The Force of Fluctuations

- Measurement of Critical Casimir Forces -

Clemens Bechinger

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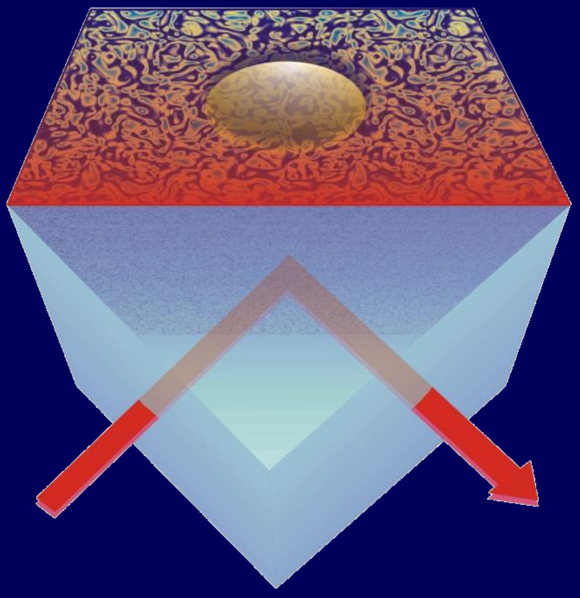
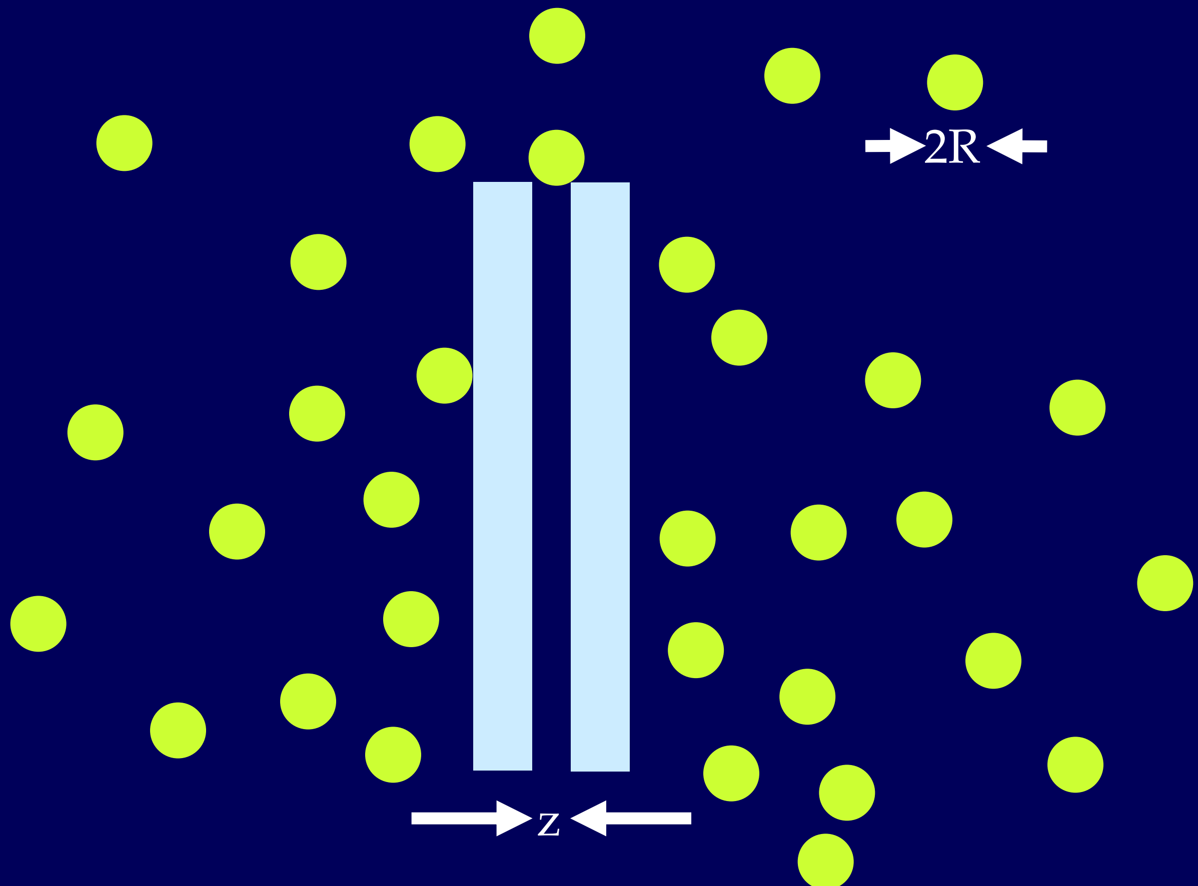
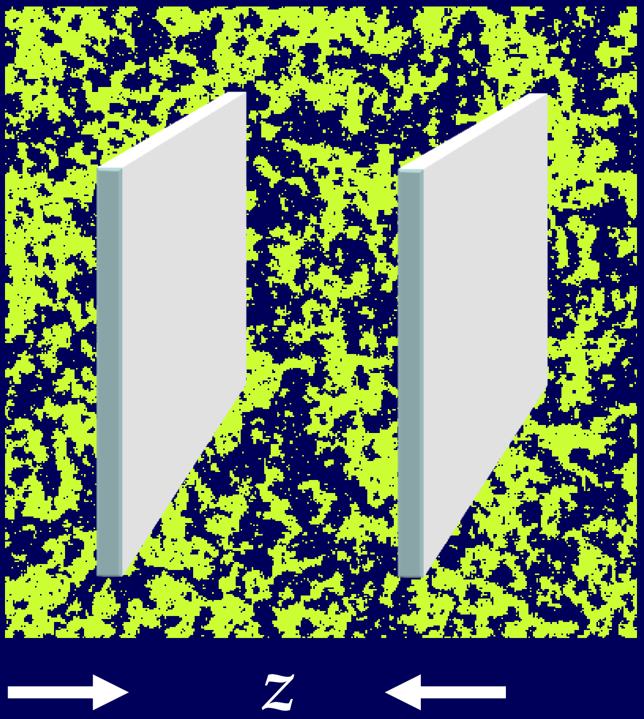


Confinement Induced Forces



particles (z < 2R) ⇒ **entropic & depletion forces**
⇒ **osmotic pressure**

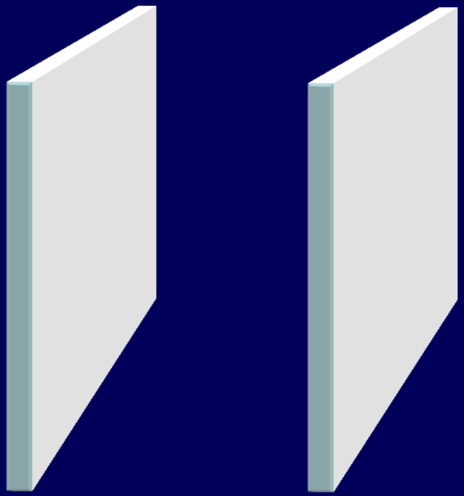
Confinement Induced Forces



binary liquid @ critical point ⇒ **critical Casimir force**

- $z \gg 2R$
- strong temperature dependence

Confinement Induced Forces



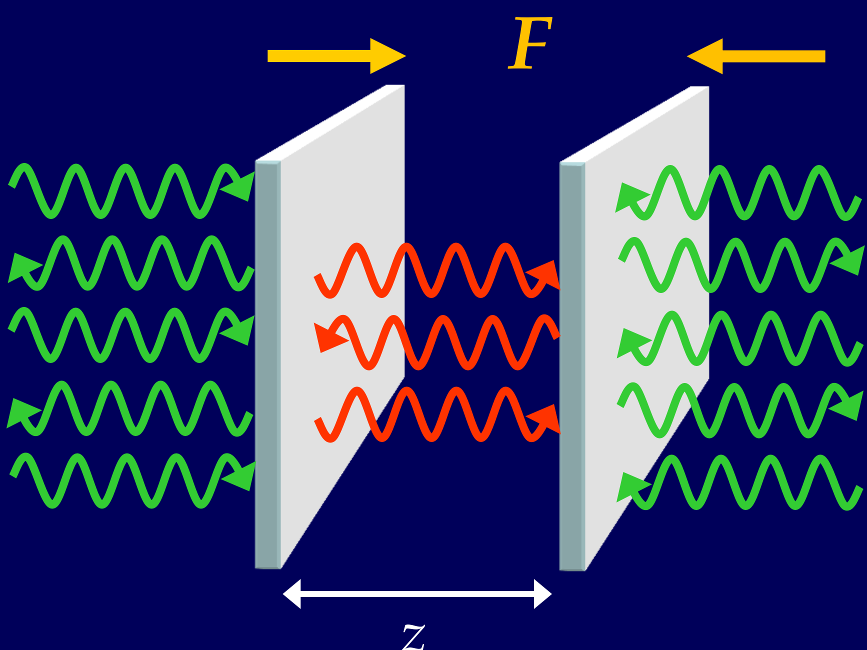
vacuum ⇨ **QED Casimir force**

Outline

- **Brief reminder to QED-Casimir forces**
  QED fluctuations in confined geometries
- **The critical Casimir effect in binary mixtures**
  Concentration fluctuations in binary mixtures
- **Total internal reflection microscopy (TIRM)**
  Measuring forces with femto Newton resolution
- **Experimental results**
  temperature dependence of critical Casimir forces
  influence of boundary conditions
- **Lateral critical Casimir forces**
  chemically patterned surfaces
- **Conclusions & future perspectives**

The QED Casimir Effect

Hendrik Casimir



$$F(z) = -\frac{\pi^2 \hbar c}{240 z^4} A$$

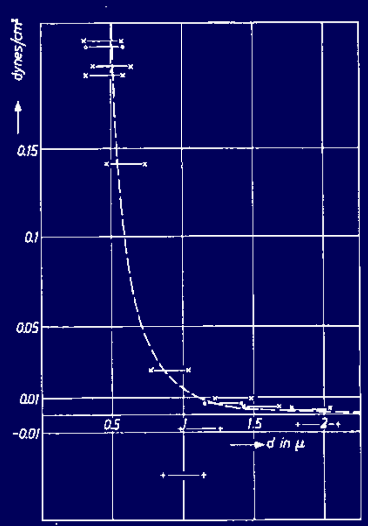
reduced spectrum of quantum mechanical vacuum fluctuations

*H. B. G. Casimir, Proc. Kon. Nederl. Akad. Wet. B**51,** 793 (1948)*

Experimental Observations

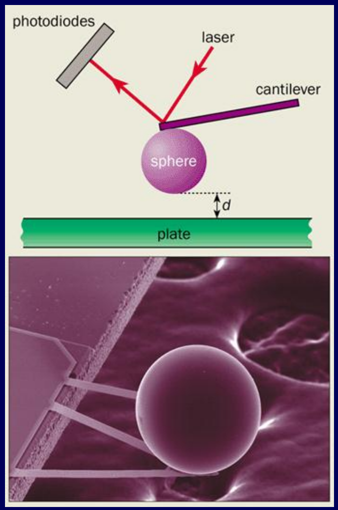
- Mechanical Balance

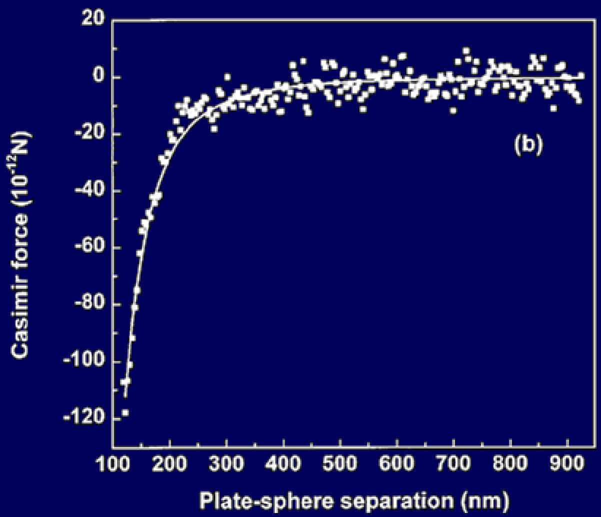
*Sparnaay, Physica **24**, 751 (1958)*



- AFM

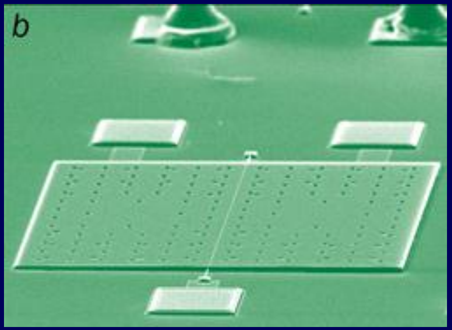
*Mohideen and Roy, PRL **81,** 4549-4552 (1998)*

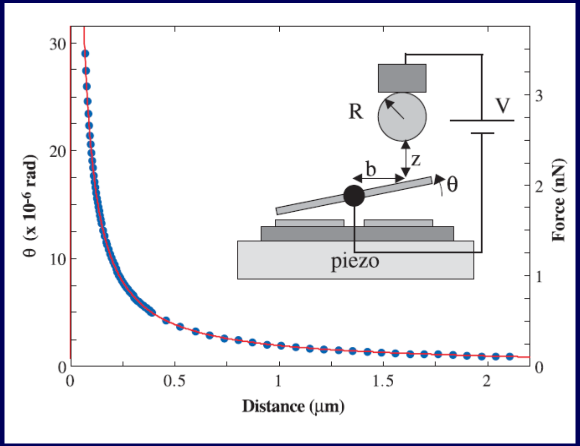




- Actuation of MEMS

*Chan, Aksyuk, Kleiman, Bishop, Capasso, Science **291,** 1941 (2001)*

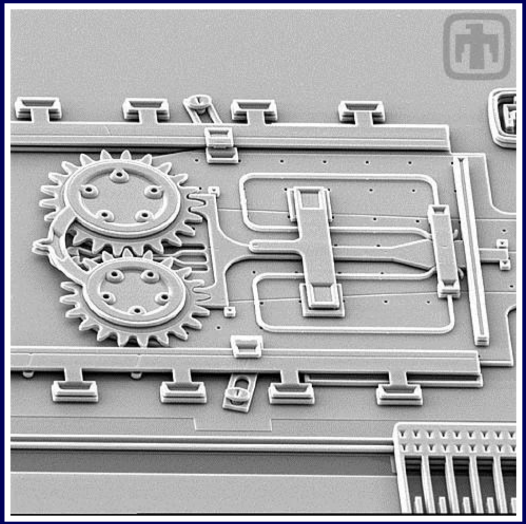




Failure Mechanisms in MEMS

Example: **parallel plates of 1mm^2 size at 10nm distance: ~ 0.1 N**

Casimir forces ⟹ STICTION



50 μm

Sandia National Laboratory

repulsive Casimir forces in vacuum:

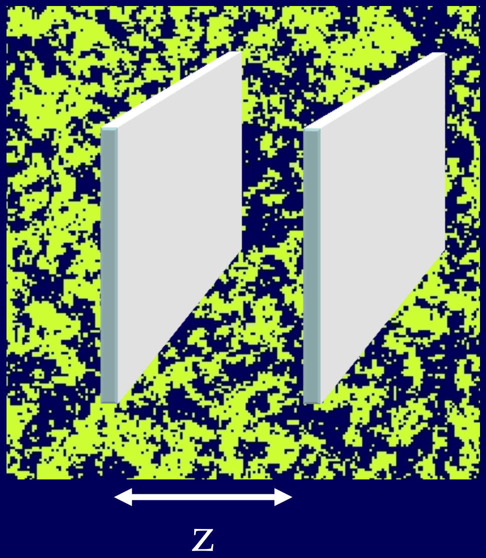
$\mu > \varepsilon$ *Kenneth et al. PRL* ***89****, 33001 (2002)*

meta-materials *Leonhardt, Philbin, New J. Phys.* ***9****, 254 (2007)*

The Critical Casimir Effect

„Phenomena at the walls in a critical binary mixture“

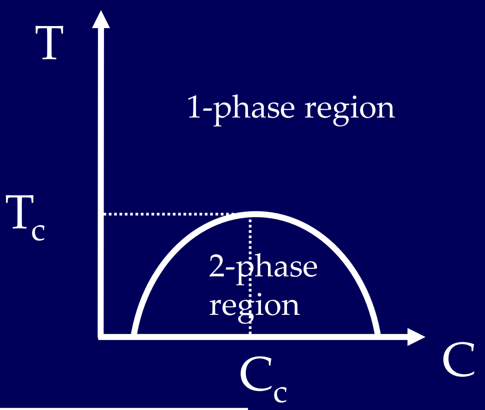
M. E. Fisher and P. G. deGennes, C. R. Acad. Sci. Paris ***B287,*** *209 (1978)*



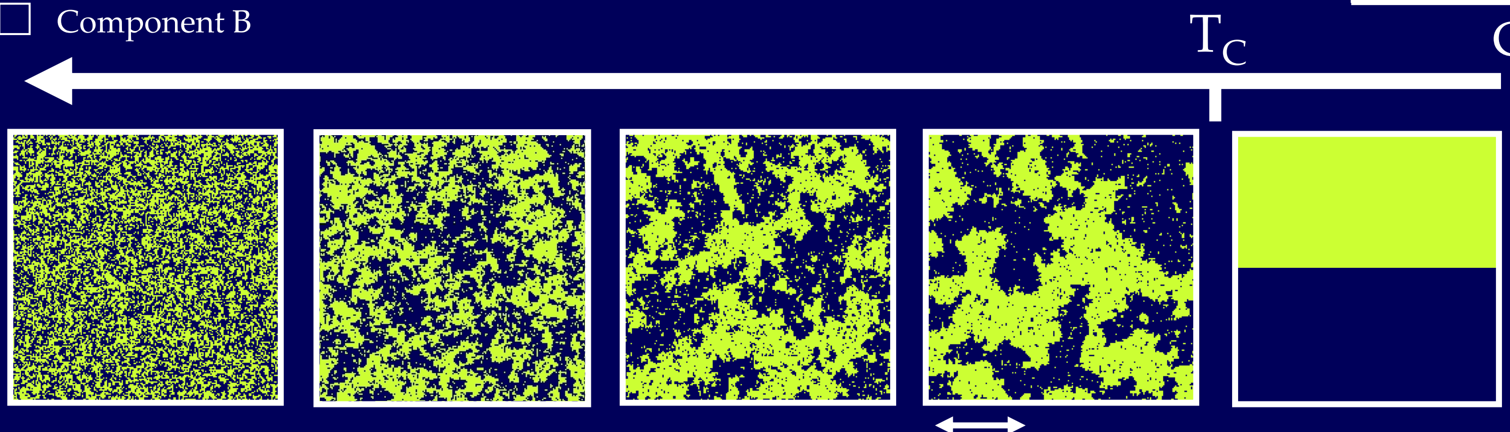
Two plates immersed in binary mixture close to the critical point

➡ Critical Casimir force

Binary Mixtures

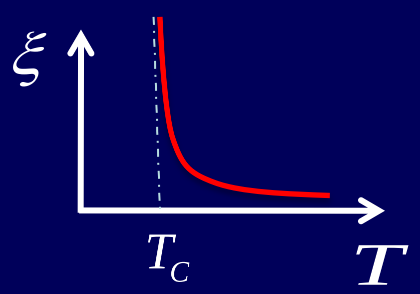


■ Component A
□ Component B



$$\xi = \xi_0 \left| \frac{T}{T_c} - 1 \right|^{-\nu}$$

3D Ising: $\nu = 0.63$



Confinement of concentration fluctuations

$$F(z, T) = A \frac{k_B T_c}{z^3} \vartheta(z / \xi)$$

⇧

universal scaling function

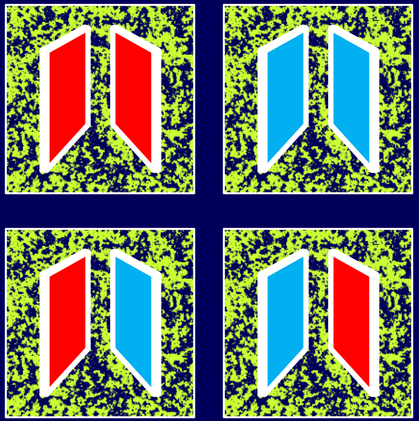
Scaling Function & Boundary Cond.

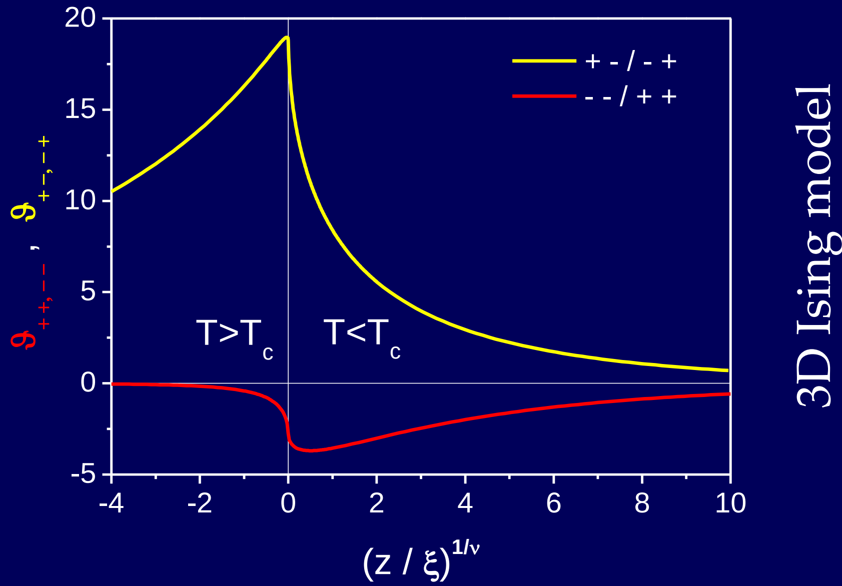
$$F(z,T) = A\,\frac{k_B T_c}{z^3}\,\vartheta(z/\xi)$$

boundary conditions set by adsorption preference of confining surfaces

symmetric BC

antisymmetric BC





*Vasilyev, Gambassi, Maciolek, Dietrich EPL **80**, 60009 (2007)*

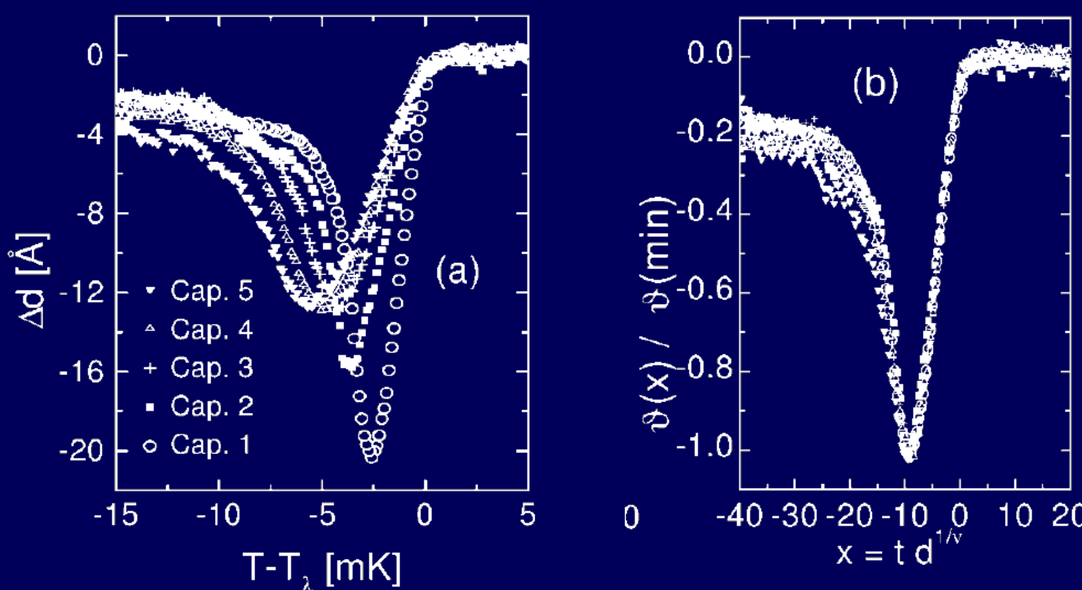
attractive and repulsive critical Casimir forces

Casimir: QED vs. Critical

	QED	Critical	
fluctuating quantity	e.m. field	local conc.	
excitation	quanta	classical	
control of fluctuation-range	NA	$\xi = \xi_0 \left\| \frac{T}{T_c} - 1 \right\|^{-\nu}$	(diverging @ T_c)
sign of force	attractive	attr./repuls.	(boundary cond.)

Critical Casimir Force in ^{4}He Films

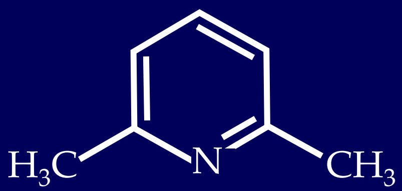
Critical fluctuations induce thinning of ^{4}He films close to $T_\lambda = 2.1768$ K

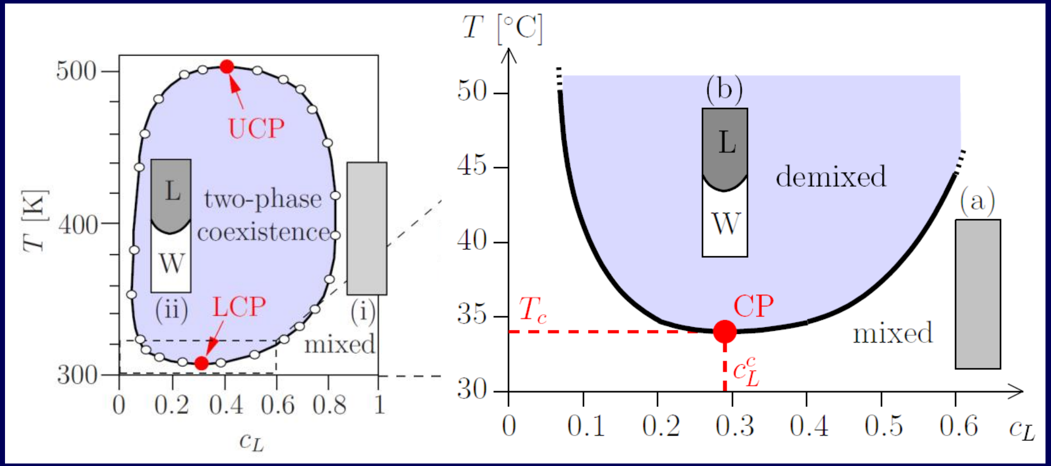


Garcia, Chan, PRL ***83,*** *1187 (1999)*
Ganhin, Scheidemantel, Garcia, Chan, PRL ***97****, 075301 (2006)*

Binary Critical Mixtures

water - lutidine





36°C

35°C

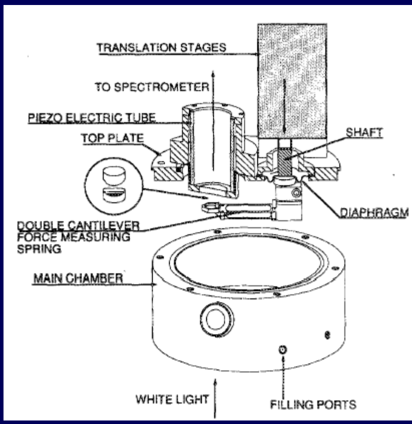
34°C

T < 33°C

critical opalescence

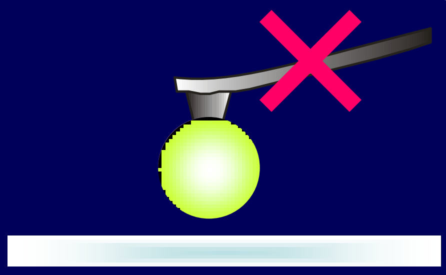
How to Measure Tiny Forces

How to resolve pico … femto Newton



- *Surface Force Apparatus (SFA)*

  J.N. Israelachvili, Intermolecular and surface forces, Academic Press (1991).



- *Atomic Force Microscopy (AFM)*

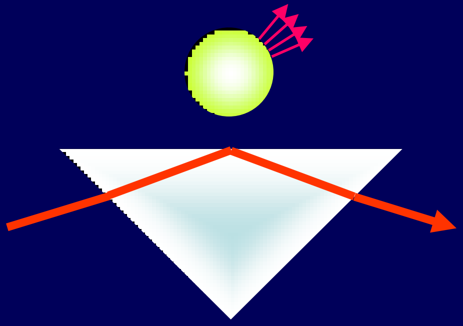
  Ducker, Senden, Pashley, Nature, **353**, 239 (1991).
  Milling,Vincent, J. Chem. Soc., Farady Trans. **93,** 3179 (1997).

resolution limited by spring constant $D \geq 0.01 N/m$

➡ ´freely´ suspended colloidal probe particle

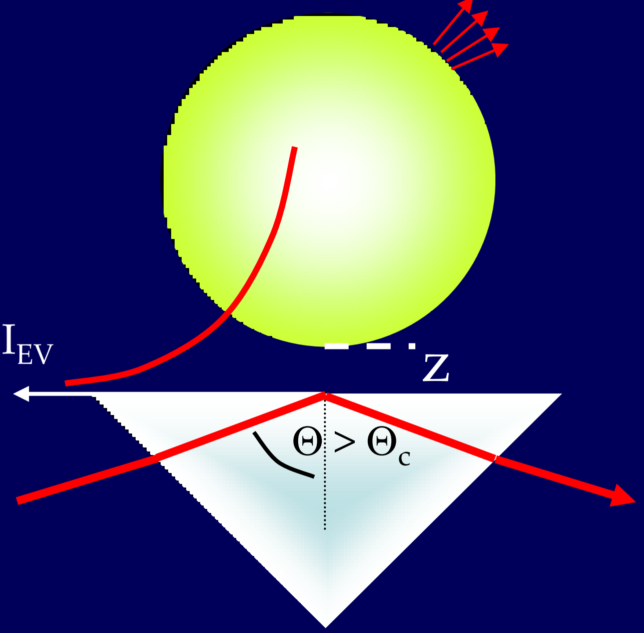
- *Total Internal Reflection Microscopy (TIRM)*

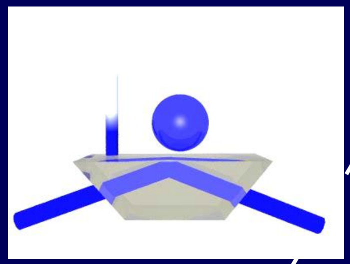
  Prieve, Walz, Current opinion in colloidal interfaces & science **2,** 600 (1997).
  Volpe, Brettschneider, Bechinger, Opt. Express (in press).



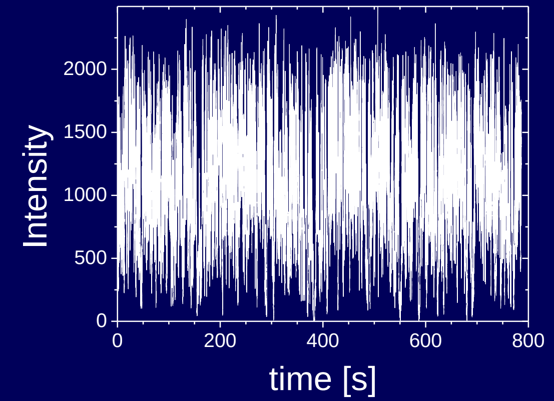
TIRM

$$I = I_0 \exp(-\beta z)$$

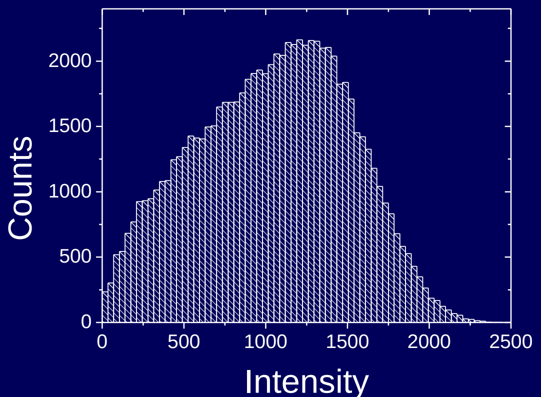




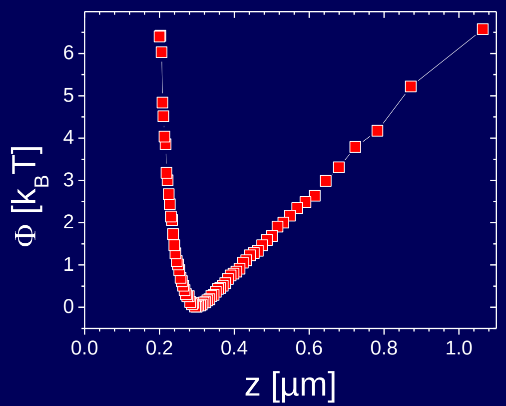
❶



❷



❸



$$\Phi(z) = A\exp(-\kappa z) + F_g z$$

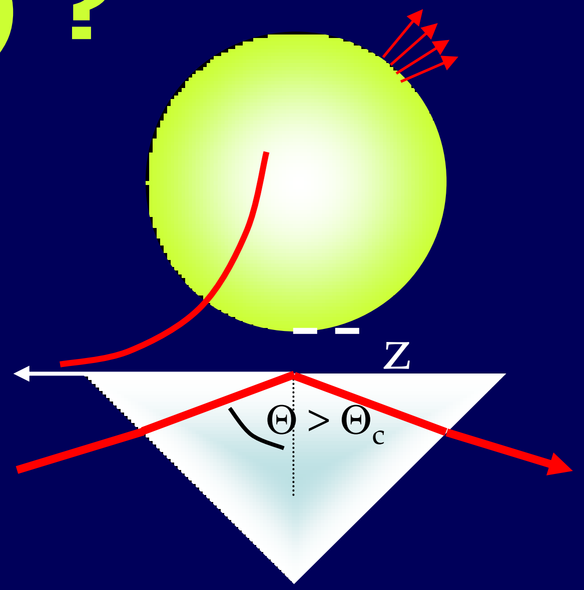
$$P(z) = P_0 \exp\left(-\frac{\Phi(z)}{k_B T}\right)$$

$$P(z)dz = N(I)dI$$

$$\frac{\Phi(z)}{k_B T} = -\ln\left(N(I)\frac{dI}{dz}\right) + \text{const.}$$

How to determine I(z) ?

complicated scattering problem $\beta^{-1} < a$



- small penetration depth
- p-polarized illumination
- dielectric surfaces

$$I = I_0 \exp(-\beta z)$$

Prieve, Walz, Appl. Opt. ***32****, 1629(1993)*
Liu, Kaiser, Lange, Schweiger, Optics Comm. ***117****, 521 (1995)*
Helden, Eremina, Riefler, Hertlein, Bechinger, Eremin, Wriedt, Appl. Opt. ***45,*** *7299 (2006)*

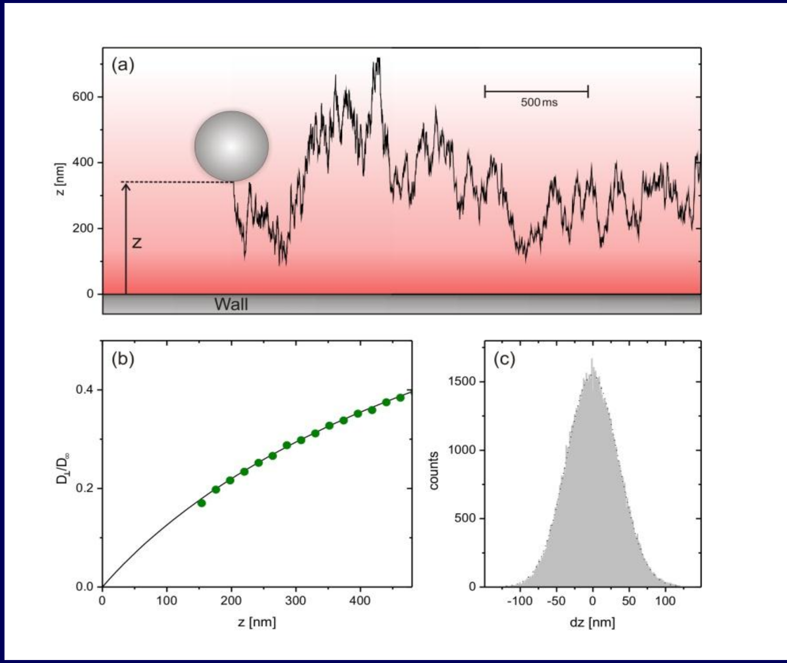
- non-homog. liquids (concentration profiles)
- highly reflecting surfaces

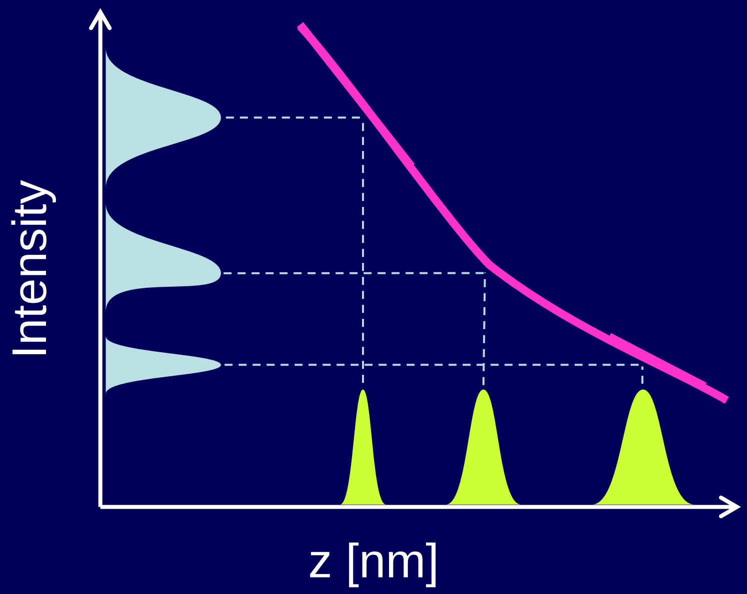
$$I(z) = ?$$

How to measure I(z)

$$p(z; z_0, \Delta t) \text{ gaussian for } \Delta t \to 0$$

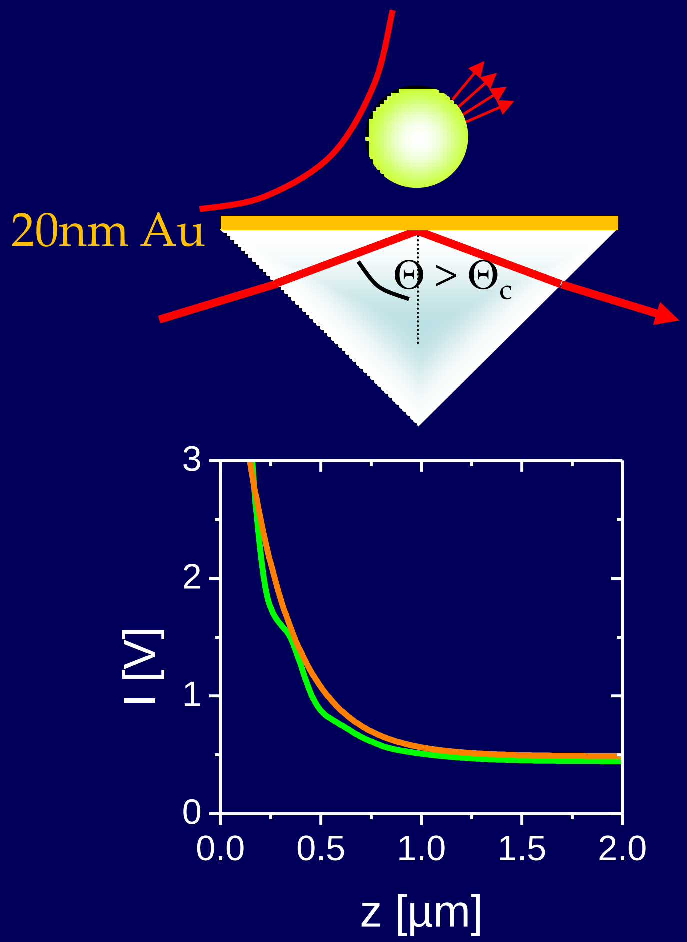
$$D_\perp(z) = \frac{1}{2dt}\left\langle \left[z(t+dt) - z(t)\right]^2 \middle| z(t) = z \right\rangle$$

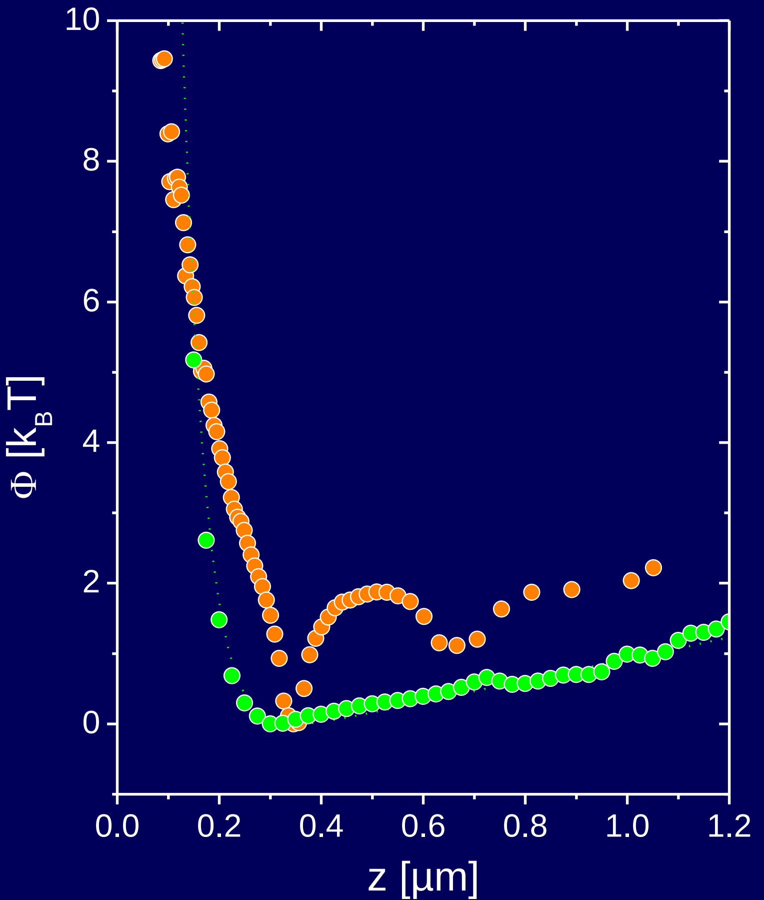




Volpe, Helden, Brettschneider, Wehr, Bechinger, *PRL* **104, 170602 (2010).**
Brettschneider, Volpe, Helden, Wehr, Bechinger. *Phys. Rev. E 83, 041113 (2011).*

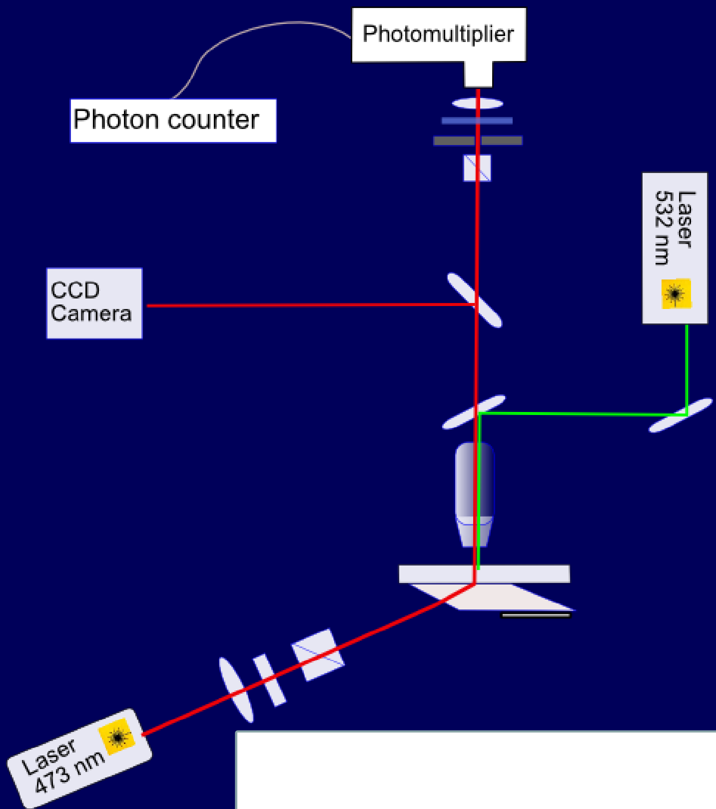
Example: TIRM on Au Surfaces

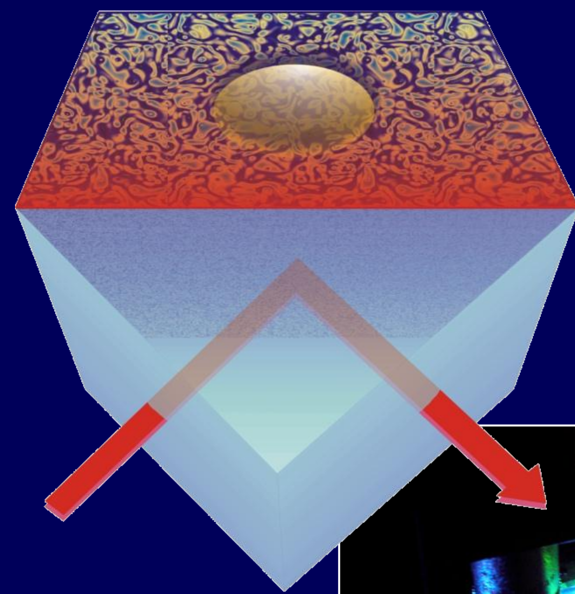


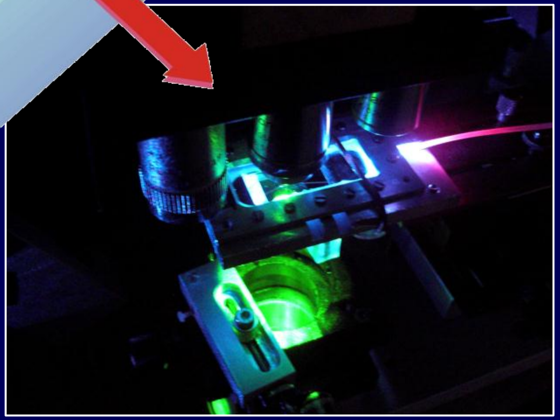


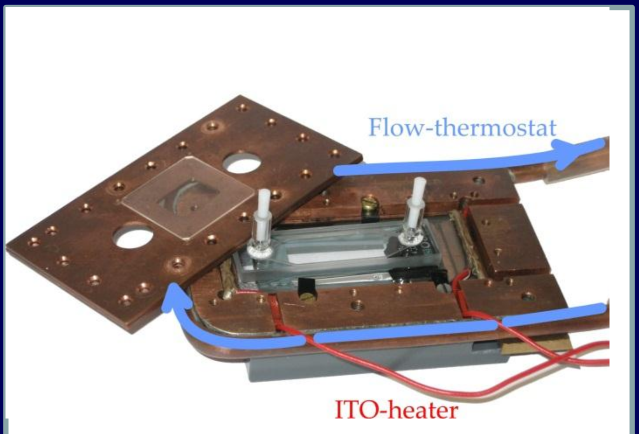
Volpe, Brettschneider, Helden, Bechinger, *Opt. Express* ***17*, 23975 (2009).**

Experimental Setup



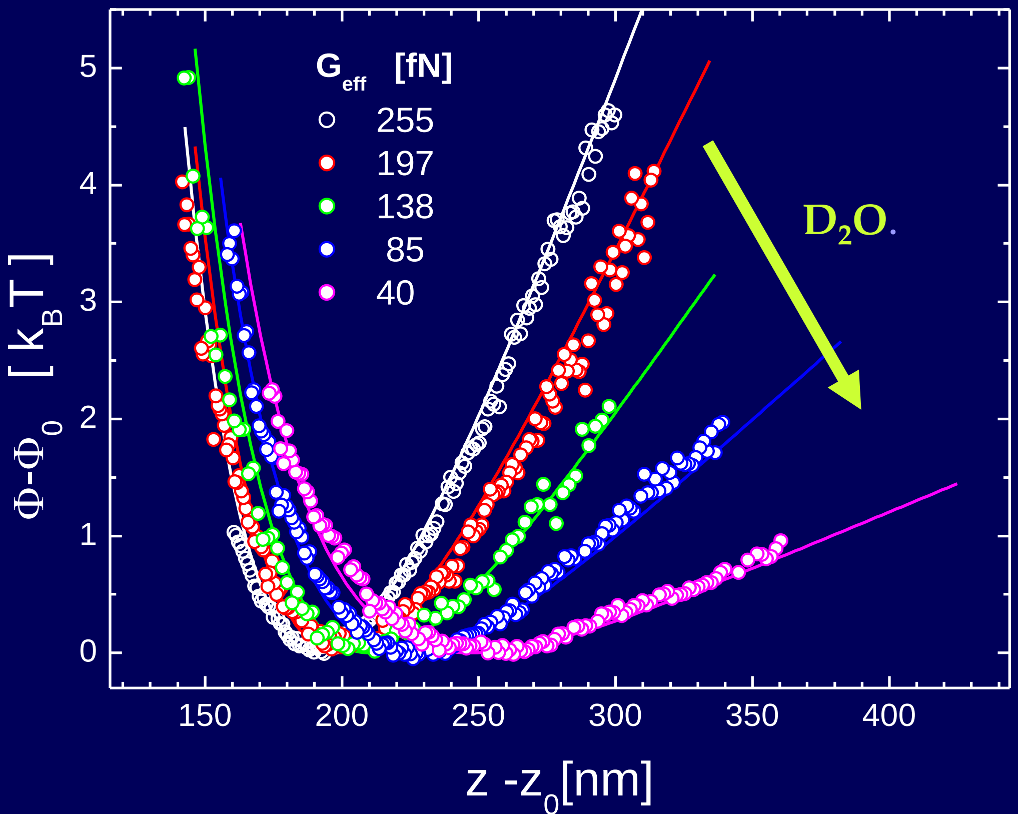






$$\Delta T = \pm 0.002°C$$

Sensitivity of TIRM



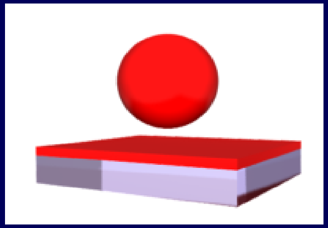
	ρ (g/cm³)
H_2O	1.0
PS	1.05
D_2O	1.1

resolution > 5 fN !

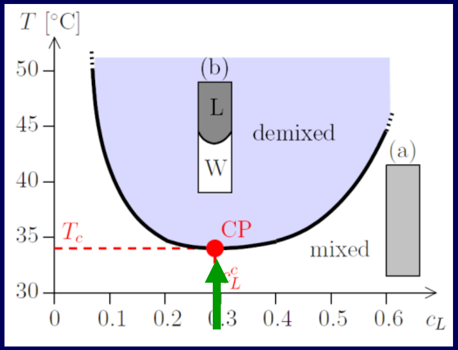
Rudhardt, Bechinger, Leiderer, J. Phys: Cond. Matt. **11, 10073 (1999)**

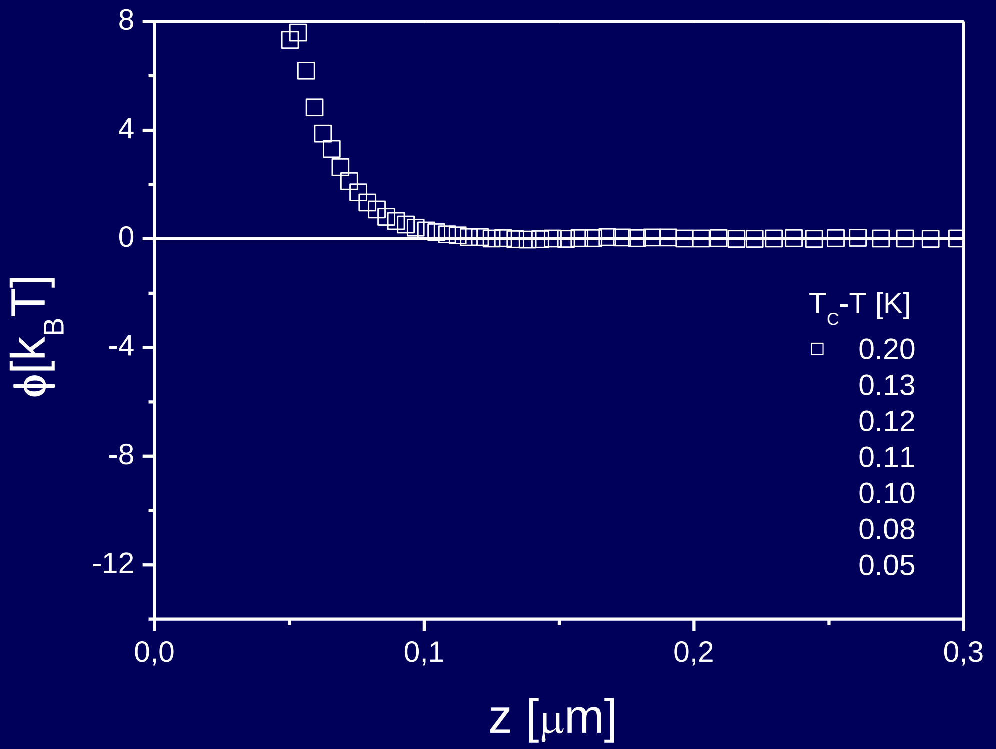
Critical Casimir Forces: ++

++: particle & wall: preferential adsorption of lutidine



PS 3.7μm (x-linked, weakly charged)
HMDS treated silica wall (hydrophobic)





$$\Phi(z) = A\exp(-\kappa z)$$

$$\kappa^{-1} \approx 15\text{nm}$$

Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature ***451****, 172 (2008)*

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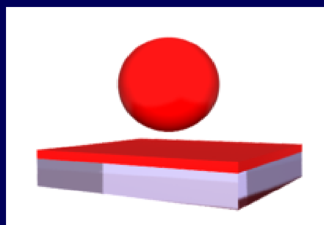

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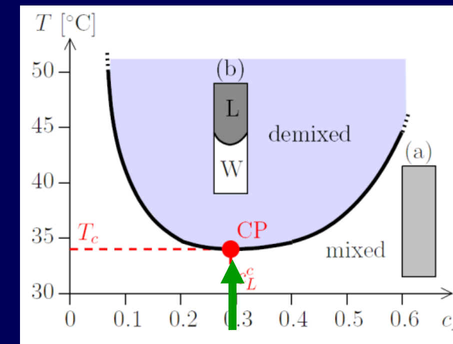

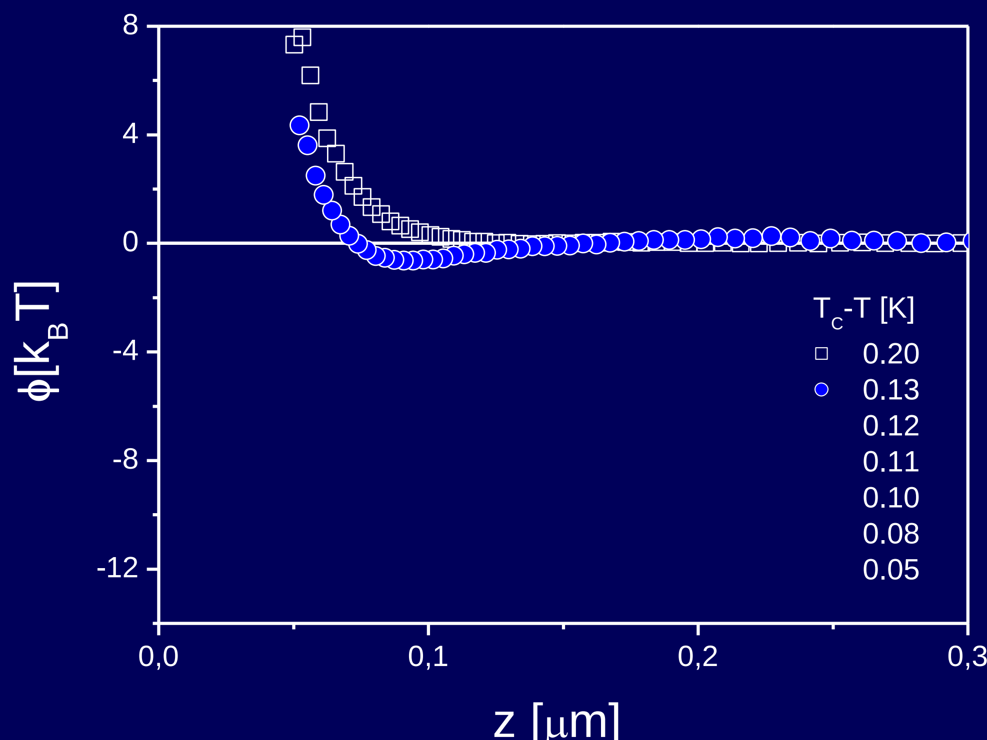

Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature ***451****, 172 (2008)*

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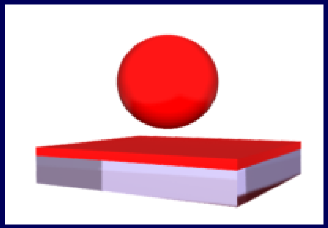

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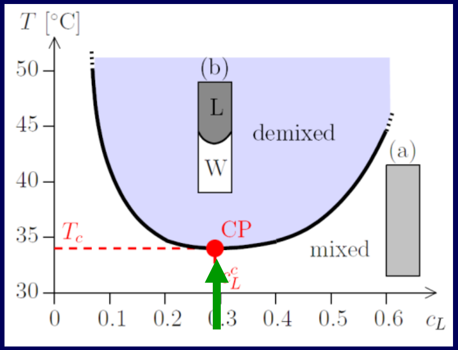

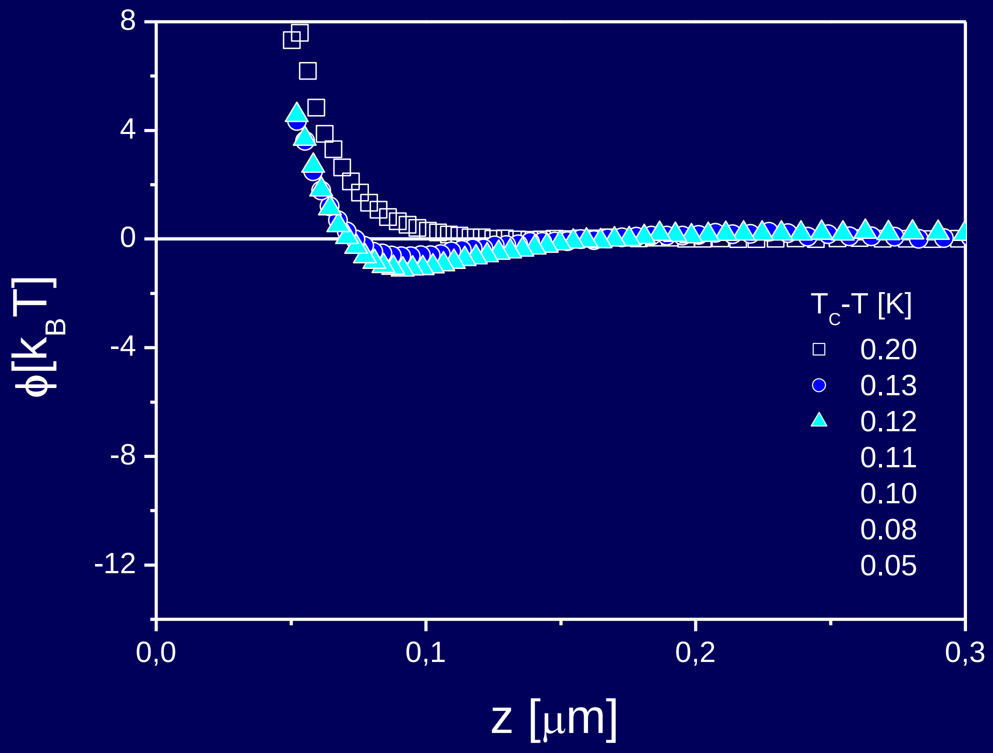

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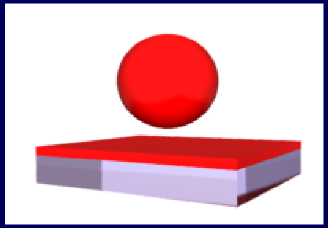

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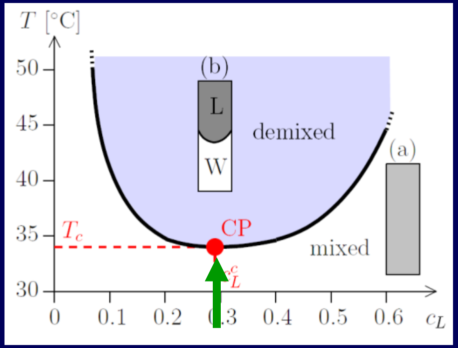

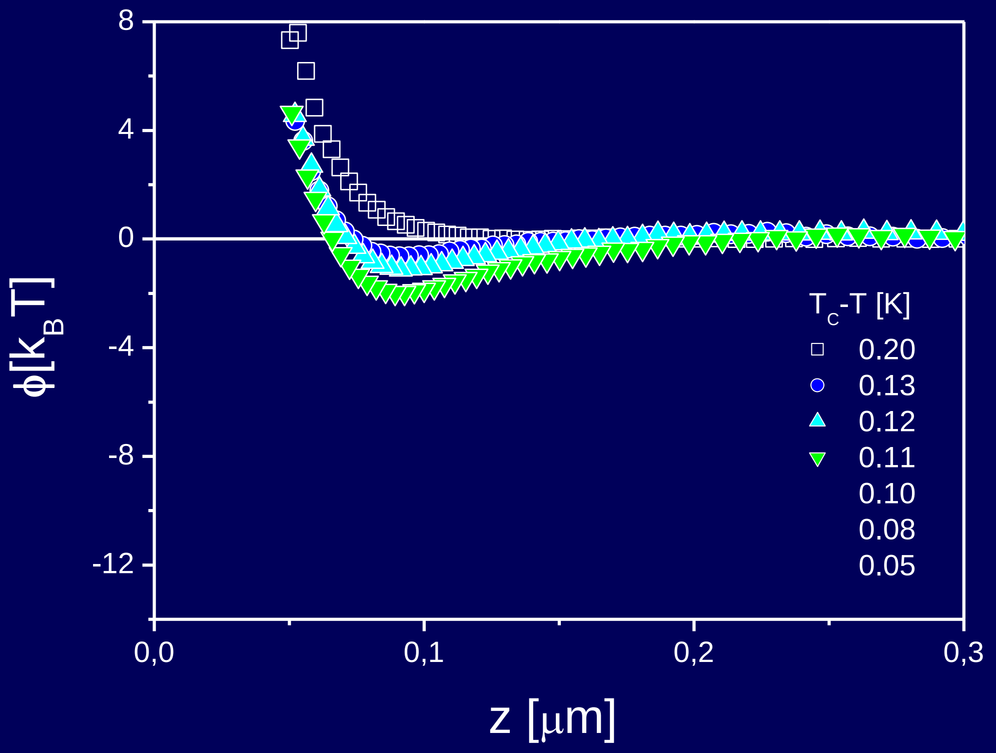

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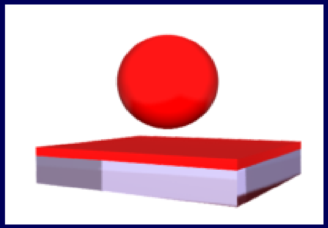

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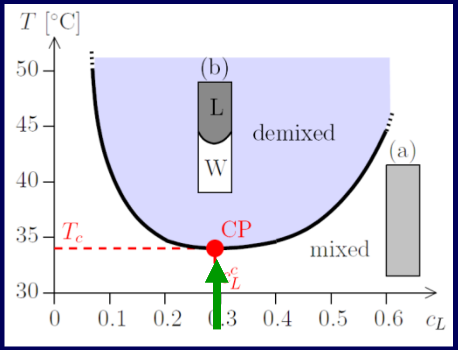

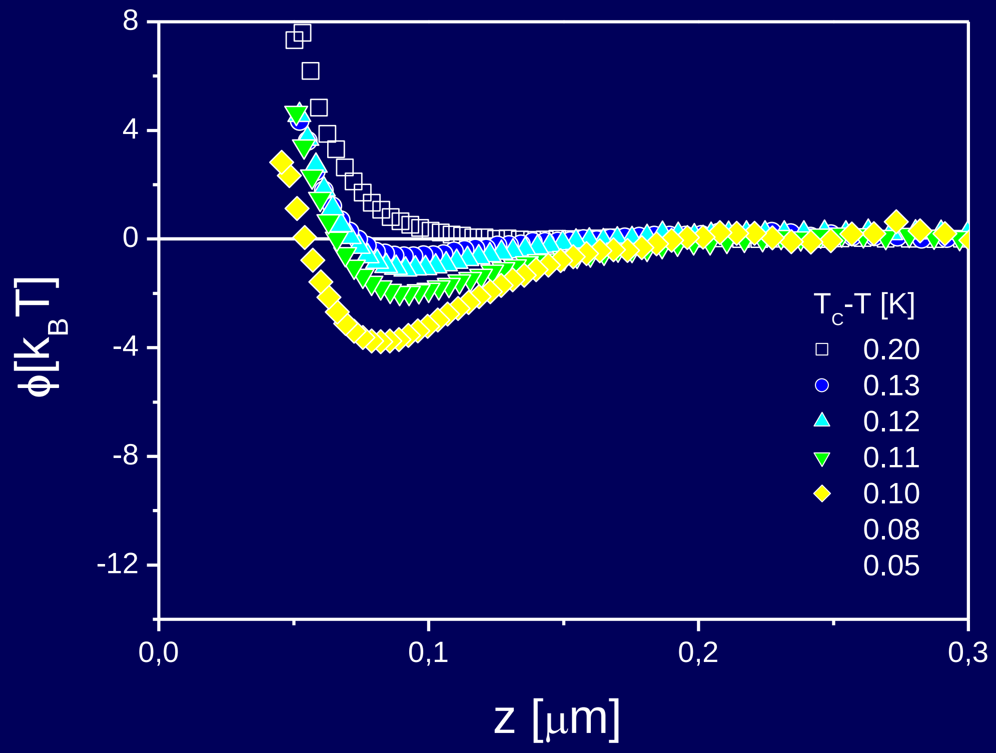

*Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature **451**, 172 (2008)*

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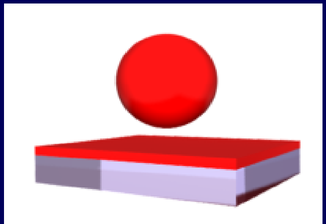

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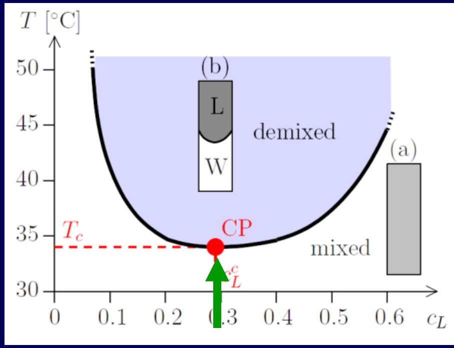
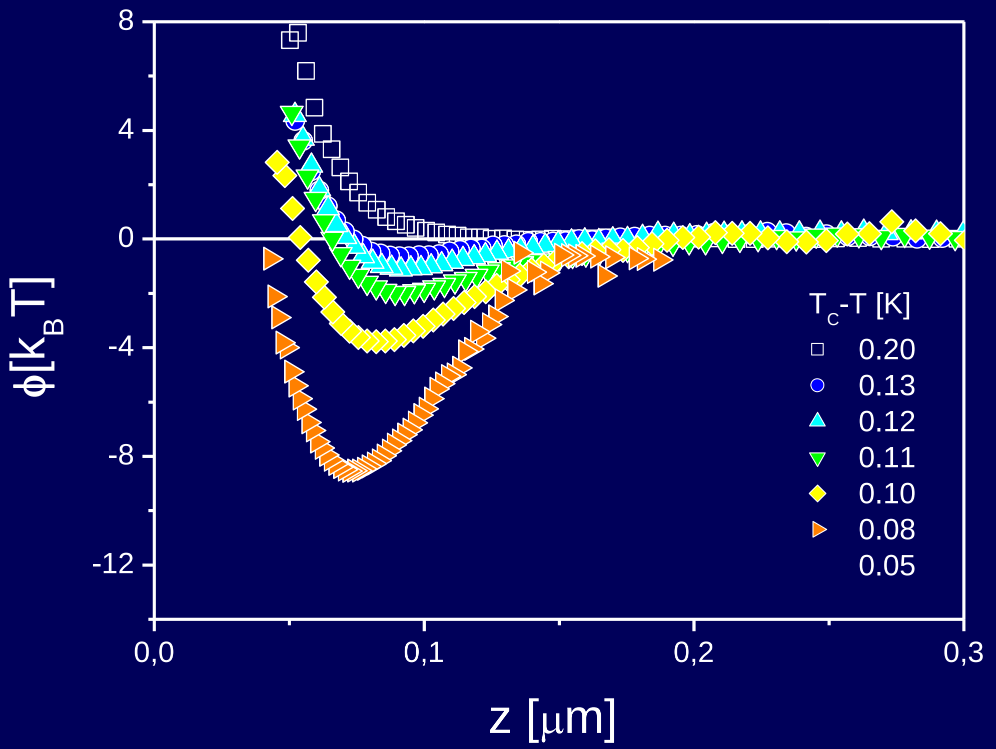
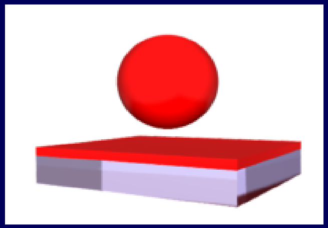




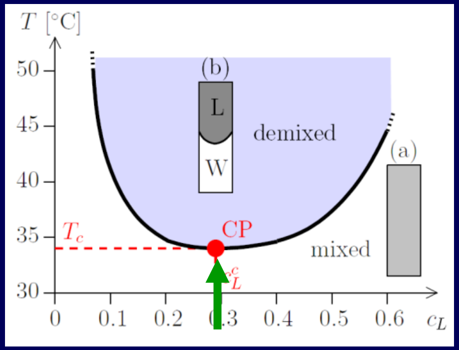
Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature ***451****, 172 (2008)*

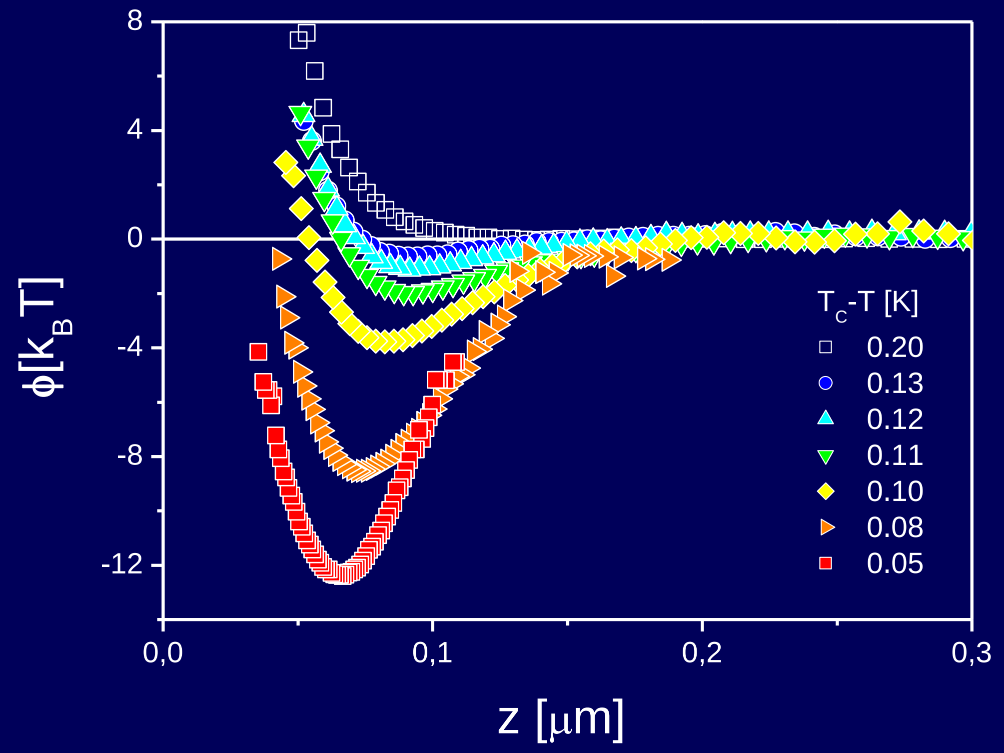
Critical Casimir Forces: ++

++: particle & wall: preferential adsorption of lutidine



PS 3.7μm (x-linked, weakly charged)
HMDS treated silica wall (hydrophobic)



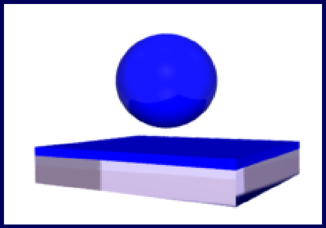


similar results for
$0.25 < c_L < 0.32$

*Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature **451**, 172 (2008)*

Critical Casimir Forces: --

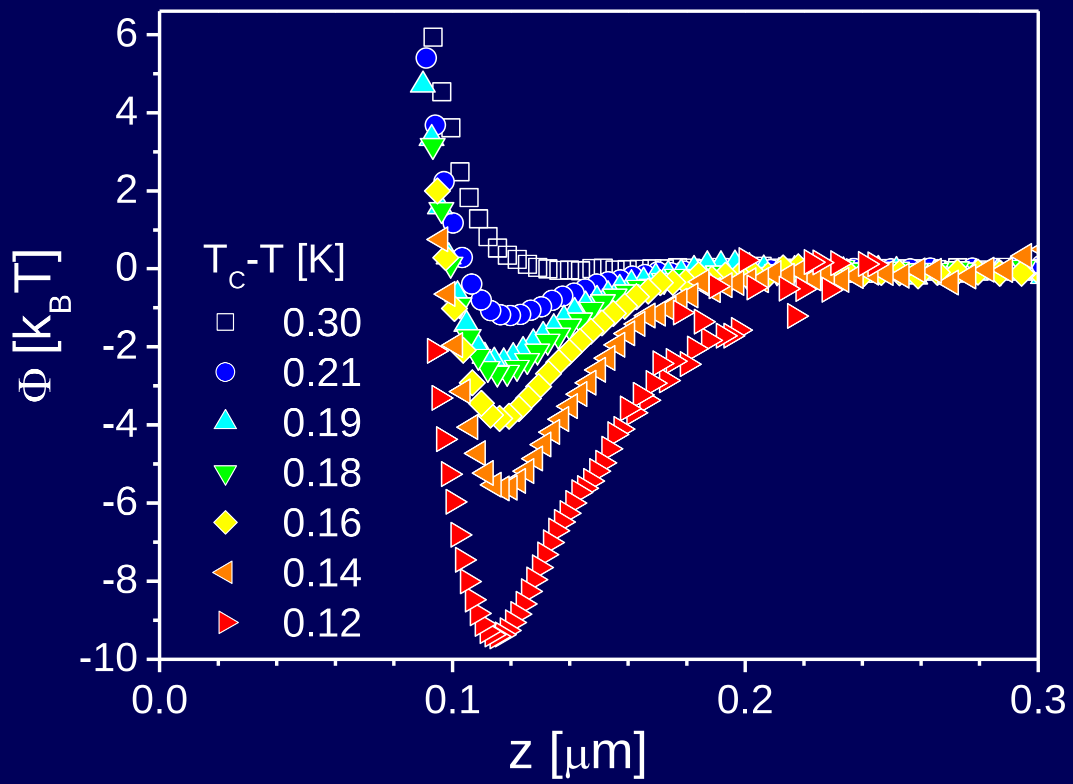
- -: particle & wall: preferential adsorption of water



sulfate-terminated PS 2.4μm (10.1μC/cm²)
hydrophilic silica wall

σ [μC/cm²]	phase
5.70	W
3.85	W
0.38	L

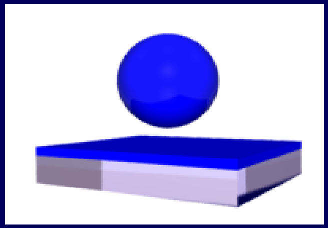
Gallagher et al. Phys. Rev. A ***46,*** *7750 (1992)*



$$\frac{\Phi}{k_B T} = \frac{R}{z}\,\vartheta\left(\frac{z}{\xi}\right)$$

Critical Casimir Forces: --

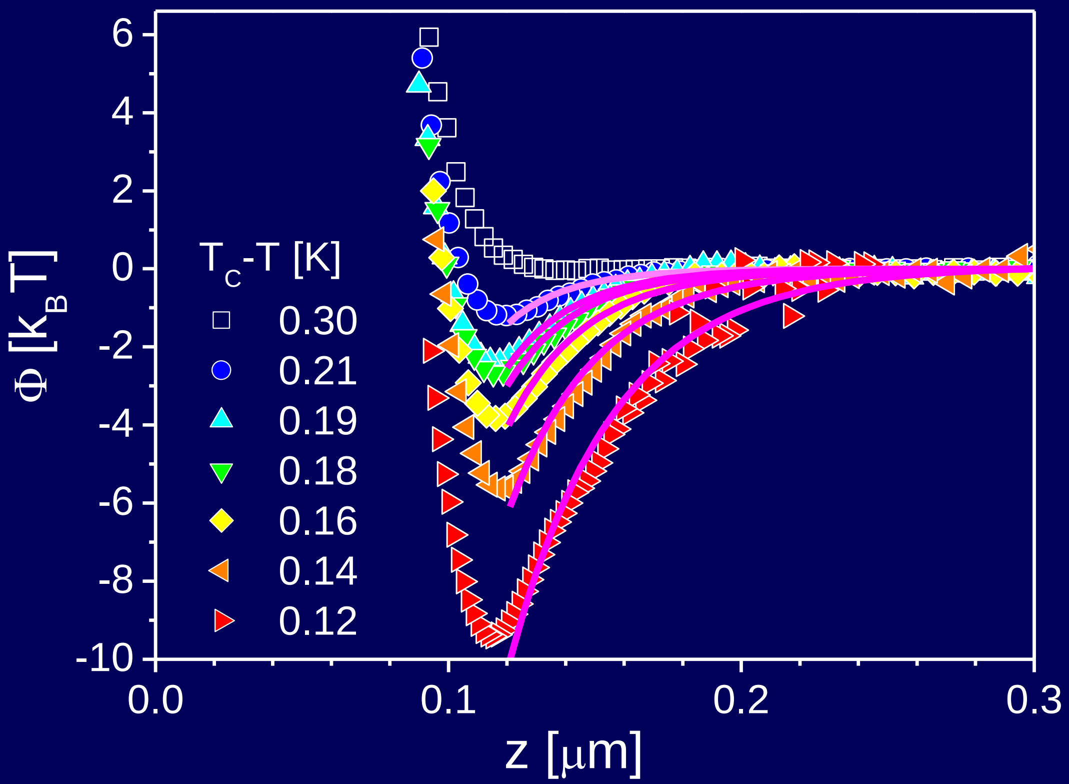
- -: particle & wall: preferential adsorption of water



sulfate-terminated PS 2.4μm (10.1μC/cm²)
hydrophilic silica wall

σ [μC/cm²]	phase
5.70	W
3.85	W
0.38	L

*Gallagher et al. Phys. Rev. A **46,** 7750 (1992)*

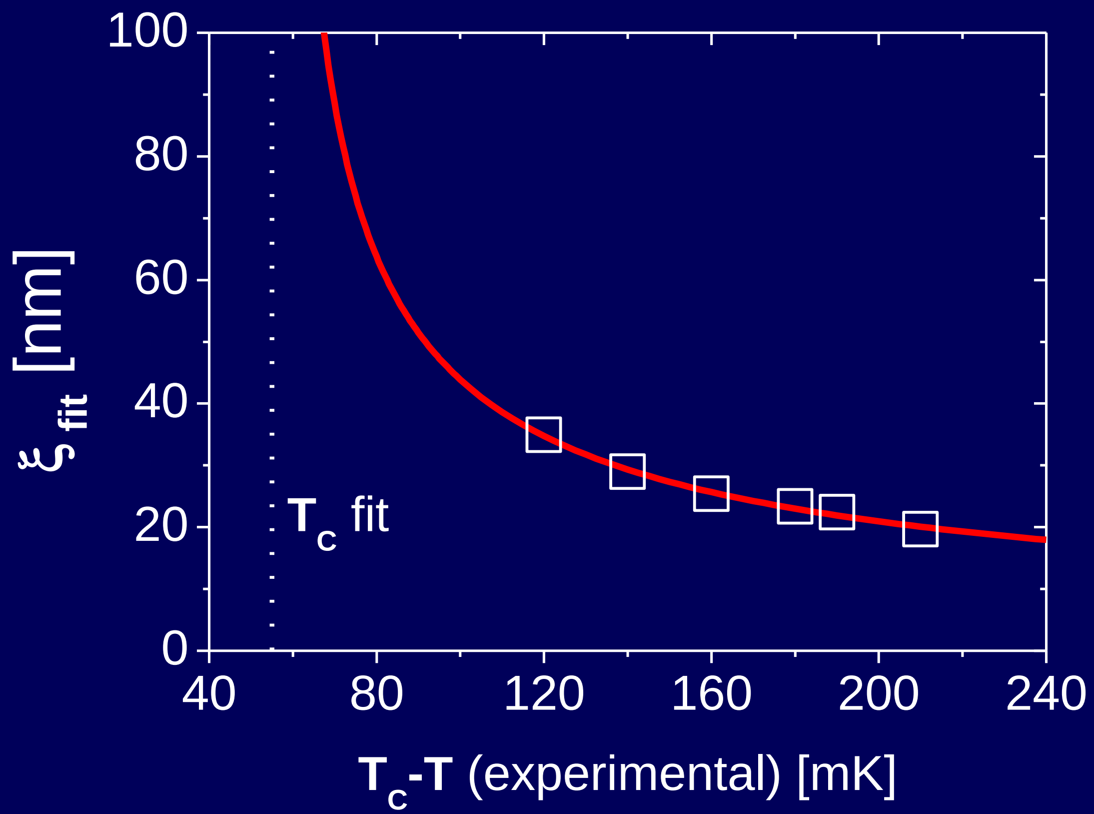


$$\frac{\Phi}{k_B T} = \frac{R}{z}\,\vartheta\left(\frac{z}{\xi}\right)$$

*Hertlein, Helden, Gambassi, Dietrich & Bechinger Nature **451**, 172 (2008)*

Correlation Length

$$\xi(T) = \xi_0 \left| \frac{T}{T_c} - 1 \right|^{-0.63}$$



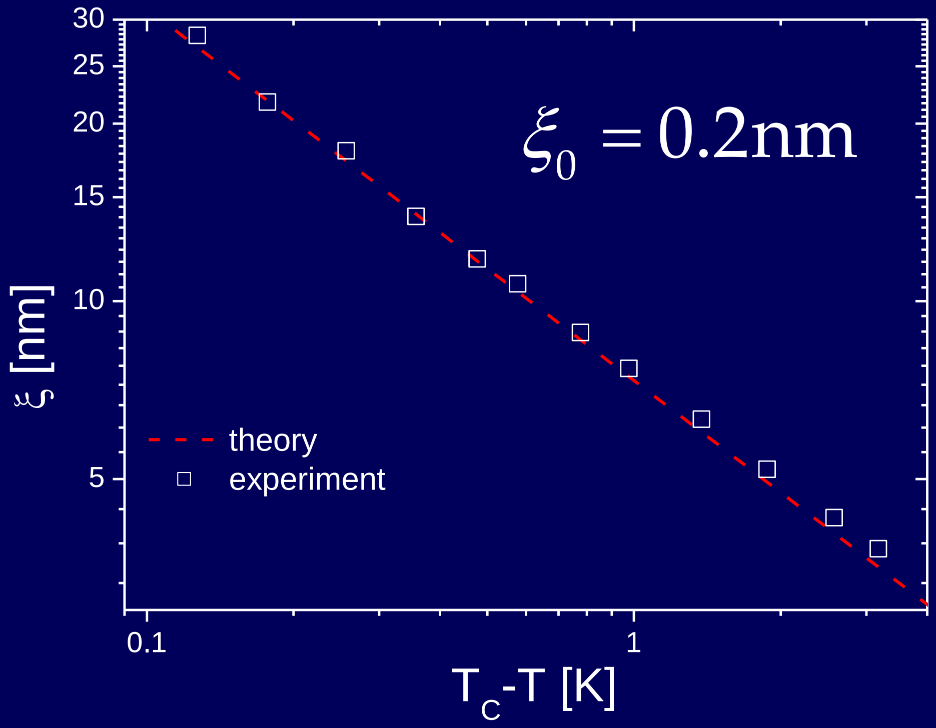
fit:

$\xi_0 = 0.18 \pm 0.02\text{nm}$

Gambassi, *Maciolek, Hertlein, Nellen, Helden, Bechinger, Dietrich Phys. Rev. E* ***80, 061143 (2009).***

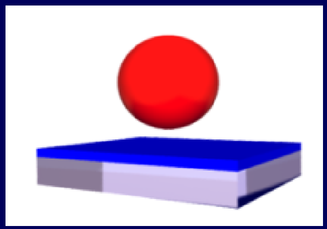
SAXS - Measurements

$$\xi(T) = \xi_0 \left| \frac{T}{T_c} - 1 \right|^{-0.63}$$



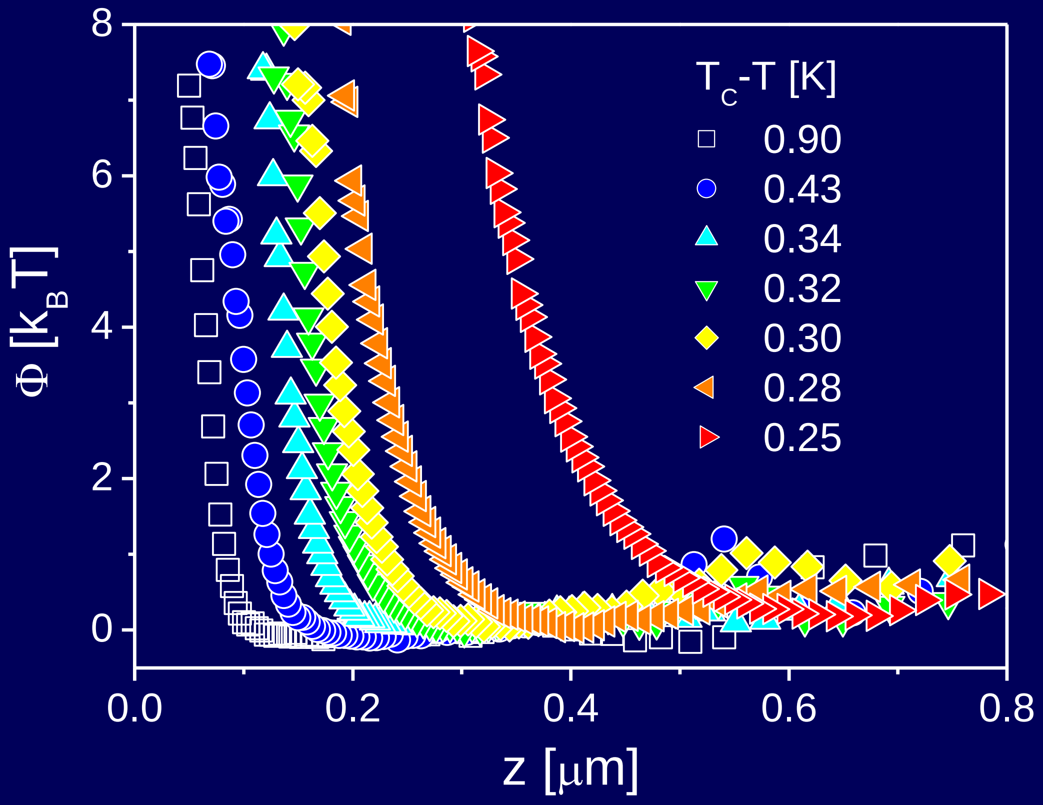
Nellen, Helden, Dietrich, Chodankar, Nygard, v.d. Veen, Bechinger, Soft Matter 7, 5360 (2011)

Critical Casimir Forces: +-

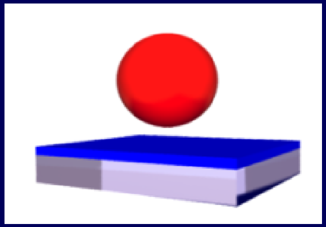


asymmetric boundary conditions

→ repulsive critical Casimir force

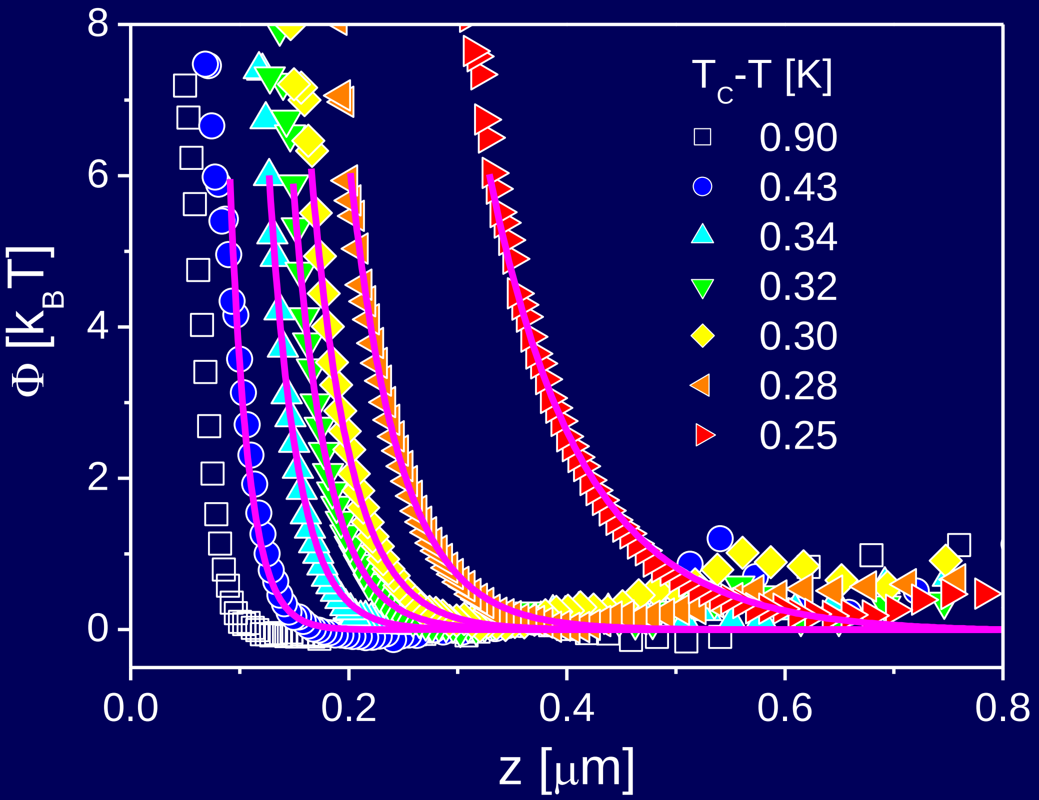


Critical Casimir Forces: +-



asymmetric boundary conditions

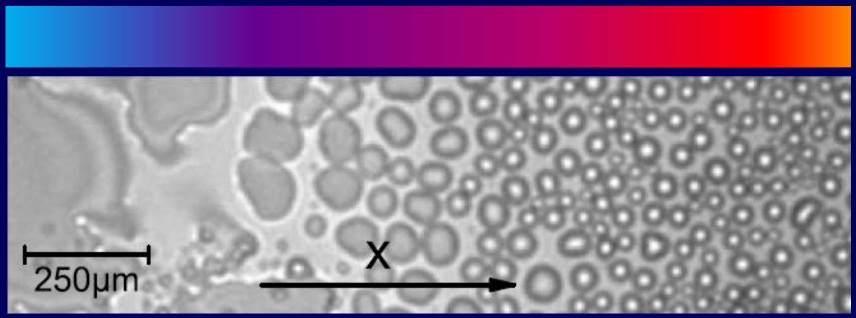
→ repulsive critical Casimir force



Dependence on BCs

Gradient in BC

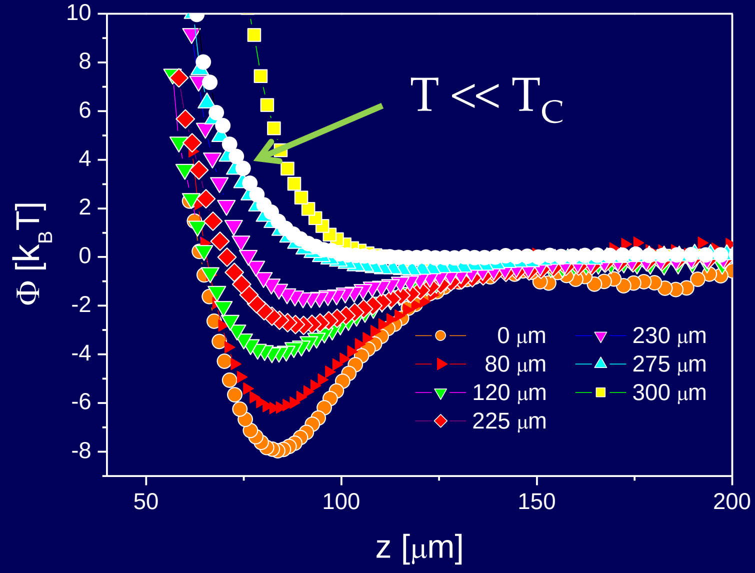
hydrophilic

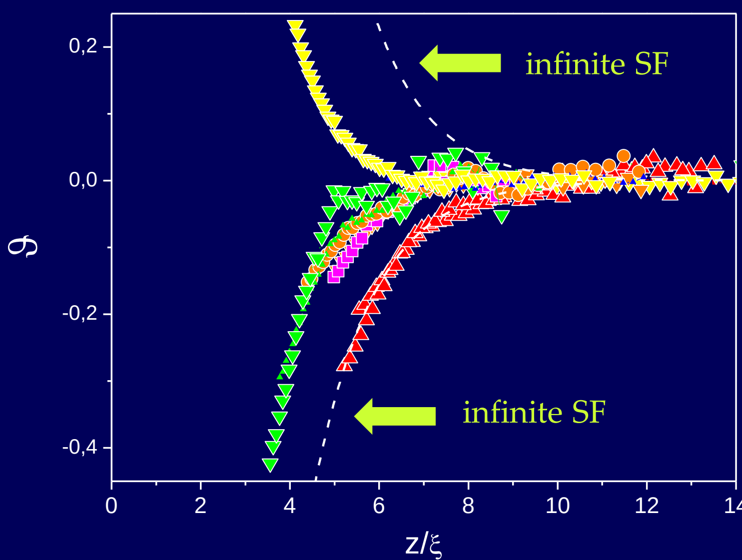


hydrophobic

$$\frac{\Phi}{k_B T} = \frac{R}{z}\,\vartheta\!\left(\frac{z}{\xi}\right)$$

hydrophilic particle $T - T_C = 0.22K$

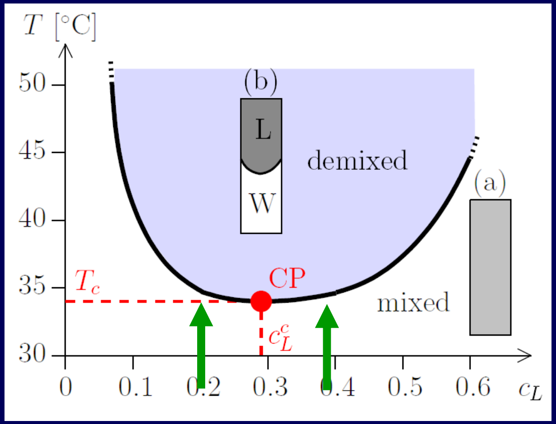


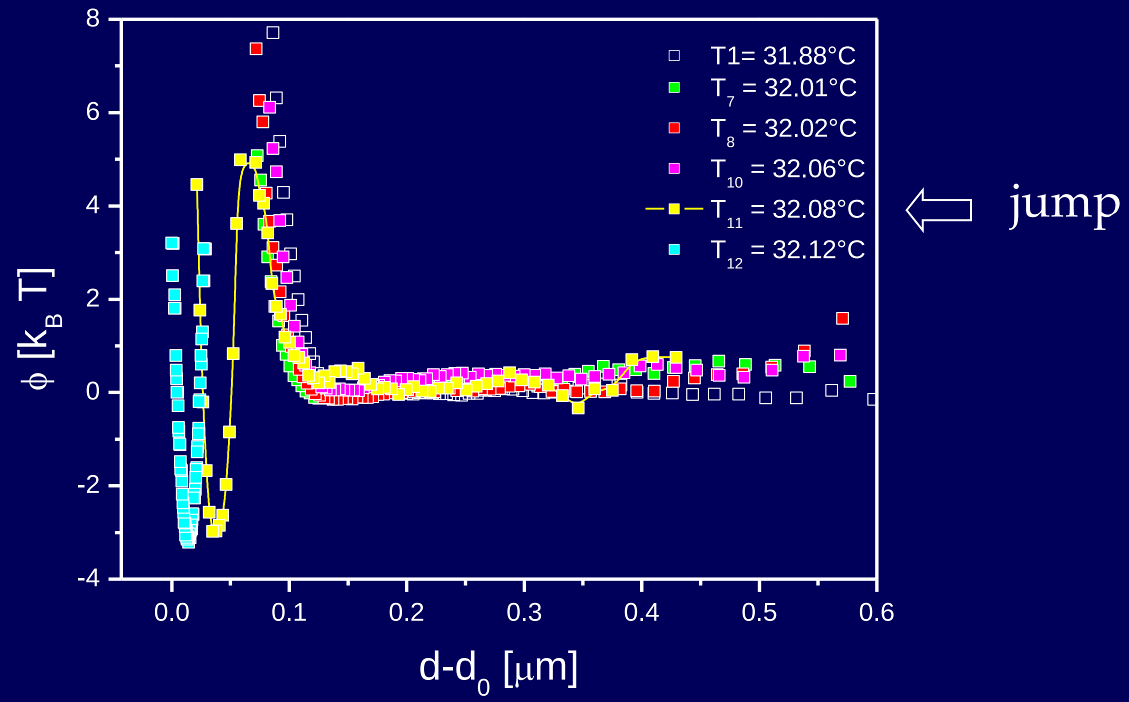


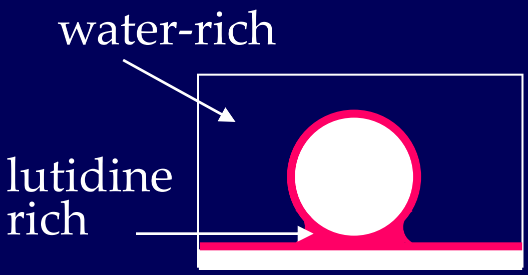
*Nellen, Helden, Bechinger, EPL **88**, 26001 (2009)*

Continuous variation of critical Casimir forces by BC

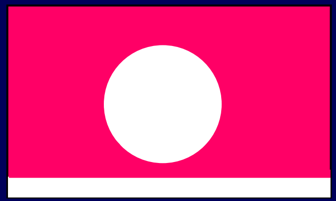
Off-Critical Composition: ++







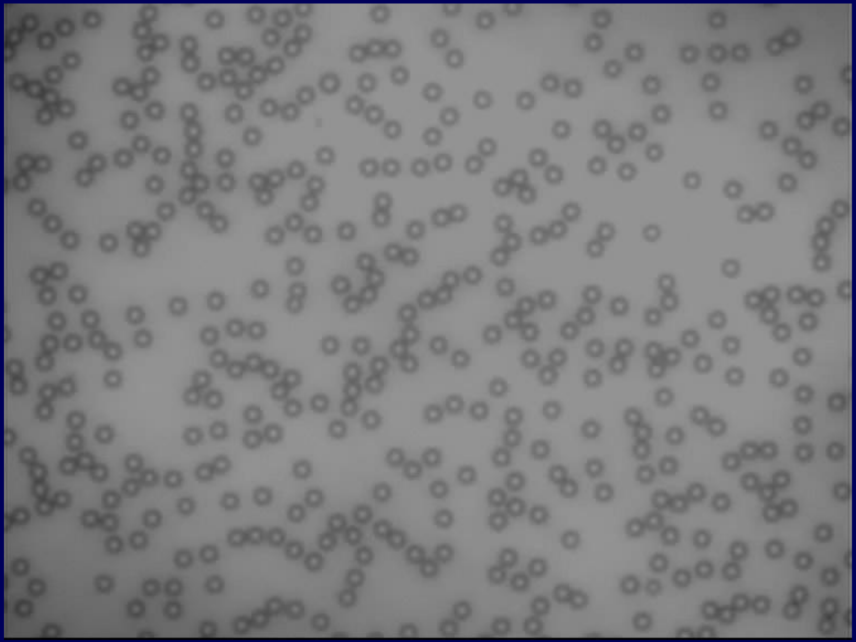
reduction of surface energy by
BRIDGE FORMATION



No bridge formation for $c_L > c_C$

Critical Casimir Forces between colloidal particles

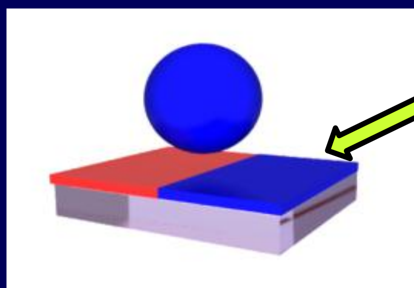
Substrate: hydrophilic
Particles: 2.4 μm hydrophobic (lutidine)



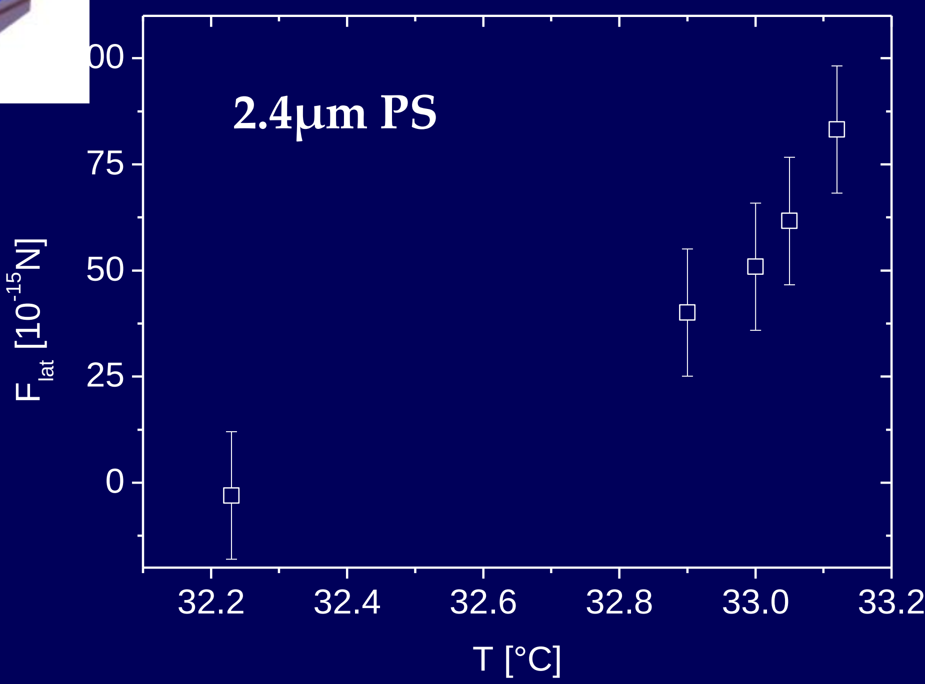
Temperature dependent pair potential

Lateral Critical Casimir Forces

1. Chemical Step

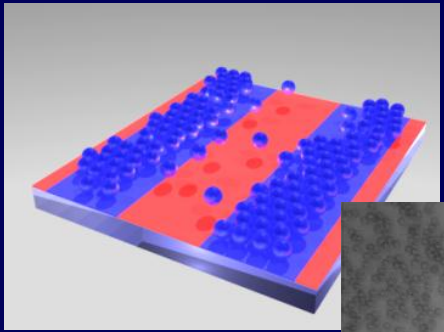


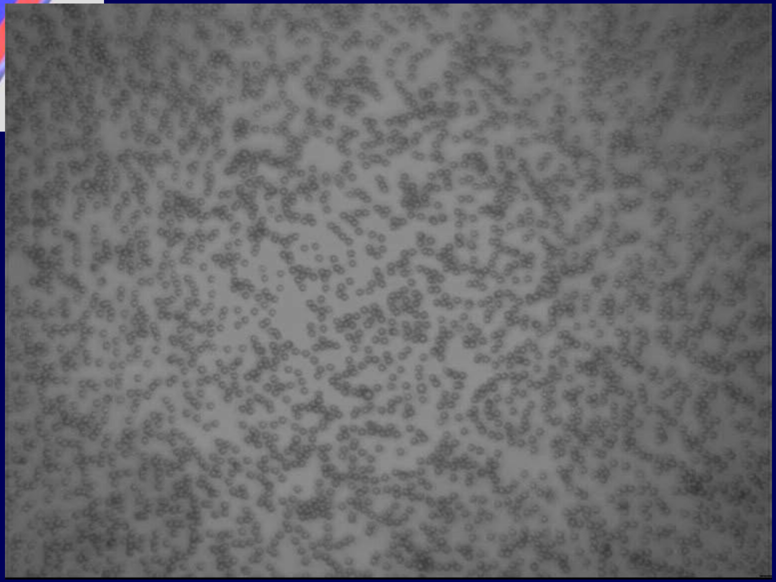
1 monolayer HMDS, FIB



Lateral Critical Casimir Forces

2. Periodic Lines

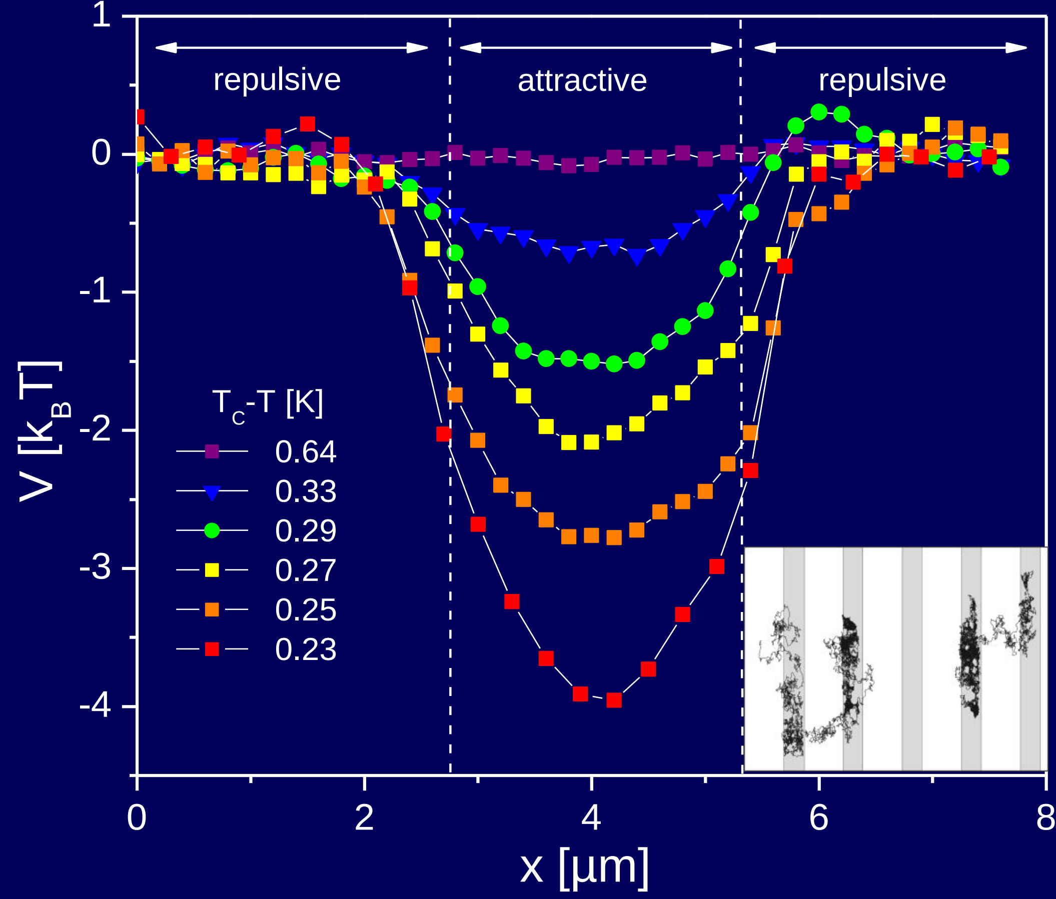




(x 8)

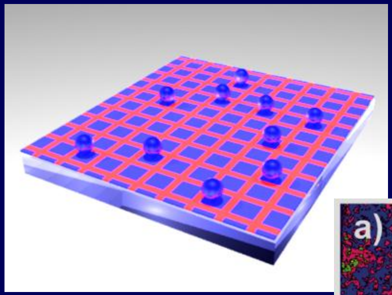
Soyka, Zvyagolskaya, Hertlein, Helden, Bechinger, PRL ***101****, 208301 (2008) .*

Critical Casimir Traps

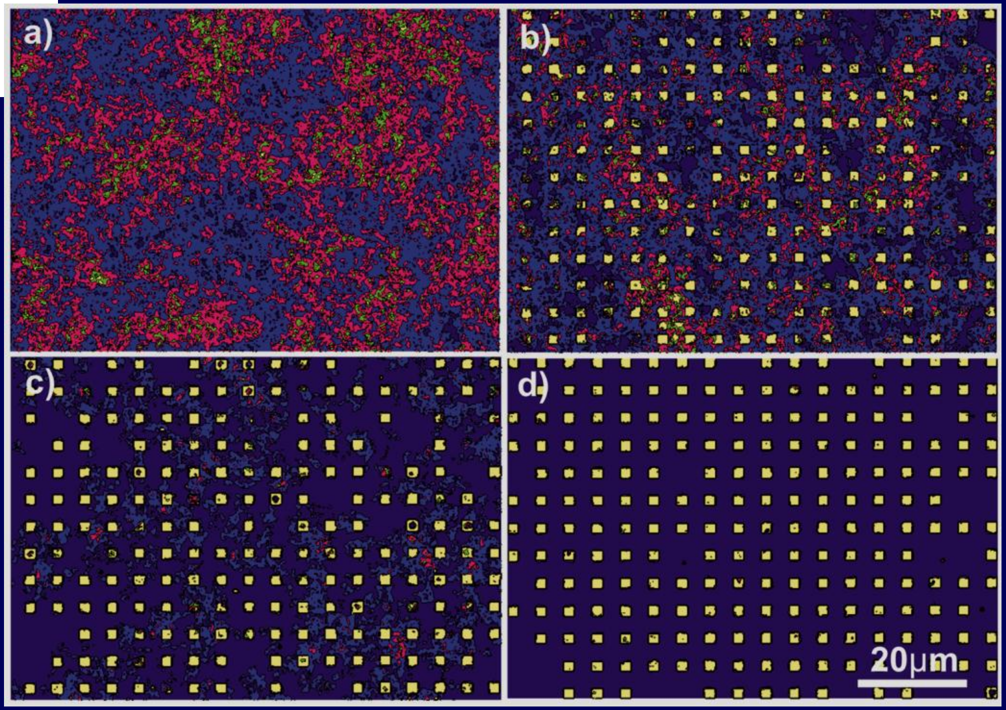


Soyka, Zvyagolskaya, Hertlein, Helden, Bechinger, PRL ***101****, 208301 (2008) .*

3. Squares



31.90 °C 32.37 °C



32.39 °C 32.48 °C

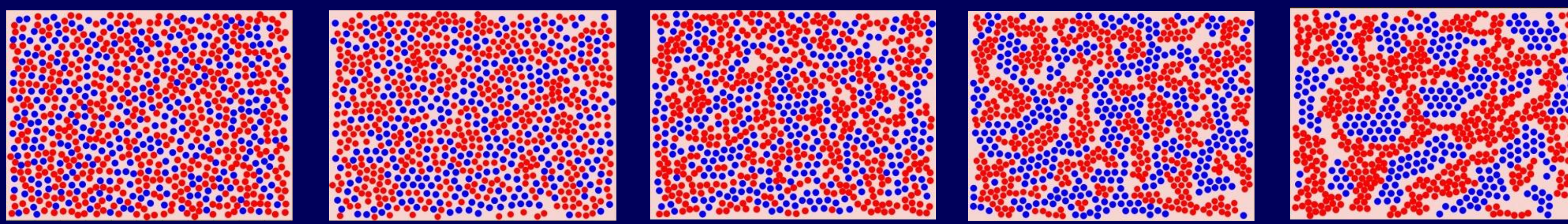
Soyka, Zvyagolskaya, Hertlein, Helden, Bechinger, PRL ***101****, 208301 (2008) .*

Demixing of binary systems

A (+)

B (-)

$\rho\sigma^2 = (\rho_A + \rho_B)\sigma^2 = 0.65$

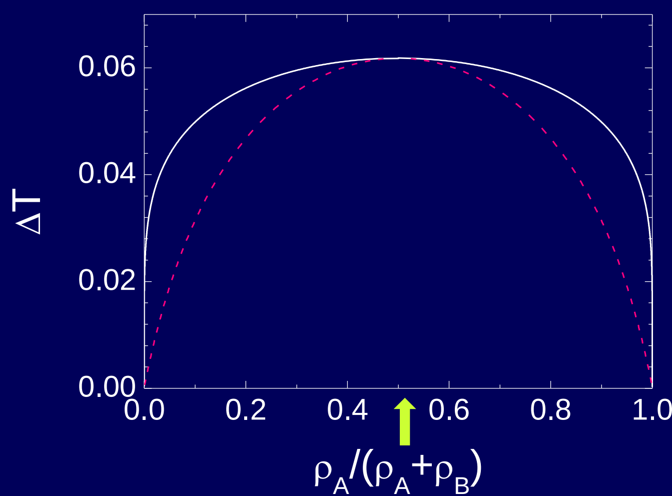


$\Delta T = 1$ K | 0.40 K | 0.08 K | 0.02 K | 0.01 K

DFT calculations

- HS

- attr./rep. crit. Casimir



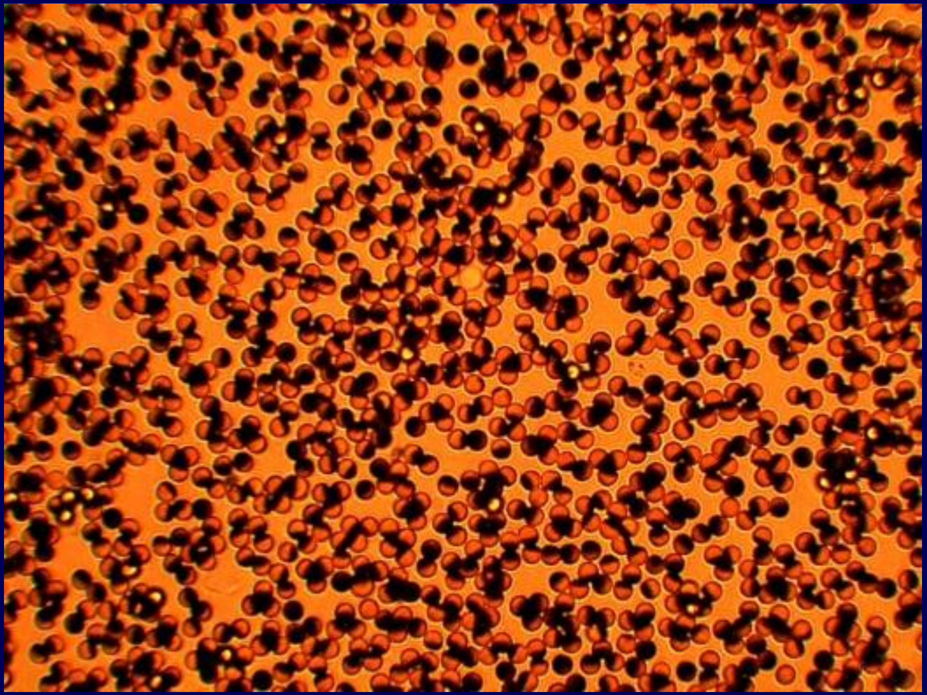
$\rho\sigma^2 = 0.65$

Andrew Archer
Loughborough, UK

critical point in solvent $\rightarrow$ critical point in colloidal mixture

Zvyagolskaya, Archer, Bechinger (submitted)

Particles with non-uniform BC



Summary

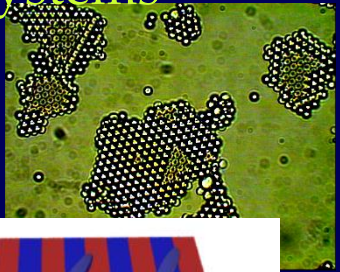
Confinement of binary liquids close to critical point lead to critical Casimir forces

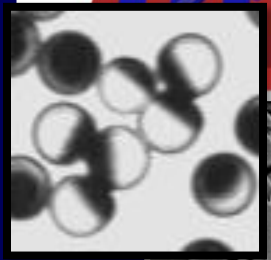
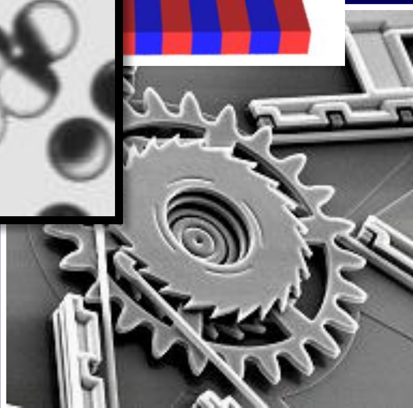
- strong temperature-dependence
- dependence on boundary conditions (single ML determines BC)
- influence of salt on critical Casimir forces

→ versatile interaction mechanism for hard and soft matter systems

Outlook

- *many body interactions, novel phases (photonic crystals)*
- *self-assembly/positional & orientational order*
- *directed bonds with patchy particles (dipolar liquids)*
- *dynamical aspects: critical slowing down*
- *anti-stiction coatings for MEMS by simple coating process*



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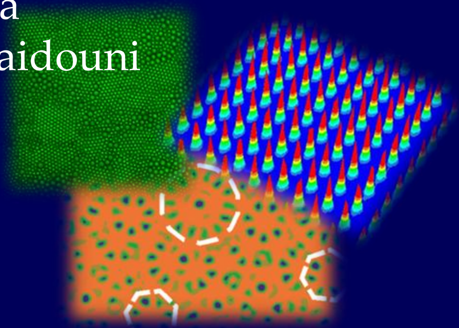
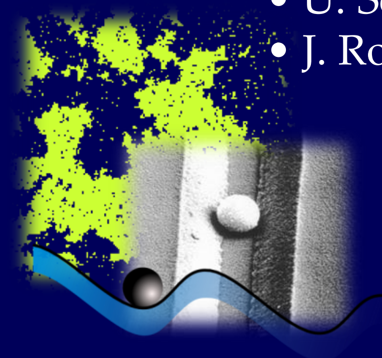
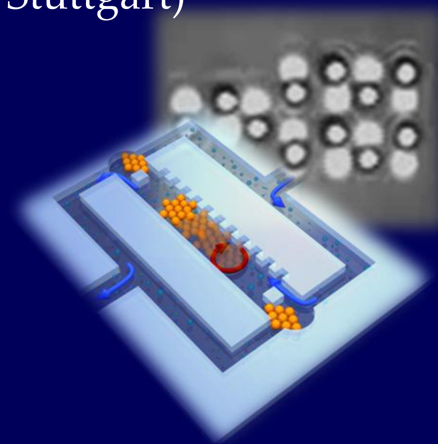


Material Science



Statistical Physics



Applied Science

DFG

MAX-PLANCK-GESELLSCHAFT

comploids
PHYSICS OF COMPLEX COLLOIDS