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.

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Health http://lpsb.nichd.nih.gov
Boyle and van der Waals gas equations

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 $a \geq 0$, $p_{vdW} \leq p_{Boyle}$
because of attractive forces;
Total volume of particles, $b \geq 0$

Thesis:
“Continuity of gas and liquid states”
Dipole-dipole interactions (1920’s – 30’s)  
van der Waals gasses

Keesom:  
permanent dipoles,  
average attractive mutual orientation.

Debye:  
permanent dipole induces a  
dipole in another, non-polar,  
molecule.

London dispersion:  
transient dipoles on polarizable bodies.
Extension to condensed media (two half-spaces: pairwise summation of dipole interactions (Derjaguin, 1934, Hamaker, 1937)
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

Modern, macroscopic point of view
Focus on electromagnetic waves
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 [Lifshitz’] 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)
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 C8
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

Interaction = \(-\frac{A(l)}{12\pi l^2}\)  
\[A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n} \left( \frac{\varepsilon_A - \varepsilon_m}{\varepsilon_A + \varepsilon_m} \right) \left( \frac{\varepsilon_B - \varepsilon_m}{\varepsilon_B + \varepsilon_m} \right) \times \text{Rel}(l)\]

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 $\varepsilon_A$, $\varepsilon_B$, $\varepsilon_m$, for interaction come from noise!

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

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

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

\[
\varepsilon(\omega) = \varepsilon'(\omega) + i \varepsilon''(\omega).
\]

Use the Kramers-Kronig transform

For “imaginary frequency”

\[
\varepsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon''(\omega)}{\omega^2 + \xi^2} d\omega
\]

\[
\xi = \xi_n \equiv \frac{2\pi kT}{\hbar} n, \quad n = 0, 1, 2, \ldots \infty
\]
Connecting van der Waals forces with spectra

The dielectric spectrum of water.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Hamaker coefficient (kT\text{room} units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbon across water</td>
<td>0.95 kT\text{room}</td>
</tr>
<tr>
<td>mica across hydrocarbon</td>
<td>2.1 kT\text{room}</td>
</tr>
<tr>
<td>mica across water</td>
<td>3.9 kT\text{room}</td>
</tr>
<tr>
<td>gold across water</td>
<td>28.9 kT\text{room}</td>
</tr>
<tr>
<td>water across vacuum</td>
<td>9.4 kT\text{room}</td>
</tr>
<tr>
<td>hydrocarbon across vacuum</td>
<td>11.6 kT\text{room}</td>
</tr>
<tr>
<td>mica across vacuum</td>
<td>21.8 kT\text{room}</td>
</tr>
<tr>
<td>gold across vacuum</td>
<td>48.6 kT\text{room}</td>
</tr>
</tbody>
</table>
Simplest form of Lifshitz interaction energy: half-spaces $A$ and $B$ across medium $m$

$$\text{Interaction} = -\frac{A(l)}{12\pi l^2} \quad A(l) = \frac{3kT}{2} \sum_{\xi_n} \left( \frac{\varepsilon_A - \varepsilon_m}{\varepsilon_A + \varepsilon_m} \right) \left( \frac{\varepsilon_B - \varepsilon_m}{\varepsilon_B + \varepsilon_m} \right) \times \text{Rel}(l)$$

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)


Forces across bilayers (Haydon & Taylor, 1968)

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

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",
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

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

The bounce of particles, observed via reflected light, gives the force between sphere and flat.
Aerosols (Marlow et al.)

V. Arunachalam, R. R. Lucchese, & W. H. Marlow
Casimir “effect” (metals)


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

K. Autumn et al. "Evidence for van der Waals adhesion in gecko setai," PNAS, 192252799
Gecko’s grip grasped


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

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\]

Inverse square dependence of the energy per unit area.
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Generalization for spatially varying polarizability $\varepsilon(z)$

$\varepsilon_A(z_A)$ $\varepsilon_m$ $\varepsilon_B(z_B)$

$\varepsilon_A$ $\varepsilon_B$

$D_A + \frac{l}{2}$ $\frac{l}{2}$ $0$ $\frac{l}{2}$ $D_B + \frac{l}{2}$

Rudi Podgornik & VAP 2001-04
E.g., Exponential variation of response in an infinitely thick layer

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

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

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 $\varepsilon$ 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 $\varepsilon$ is constant across planar regions.


- Inhomogeneous Graded Layers
  - Variations in epsilon in layer
  
  \[
  \varepsilon_A(z_A) = \varepsilon_m + \frac{(\varepsilon_A - \varepsilon_m)}{a^2} (z_A - \frac{l}{2})^2, \quad \varepsilon_B(z_B) = \varepsilon_m + \frac{(\varepsilon_B - \varepsilon_m)}{b^2} (z_B - \frac{l}{2})^2.
  \]

- 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
Example 2. Lipid bilayers, solutes control spectra
Multilayers: Neutral lipid bilayers in salt water

Small-angle x-ray scattering

$D = 2\pi/q \sim 60\text{Å}$

locally flat, multilayer stacks

$D$ (repeat spacing, $\sim 60$ Ang)

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)

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**Graph:**
- DLPC/KBr
- DLPC/KCl

**Lines:**
- "charge regulation" fit (Ninham and VAP, 1971)
- Br⁻ “binding” $K_{assoc} \approx 0.2 \text{ M}^{-1}$
Example 3.
Kevin Cahill:
“Only Keesom, Debye, London power law? How about first-order interactions?”

Landau & Lifshitz, Quantum Mechanics, footnote page 341
First-order van der Waals forces atom-atom attraction

A Rydberg-like potential $V_{\text{Rydb}}$,

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

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

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


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

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


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


Title and Authors

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.