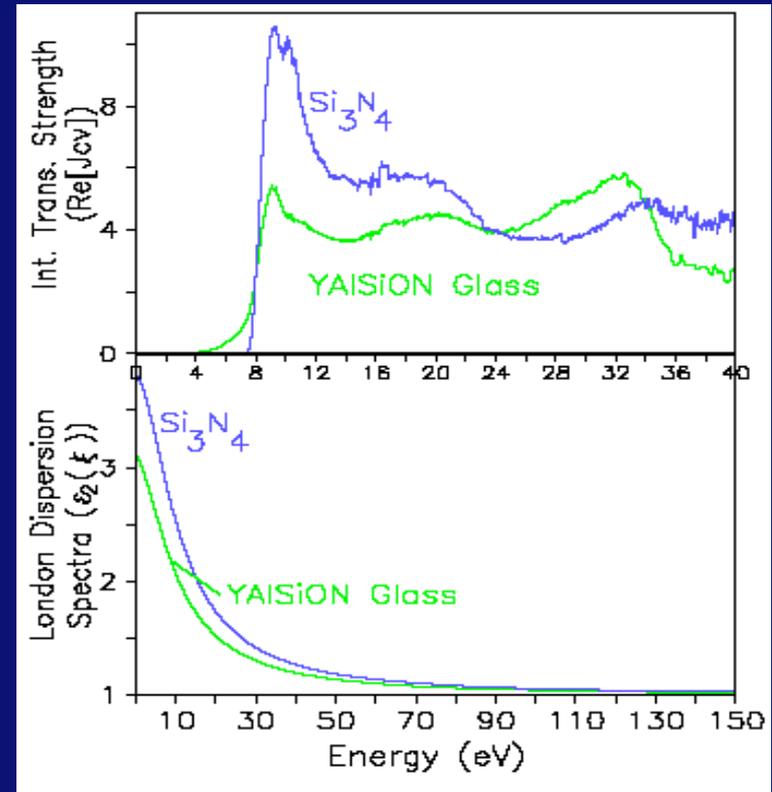
$$\epsilon_2(\xi) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \epsilon_2(\omega)}{\omega^2 + \xi^2} d\omega$$

- ◆ Then Hamaker Constant
  - Calc'd by Spectral Differences
  - of London Disp. Spectra

$$A = \frac{-3\hbar L^2}{\pi} \int_0^{\infty} \rho d\rho \int_0^{\infty} \ln G(\xi) d\xi$$

$$G_{121}^{NR}(\xi) = 1 - \Delta_{12}^2 e^{-2a\rho}$$

$$\Delta_{kj} = \frac{\epsilon_{2,k}(\xi) - \epsilon_{2,j}(\xi)}{\epsilon_{2,k}(\xi) + \epsilon_{2,j}(\xi)}$$



R. French, 2003.

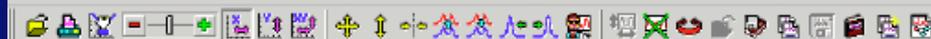
## Hamaker Constant $A_{121}^{NR}$ (zJ)

SrTiO <sub>3</sub>   Vacuum   SrTiO <sub>3</sub>	<b>245 zJ</b>
SrTiO <sub>3</sub>   <b>Σ13 Boundary</b>   SrTiO <sub>3</sub>	<b>78.6 zJ</b>
SrTiO <sub>3</sub>   <b>Σ5 Boundary</b>   SrTiO <sub>3</sub>	<b>34.5 zJ</b>

Project acronym: INCEMS

Project full title: Interfacial Materials – Computations and Experimental Multi-Scale Studies

Proposal/Contract no.: Proposal 013862 /



Sort [Up] [Dn] [Up] [Dn] Database contains 120 rows

Layer	SpectrumName	SpectrumData	nVis	DSpectrumData	Comment
1	PBRUOT		n=3.56,Ln250,Lw3,Hw3		552 Pb2Ru207 L SILVERMAN 300 HP-KKn30 @1240,Hew6.55.
2	TIO2RUTT		n=2.41,Ln250,Lw3,Hw3		527 TiO2 YET 300 RUTILE-1M/OSN-ANN4KKn2.55
3	KH9GLT		n=1.62,Ln250,Lw3,Hw3		432 KH9GLASS 65SiO2 34PbO 1 Al2O3 Lee KKn1.8 @633,Hew6.83.
4	TIO2RUTT		n=2.41,Ln250,Lw3,Hw3		527 TiO2 YET 300 RUTILE-1M/OSN-ANN4KKn2.55
5	PBRUOT		n=3.56,Ln250,Lw3,Hw3		552 Pb2Ru207 L SILVERMAN 300 HP-KKn30 @1240,Hew6.55.
999	PDN7ST		n=1.55,Ln250,Lw1,Hw3		#360-323.PDN7S heptM_methfl_300_1090391 compKKn1.54
999	CDST		n=2.27,Ln250,Lw3,Hw3		#272.CdS,YWong,Single_300,KKn2.4 @633_Hew6.33.
999	CDMOO4T		n=1.95,Ln250,Lw3,Hw3		#367B.cDmOo4.Brixs_xtdLC ovs_300KKn1.85 @600_Hew7.33.
999	CAF2T		n=1.44,Ln250,Lw3,Hw3		549 CAF HARRICKWINDOW 0 KKn1.46 @633_Hew6.33.
999	CAW04T		n=1.74,Ln250,Lw3,Hw3		#332.CaWO4.briener,Sxtol_300,1uKKn1.71 @600_Hew6
999	CAM004T		n=1.88,Ln250,Lw3,Hw3		#333.CaMoO4.Brix_sxtal_300,1UKKn1.95 @633_Hew6.77.
999	icedT		n=2.15,Ln250,Lw1,Hw3		-LOs (01.08.00)(11.05.00)(40.02.00)(8.6.73) #404.cdiocytSilane_methfl_300.1
999	PDN8ST		n=1.53,Ln250,Lw1,Hw3		

HAMAKER DASHBOARD

Open DB Save As Close DB View Log

Add Spectrum Create Dispersion Spec Vers

Delete Row Clone Row Extract Spc Help

Add A Layer

Highlight Database Row, then push layer button.

Layer 1 PBRUOT nVis=n=3.56,Ln250,Lw3 X

Layer 2 TIO2RUTT nVis=n=2.41,Ln250,L X

Layer 3 KH9GLT nVis=n=1.62,Ln250,Lw3 X

Layer 4 TIO2RUTT nVis=n=2.41,Ln250,L X

Layer 5 PBRUOT nVis=n=3.56,Ln250,Lw3 X

Layer 6 SpectrumName nVis X

Layer n SpectrumName nVis X

Hamaker Coefficients

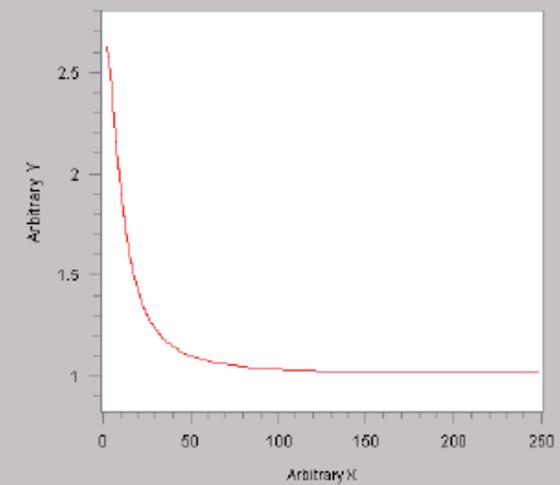
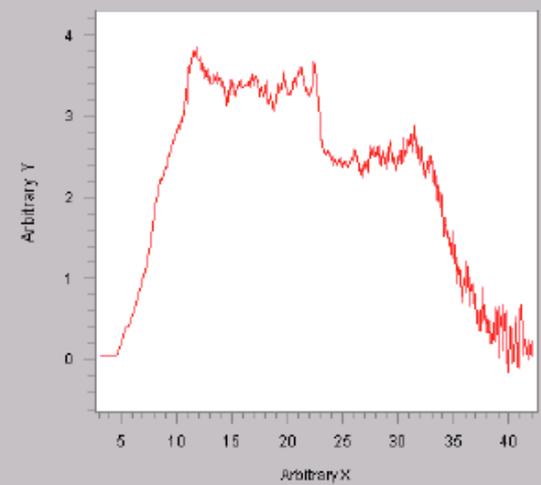
NonRetarded Retarded Add A Layer

N-121 R-121 Calculate

N-123 R-123

N-12321

Contact Angle 1-on-2



# Some “modern” developments

The pseudo-Casimir effect.  $n=0$  (classical) term.

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

Critical Hamiltonian

$$\delta\mathcal{F}(H) = -k_B T \times \frac{A}{H^2} \times \Delta.$$

$$\mathcal{H}[\phi] = \frac{K}{2} \int d^3\mathbf{x} (\nabla\phi)^2,$$

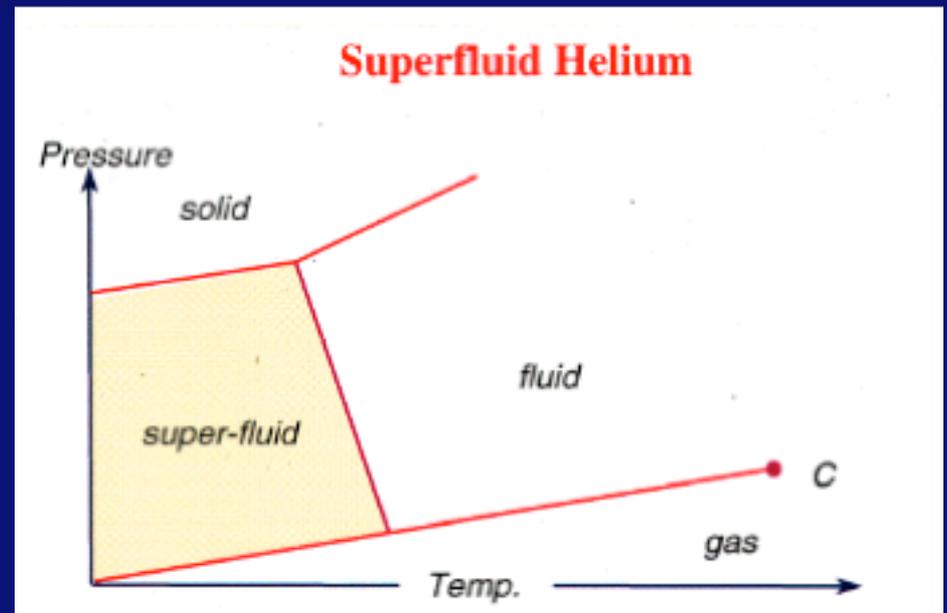
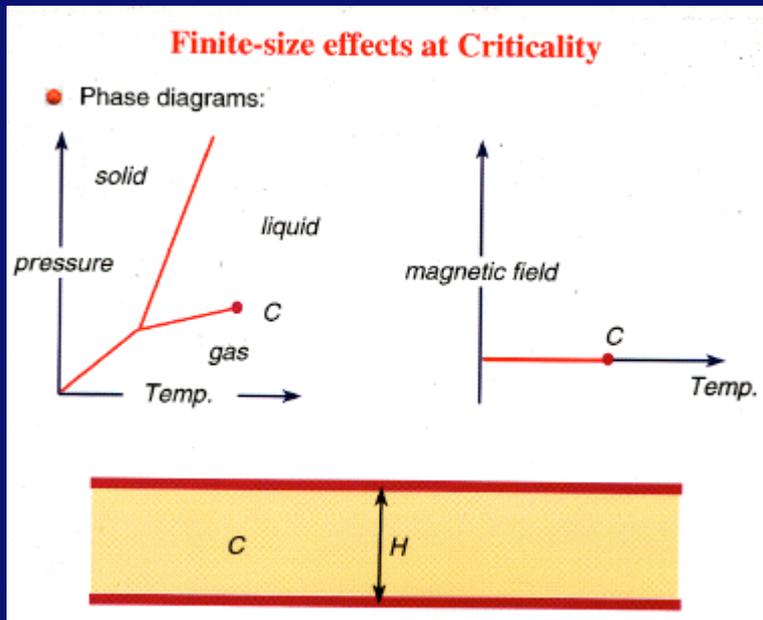
$$\delta\mathcal{F}(H) = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi}.$$

Critical fluids (Fisher and de Gennes, 1978).

Superfluid films (Li and Kardar, 1991).

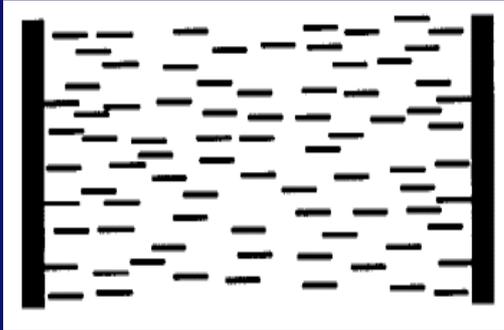
Critical density fluctuations.

Superfluid He Goldstone (massless) bosons associated with the phase of the condensate.

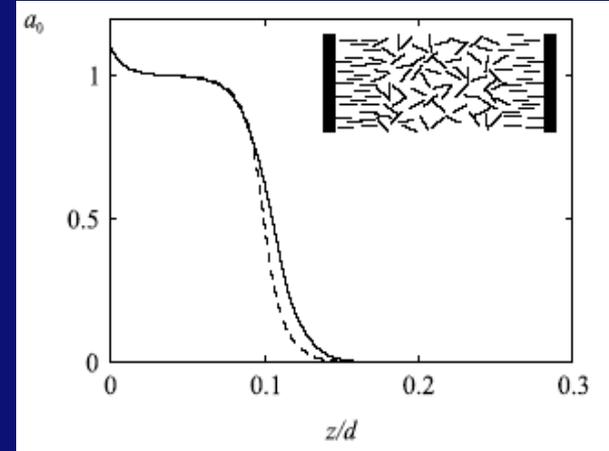


# Nematic and smectic pseudo-Casimir interactions

Nematic liquid crystals.



Critical fluctuations  
in the director field.



$$\mathcal{H}_N = \frac{1}{2} \int d^3 \mathbf{r} [\kappa_1 (\nabla \cdot \mathbf{n})^2 + \kappa_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \kappa_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2].$$

$$\delta \mathcal{E}_N = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi} \left( \frac{\kappa_3}{\kappa_1} + \frac{\kappa_3}{\kappa_2} \right).$$

Nematic film with stiff boundaries (Mikheev, 1989).

$$\mathcal{F} = -\frac{kTS}{8\pi d^3} \zeta(3) - \frac{kTS}{4\pi \xi^2 d} \exp(-2d/\xi)$$

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

Smectic LC

$$\mathcal{H}_S = \frac{1}{2} \int d^3 \mathbf{r} \left[ B \left( \frac{\partial u}{\partial z} \right)^2 + \kappa (\nabla^2 u)^2 \right].$$

$$\delta \mathcal{E}_S = -k_B T \times \frac{A}{H\lambda} \times \frac{\zeta(2)}{16\pi}, \quad \text{with } \lambda \equiv \sqrt{\frac{\kappa}{B}}$$

Smectic films (Li and Kardar, 1992).

# Ionic pseudo-Casimir interactions

Charged fluids  
(Podgornik and Zeks, 1989).

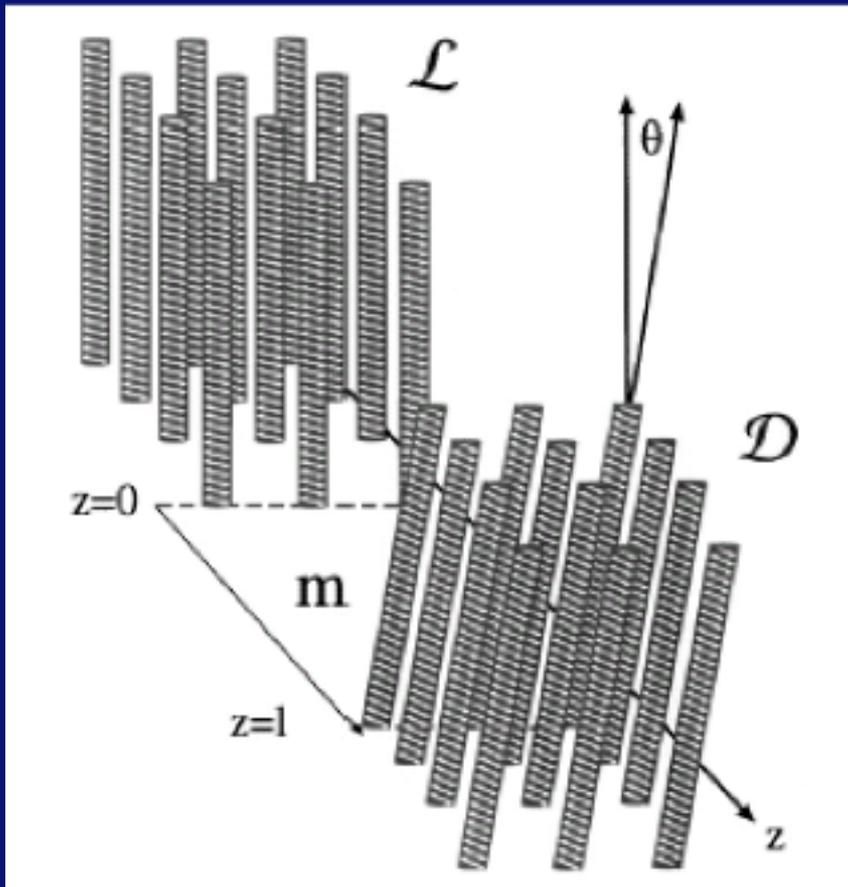
$$\mathcal{F}[n_0, \phi, \nabla\phi] = \int_V \left( \frac{1}{2} \epsilon \epsilon_0 \int_V \nabla\phi^2 - kT n_0 (e^{-\frac{e_0\phi}{kT}} - 1) \right) d^3\mathbf{r}$$

$$F_{\text{FI}} = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi}$$

(Podgornik and Zeks, 1989).

$$F_{\text{FI}} = k_B T \times \frac{A}{\lambda_{\text{GC}}^2} \times \Delta_c \times \ln\left(\frac{H}{\lambda_{\text{GC}}}\right),$$

(Golestanian and Kardar, 1998).



This is part of the weak coupling approximation  
in the theory of coulomb fluids  
(Netz and Moreira, 2000)

Pseudo-Casimir interaction coincides with  
the  $n=0$  Lifshitz result exactly.

Fluctuation (pseudo-Casimir) interactions are non-  
pairwise additive. The total energy of an assembly is  
difficult to calculate.

(Podgornik and Parsegian, 2001)

Non-pairwise additive effects are essential in all  
fluctuation driven interactions.

# Elastic pseudo-Casimir interactions

Membrane inclusions (Goulian et al. 1993).

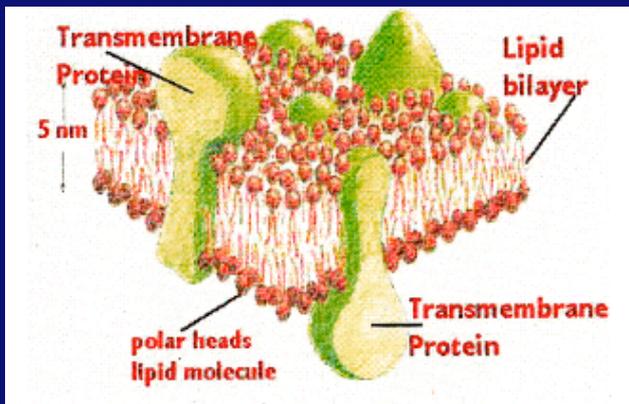
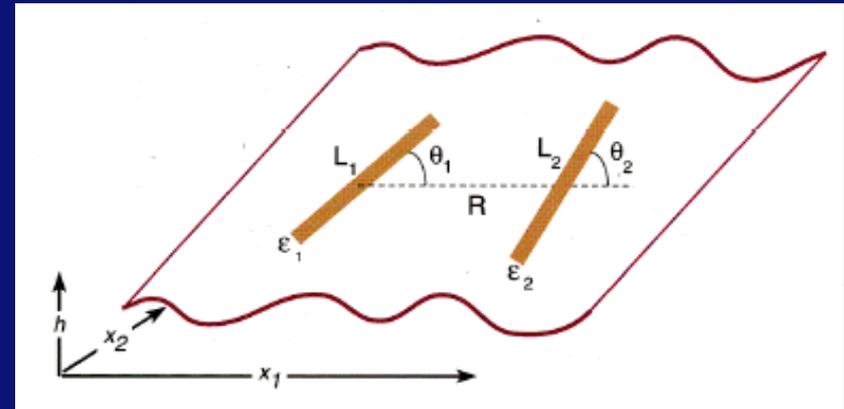
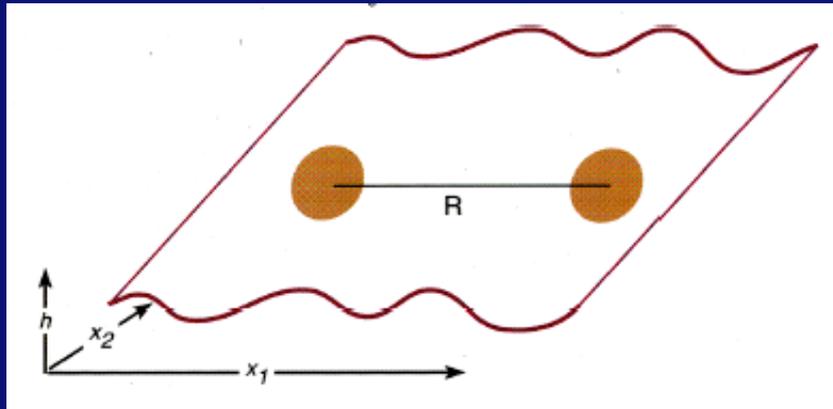
$$\mathcal{H} = \frac{\kappa}{2} \int d^2\mathbf{x} (\nabla^2 h(\mathbf{x}))^2,$$

$$\mathcal{V}(R) = -k_B T \times \frac{A^2}{R^4} \times \frac{6}{\pi^2},$$

(Goulian, Bruinsma, Pincus . 1993).

$$V^T(R, \theta_1, \theta_2) = -\frac{k_B T}{128} \times \frac{L_1^2 L_2^2}{R^4} \times \cos^2[2(\theta_1 + \theta_2)],$$

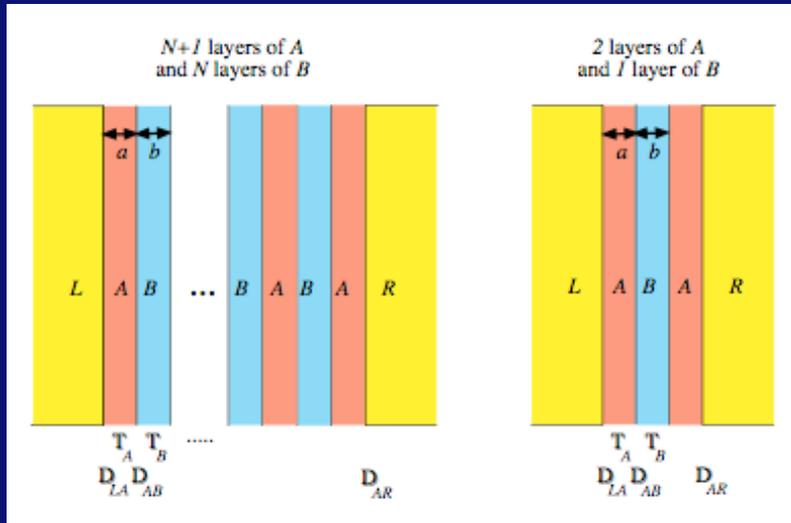
(Golestanian, Goulian and Kardar, 1996).



Interaction between (lipid) membrane inclusions such as proteins.

Important in understanding aggregation of membrane proteins.

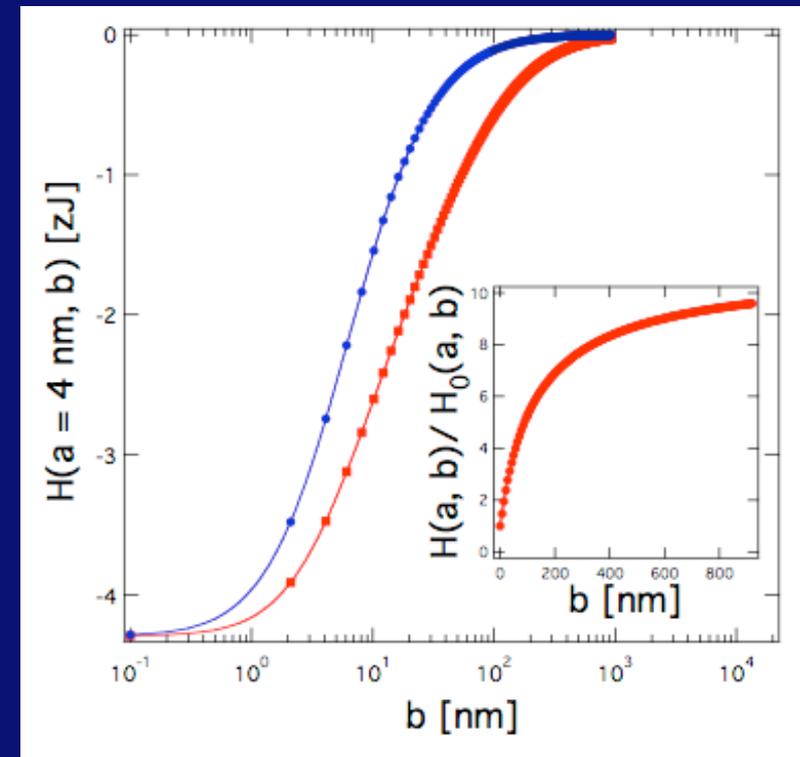
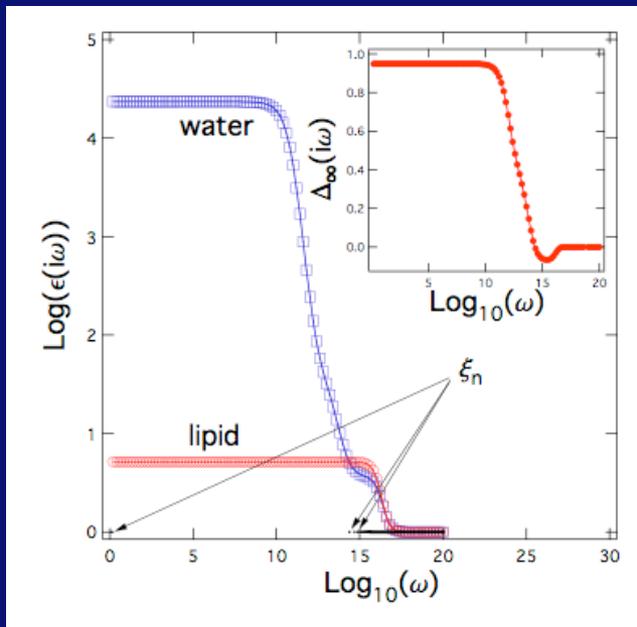
# Van der Waals interactions in modulated systems



Strong non-pairwise additive effects and also retardation effects (?).

The effective Hamaker coefficient is 4.3 zJ.

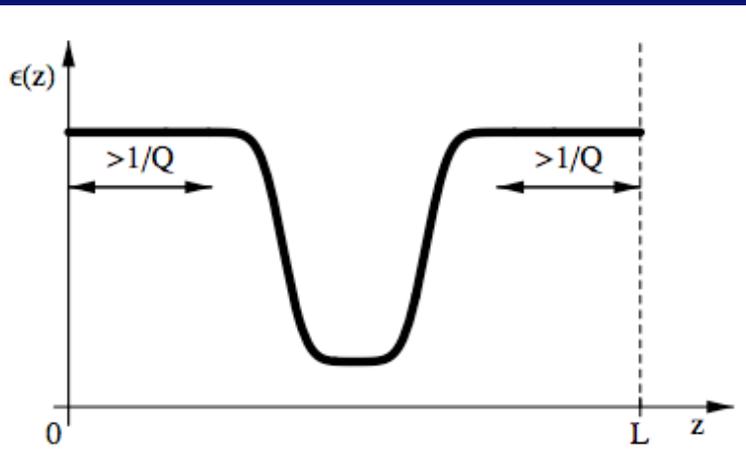
The best value currently available in the literature.  
R.Podgornik, R.H. French and V.A. Parsegian, J. Chem. Phys. Vol. 124, 044709 (2006).



Cholesteric arrays (Dzyaloshinski and Kats, 2006)

# Van der Waals interactions in continuous systems

A continuous spatial variation in the dielectric response.  
Two jellium slabs with a electron density spillover.



DFT formalism: Lundqvist, Langreth, Dobson and others...  
(2006)

$$F/A = \int_0^\infty \frac{d\xi}{2\pi} \int \frac{d^2Q}{(2\pi)^2} \ln \frac{D_M(i\xi; L)}{D_M^{(0)}(i\xi)},$$

$$D_M(i\xi; L) = (\tilde{\varphi}'(0))^{-1},$$

$$\tilde{\varphi}'' + \frac{\epsilon'}{\epsilon} \tilde{\varphi}' - Q^2 \tilde{\varphi} = 0.$$

Lifshitz (field) formalism: Podgornik, Hansen,, Parsegian, Veble ... (2006)

$$F/A = \int_0^\infty \frac{d\xi}{2\pi} \int \frac{d^2Q}{(2\pi)^2} \ln \frac{D_F(i\xi; L)}{D_F^{(0)}(i\xi)},$$

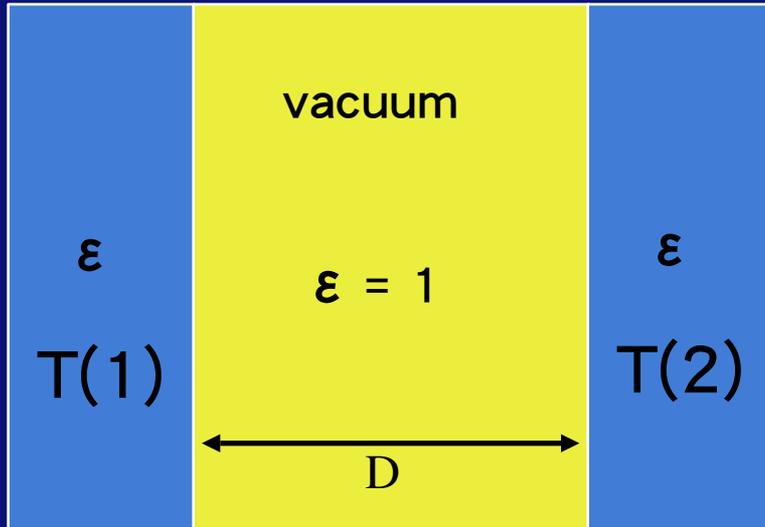
$$M = \dots T_{i+1} D_{i+1} T_i D_i \dots,$$

$$T_i = \begin{bmatrix} 1 & 0 \\ 0 & \exp(-2\rho_i \delta z_i) \end{bmatrix}, \quad D_i = \begin{bmatrix} 1 & -\Delta_i \\ -\Delta_i & 1 \end{bmatrix},$$

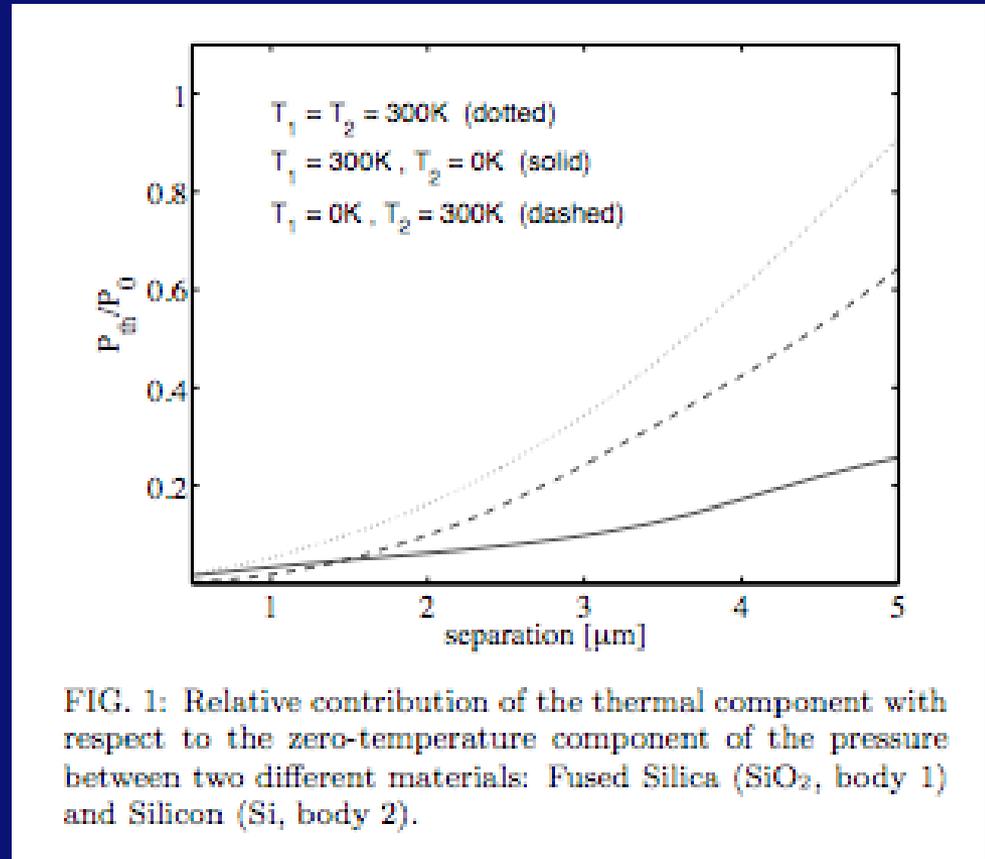
The two approaches can be shown to coincide exactly  
but are not equivalent in terms of numerical implementation.

# Van der Waals interactions in non-equilibrium systems

Recent work of Pitaevskii and the Trento group (2006).



The two semi-infinite slabs are not at the same temperature and thus the system is not at a thermodynamic equilibrium.

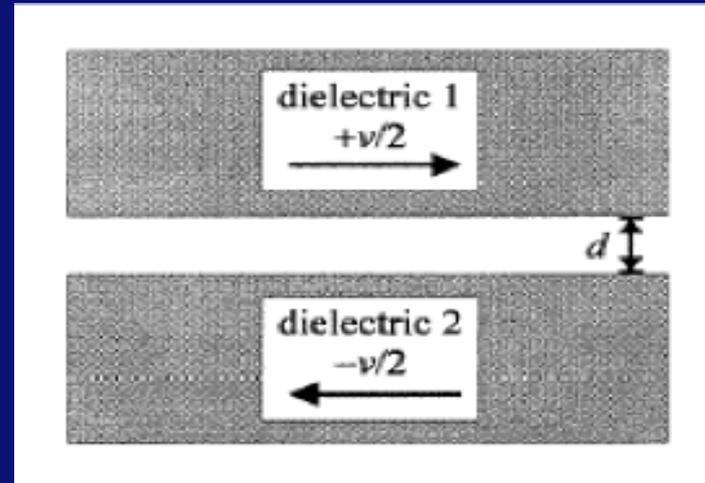
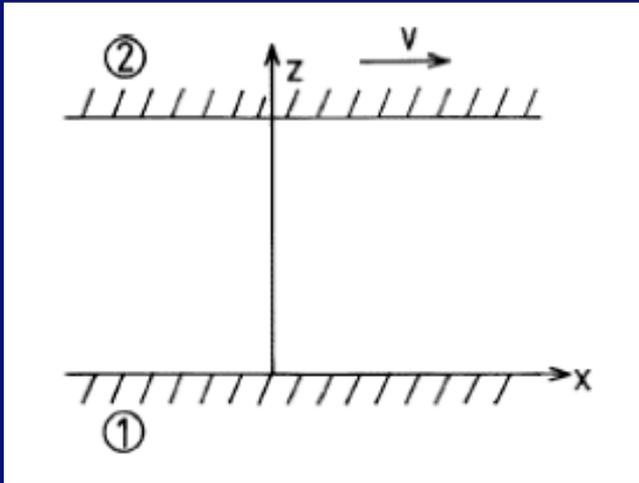


In this case there is a big difference between the propagating modes and the evanescent modes that cancel in the equilibrium case since they have different signs.

The non-equilibrium case leads usually to smaller interactions, except if one of the components is a rarefied gas...

# The dissipative Lifshitz interactions

The dissipative component of the Casimir effect in general.  
Velocity dependent Casimir effect.



Not to forget:  $\epsilon(\omega)$  is defined in a rest-frame!

$$\mathbf{E}'_{\parallel} = \mathbf{E}_{\parallel}$$

$$\mathbf{E}'_{\perp} = \gamma (\mathbf{E}_{\perp} + (\mathbf{v} \times \mathbf{B}))$$

Lorentz boost  
for boundary conditions

$$\mathbf{B}'_{\parallel} = \mathbf{B}_{\parallel}$$

$$\mathbf{B}'_{\perp} = \gamma \left( \mathbf{B}_{\perp} - \frac{1}{c^2} (\mathbf{v} \times \mathbf{E}) \right)$$

Again consider the (averaged) Maxwell stress tensor

$$T_{ij} = \frac{1}{2} \left\{ +\epsilon_0 E_i E_j^* + \epsilon_0 E_i^* E_j - \epsilon_0 \delta_{ij} \mathbf{E} \cdot \mathbf{E}^* + \mu_0 H_i H_j^* + \mu_0 H_i^* H_j - \mu_0 \mathbf{H} \cdot \mathbf{H}^* \right\}.$$

# Transverse and longitudinal Lifshitz interactions

Transverse and longitudinal component of the force:  
Intervening vacuum. Pendry, 1997.

$$F_x = \frac{\hbar}{\pi} \sum_{k_x k_y} \int_{-\infty}^{+\infty} \exp(-2kd) k_x \Im \left[ \frac{\varepsilon(k_x v - \omega) - 1}{\varepsilon(k_x v - \omega) + 1} \right] \Im \left[ \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \right] d\omega.$$

In the limit of frequency independent dielectric function:

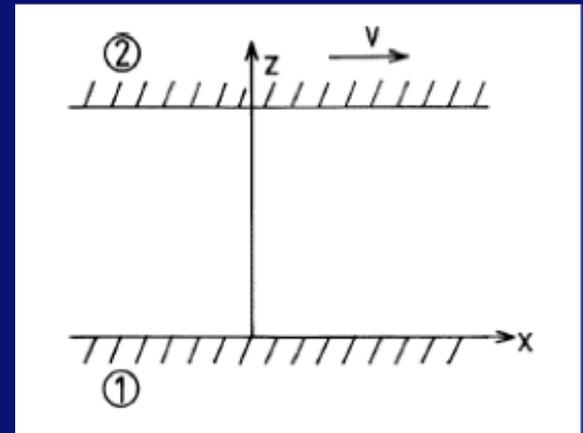
$$F = \left[ \Im \frac{\varepsilon - 1}{\varepsilon + 1} \right]^2 \frac{3\hbar v}{2^6 \pi^2 d^4}.$$

Compare this with Stokes formula and one has viscosity.

The “viscosity” of vacuum is in general small. Mkrтчian, 1995.

$$\eta = \frac{a}{c} \left( \bar{T}_{xz} \right) \Big|_{z = -a/2}.$$

“Viscosity” of vacuum.



$$\frac{f_{\max}}{f_{\text{Casimir}}} \sim \frac{v}{c}.$$

Large planar bodies.

“Viscosity” depends on the separation between the bodies.  
Of course it is a missnomer. Vacuum has no viscosity!

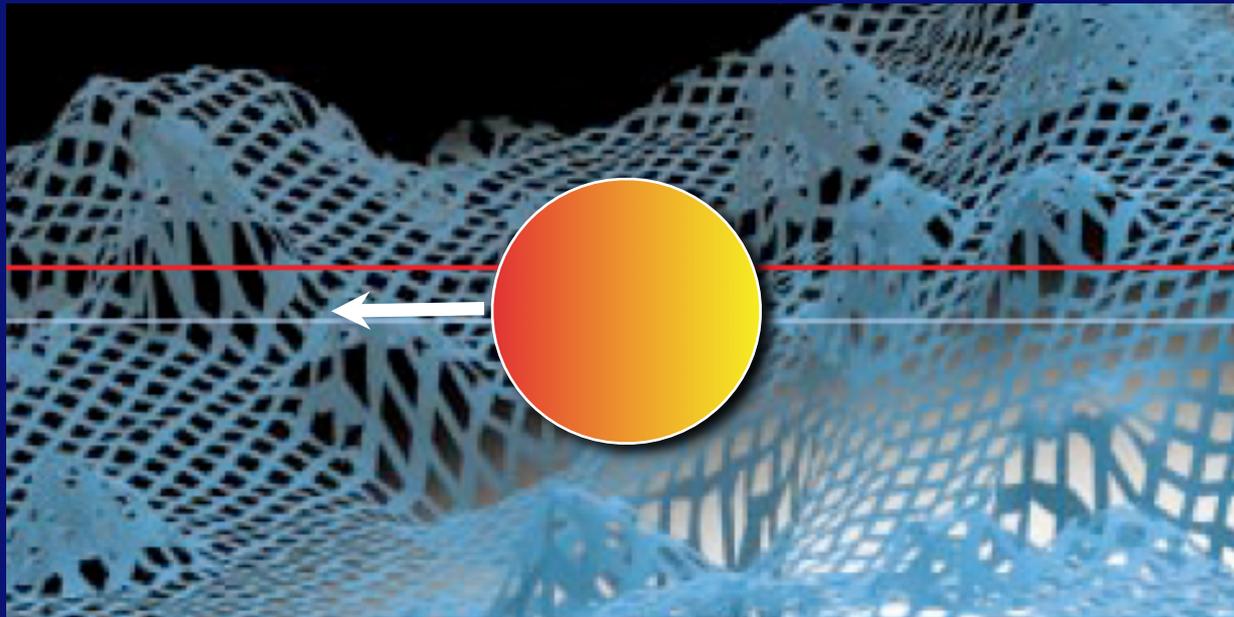
# The “viscosity” of vacuum

Increase the separation between the bodies.  
What happens to “viscosity” quantified as the relaxation time.  
(remember it is a missnomer)

$$\langle \vec{F} \rangle = V \vec{v} \left( \frac{\beta \hbar^2}{3 \pi c^5} \right) \int_0^\infty d\omega \frac{\omega^5 \chi_e''(\omega)}{\sinh^2(\frac{1}{2} \beta \hbar \omega)}.$$

$$\frac{1}{\tau} = \left( \frac{\beta \hbar^2}{3 \pi \rho_M c^5} \right) \int_0^\infty d\omega \frac{\omega^5 \chi_e''(\omega)}{\sinh^2(\frac{1}{2} \beta \hbar \omega)}.$$

It reaches a finite limit! Mkrтчian et al. 2003.



$$\varepsilon(\omega) = 1 + \chi(\omega)$$

The object moves with respect to the coordinate frame in which the Planck spectrum is stationary.

For a non-dissipative particle, there is no viscosity of the vacuum!

The effect persists only at finite temperatures.

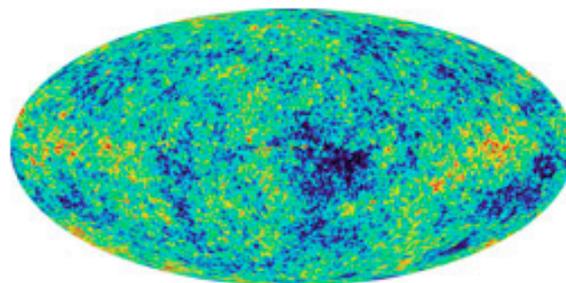
[Phys. Rev. Lett. 91, 220801](#)  
(issue of 28 November 2003)  
[Title and Authors](#)

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.

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.



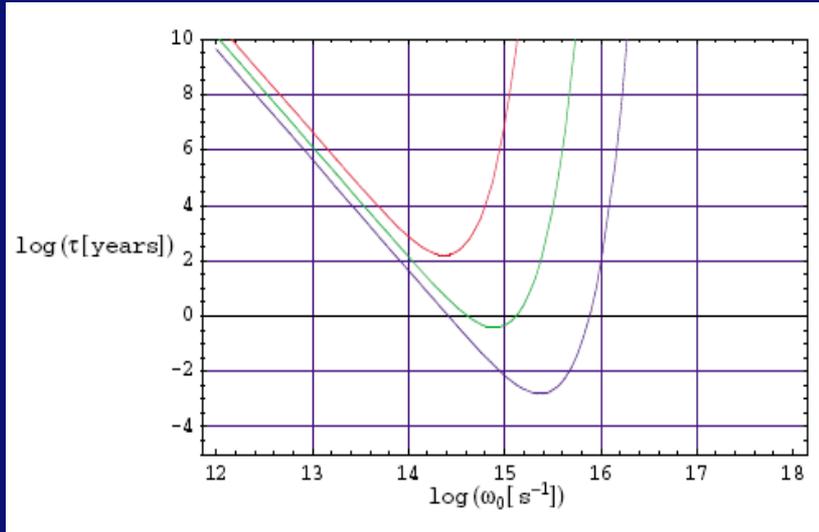
NASA/WMAP Science Team

**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.)

# “Hydrodynamic” Lifshitz drag

$$\chi_e''(\omega) = \chi_0 \delta(\omega/\omega_0 - 1), \text{ where } \chi_0 = \rho_N \alpha_m / \epsilon_0$$

Use different model expressions for the material dielectric or metallic response.



Dependence of characteristic time on absorption frequency for a single sharp absorption line:

$$\tau = \left( \frac{3\pi\rho_M c^5 \hbar^4}{2^6 \chi_0 (k_B T)^5} \right) \frac{\sinh^2(x)}{x^6}.$$

More realistic Lorentzian model.  
No drastic changes in result!

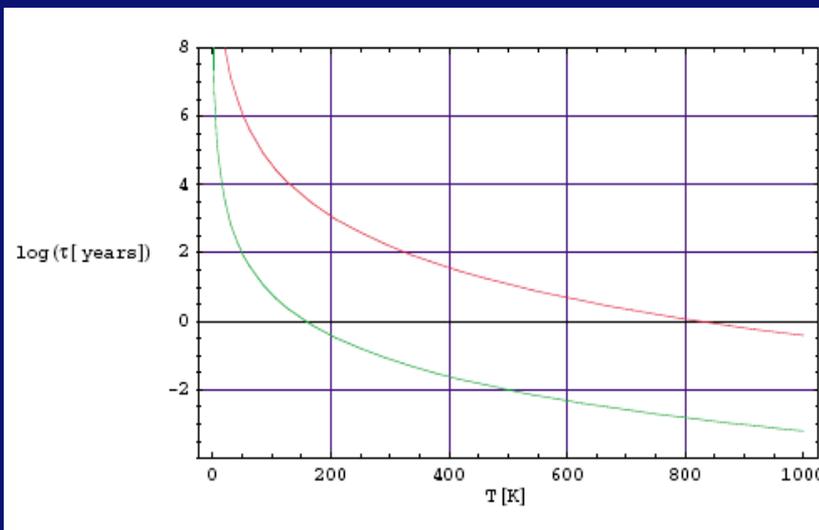
$$\chi''(\omega) = \frac{Ne^2}{\epsilon_0 m} \sum_j \frac{\gamma_0 \omega}{(\omega_j^2 - \omega^2)^2 + (\gamma_0 \omega)^2}$$

Dependence of characteristic time on temperature.

$$\tau = \frac{C}{T^5},$$

$$\tau = \frac{C'}{T^4},$$

Dielectric vs. metal.



# Casimir friction and cosmology

Does not make everybody happy.

"I thought that the paper was great fun," says John Pendry, of Imperial College in London. "The idea that [photons] are in fact a viscous fluid is an intriguing notion." Cosmologist Jim Peebles, of Princeton University in New Jersey is less impressed. He says the effect is real but was accounted for by cosmologists long ago. Referring to Saslow, Peebles says, "Either he or we are out to lunch." Saslow replies that the drag he and his colleagues describe involves a photon absorption process that is different from Rayleigh scattering, the photon interaction cosmologists usually refer to. If the team's predictions about the early Universe are correct, says cosmologist Fred Adams of the University of Michigan in Ann Arbor, "then their result would be quite important."

The Rayleigh force. S. Prasad, 2004.

$$\vec{F} = \frac{512\pi^6 \mu_0 e^4 k_B^8 T^8}{405 \epsilon_0 m^2 c^6 \hbar^7 \omega_0^4} \vec{v}$$

Rayleigh vs. Casimir

$$\frac{F_C}{F_R} = \frac{405 m c^3 \epsilon_0 \hbar^2 \gamma_0}{504 \pi e^2 k_B^2} \frac{1}{T^2}$$

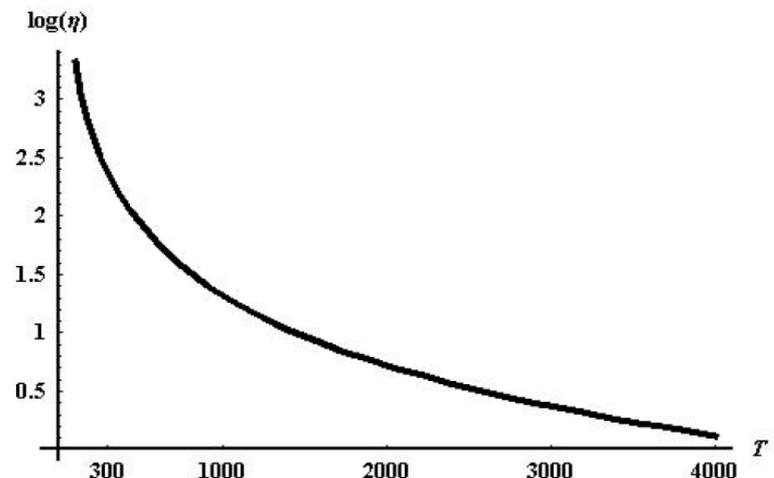


Figure 1:  $\log_{10} \eta$  Vs.  $T$  for  $\omega_0 = 167$  MHz.

The Casimir Force appears to be different from the scattering mechanism, and is by far the stronger force at temperatures lower than the recombination temperature of about 3000 K.



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FINIS

value of  $J$ , the positive level is below the negative one, then in the doublet for  $J=1$  the order is opposite, the positive level being above the negative one, and so on; the order varies alternately as the total angular momentum takes successive values. We are speaking here of case *a* terms; for case *b*, the same holds for successive values of the angular momentum  $K$ .

#### PROBLEM

Determine the  $A$ -splitting for a  $^4D$  term.

**SOLUTION.** Here the effect appears in the fourth approximation of perturbation theory. Its dependence on  $K$  is determined by the products of the four matrix elements (88.1) for transitions with change of  $A: 2 \rightarrow 1, 1 \rightarrow 0, 0 \rightarrow -1, -1 \rightarrow -2$ . This gives

$$\Delta E = \text{constant} \times (K-1)K(K+1)(K+2),$$

where the constant is of order of  $8^4/r^2$ .

#### §89. The interaction of atoms at large distances

Let us consider two atoms which are at a great distance from each other (DISTANCE); we may, therefore, find the energy of their interaction. In

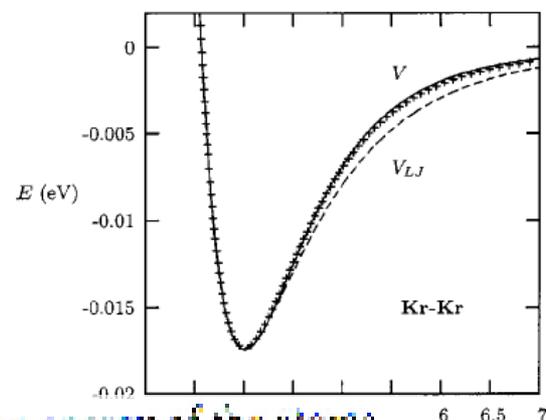
† This, of course, does not imply that the mean value of the interaction energy of the atoms is precisely zero. It diminishes exponentially with distance, i.e. more rapidly than every finite power of  $1/r$ , and hence each term of the expansion vanishes. This occurs because the expansion of the interaction 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.

of perturbation theory. The energy of the interaction of the atoms is there determined as the diagonal matrix element of the perturbation operator, calculated with respect to the unperturbed wave functions of the system (expressed in terms of products of unperturbed wave functions for the two atoms).† In  $S$  states, however, the diagonal matrix elements, i.e. the mean values of the dipole, quadrupole, etc., moments, are zero; this follows immediately, since the distribution of charge density in the atoms is spherically symmetrical. Hence each term of the expansion of the perturbation operator in powers of  $1/r$  is zero in the first approximation of perturbation theory.‡

† Here we neglect the exchange effects, which decrease exponentially with increasing 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.

## The Cahill - Parsegian calculation, 2004.



ground state with  $a = 78.214 \text{ eV } \text{\AA}^6$ , and  $e$  (pluses, blue) with the m, the Lennard-Jones  $0.017338 \text{ eV}$ ] (dashes,

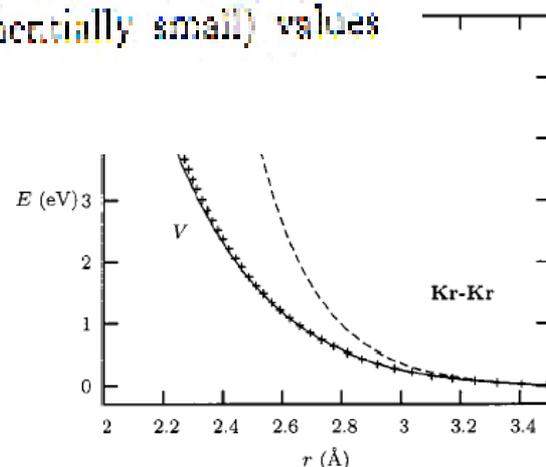
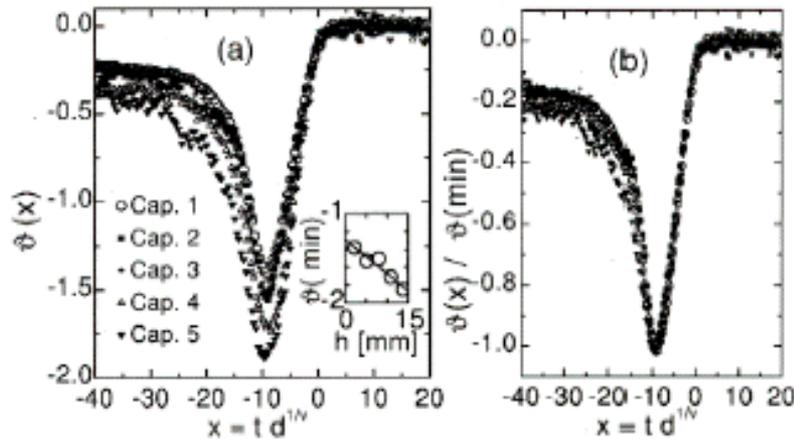


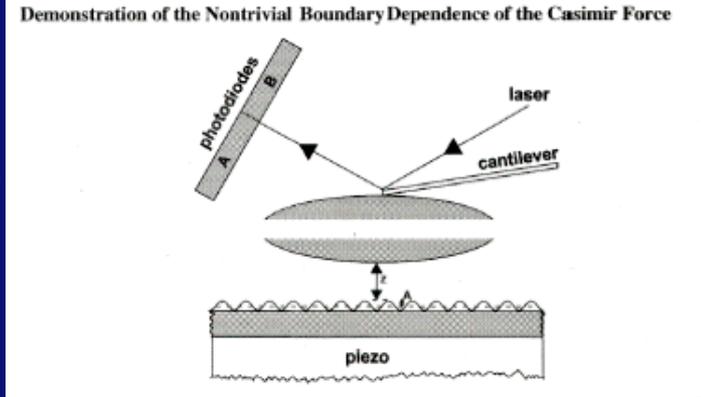
FIG. 8. Positive potential  $V$  [Eq. (6) as in Fig. 7],  $\text{Kr}_2$  Aziz points (pluses, blue), L-J form  $V_{LJ}$  [Eq. (1) as in Fig. 7].

# Some "modern" developments ...

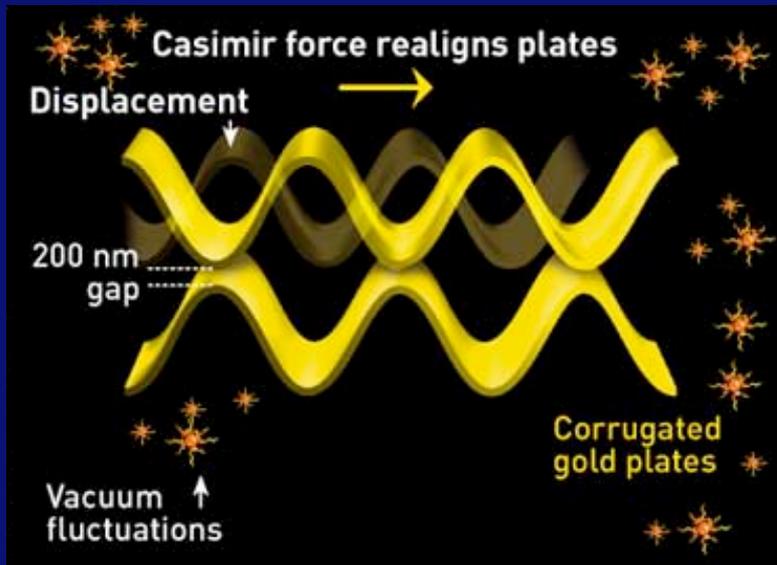
- The data for thinning of superfluid films can be collapsed assuming a roughness of  $w \sim 130 \text{ \AA}$



• A. Roy and U. Mohideen, Phys. Rev. Lett. 82, 4380 (1999).



Effects of boundary conditions.



$$\frac{f(H)}{kT} = -\frac{\zeta(3)}{16\pi} \frac{1}{H^2} - \frac{3\zeta(3)}{16\pi} \frac{A_S L^{2\zeta_S}}{H^4} + \frac{C_1}{4} \frac{A_S}{H^{4-2\zeta_S}}$$

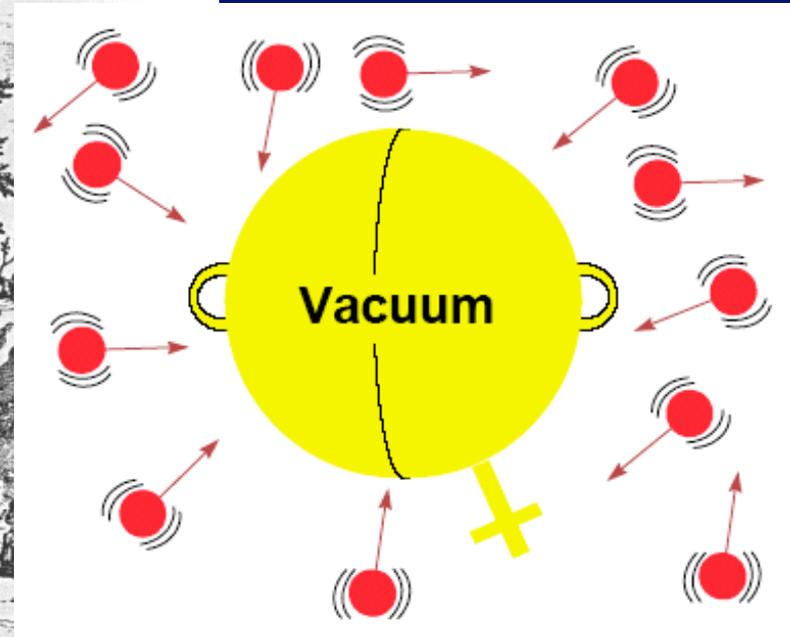
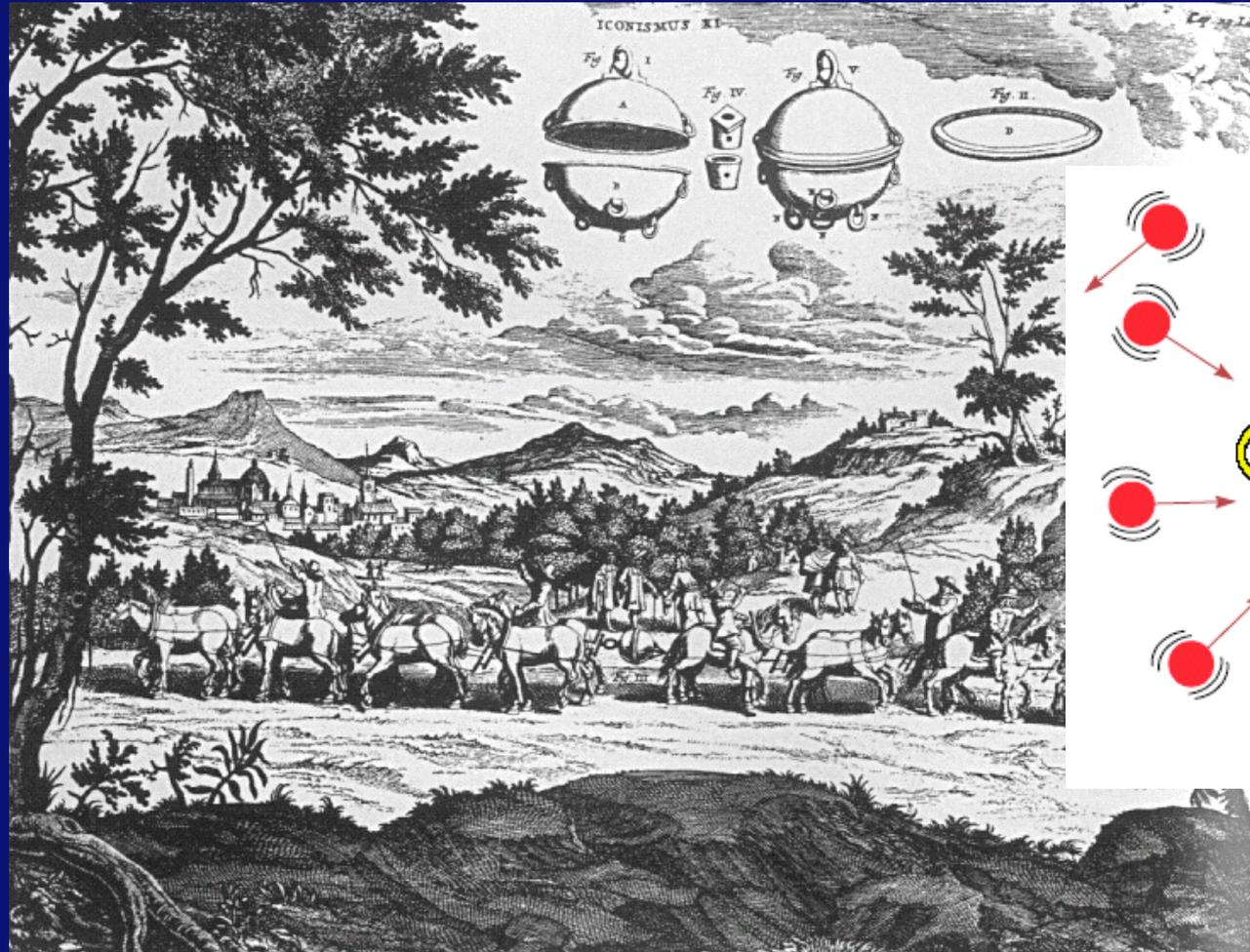
$$\overline{[h(\mathbf{x}) - h(\mathbf{y})]^2} = A_S |\mathbf{x} - \mathbf{y}|^{2\zeta_S}$$

Li and Kardar, 1991.

BC can qualitatively change vdW interactions.

T. Emig, 2003.

# Von Guericke (1602-1686) and the Magdeburg sphere.



Scattering of EM waves!

Casimir model (1956) of the electron.  
Electrostatic repulsion and Casimir attraction  
have to balance!

Sometimes even the sign is difficult to guess.  
Spherical geometry.

$$E = \frac{e_0^2}{4\pi\epsilon_0 a} - Z \frac{\hbar c}{a}$$

Boyer, Davies, Balian and Duplantier,  
Milton, DeRaad and Schwinger (1978)  
 $Z < 0!$