

The *universal* force of critical fluctuations: Casimir, wetting, colloids and all that...

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Trieste (Italy)**



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February 3, 2012

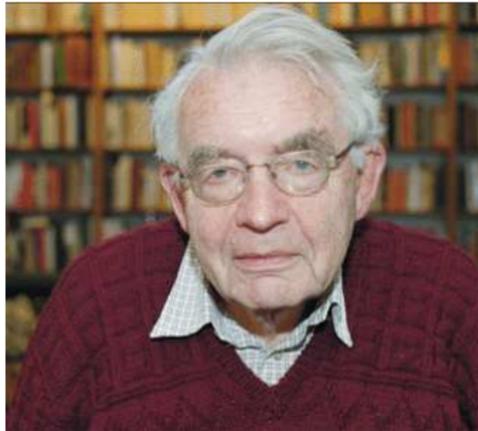
QED \longleftrightarrow Stat Phys

- » Casimir in quantum electrodynamics (QED)
- » Casimir in stat. phys. / critical phenomena *leadsto* *universality*
- » Indirect & *direct* measurement of *critical* Casimir forces
- » Applications in soft matter

H. B. G. Casimir (1909 – 2000)

“On the attraction between two perfectly conducting plates”

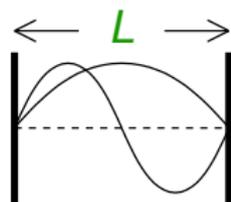
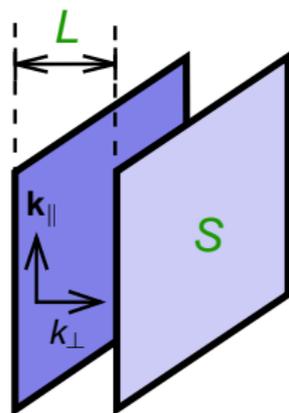
Proc. Kon. Nederland. Akad. Wetensch. **B51**, 793 (1948)



~> **Casimir effect**

Casimir in QED

Plates $\Rightarrow \mathbf{E}_{\parallel}, B_{\perp} = 0$, *Boundary conditions!*



\rightsquigarrow allowed modes:

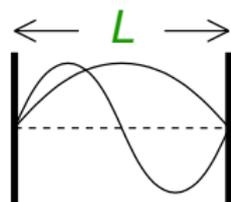
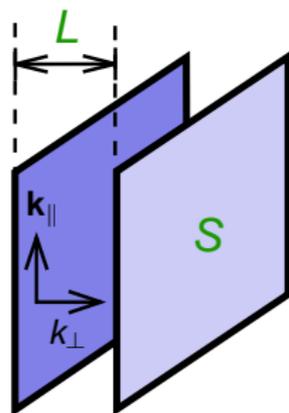
$$k_{\perp} = \frac{\pi n}{L}, \quad n = 1, 2, \dots$$

QED:
$$\mathcal{E} = \sum_{\text{modes}} \frac{1}{2} \hbar c |\mathbf{k}|_{\text{modes}}$$

c = speed of light

Casimir in QED

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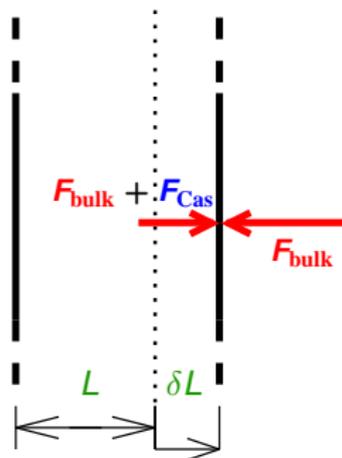
c = speed of light

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_{\text{bulk}} + \mathcal{E}_{\text{surf}}^{(L+R)} + \mathcal{S} \frac{\hbar c}{L^3} \left[-\frac{\pi^2}{1440} + \mathcal{O}((\kappa L)^{-2}) \right] \\ &\sim \mathcal{S} L^1 \quad \sim \mathcal{S} L^0 \quad \mathcal{E}_{\text{Cas}} \sim \mathcal{S} L^{-3} \end{aligned}$$

Casimir in QED: “Measurement”



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$$\text{force} \equiv -\frac{\delta\mathcal{E}}{\delta L} = F_{\text{bulk}} + F_{\text{Cas}}$$

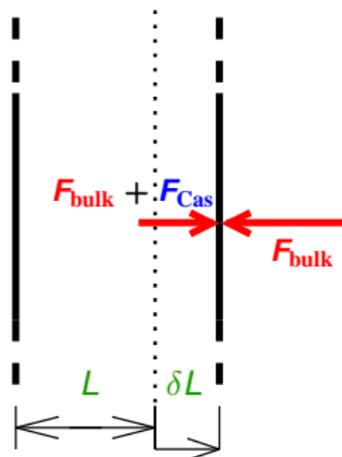
$$\frac{F_{\text{Cas}}}{S} = -\frac{\pi^2}{480} \frac{\hbar c}{L^4} \quad \text{for } L \gg \kappa^{-1}$$

Universal!

Q: $\kappa^{-1} = ??$ $c\kappa \simeq \omega_p \simeq 3 \cdot 10^{15} \text{Hz (Cu)}$

$$\rightsquigarrow \kappa^{-1} \simeq 0.3 \mu\text{m}$$

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Exp: Sparnaay (1958)

Lamoreaux PRL **78**, 5 (1997)

Bressi *et al.* PRL **88**, 041804 (2002)

$$0.5 \mu\text{m} \lesssim L \lesssim 6 \mu\text{m}$$

Revs.: Lamoreaux, Physics Today, Feb 2007
Ball, Nature **447**, 772 (2007)

M. E. Fisher and P.-G. de Gennes

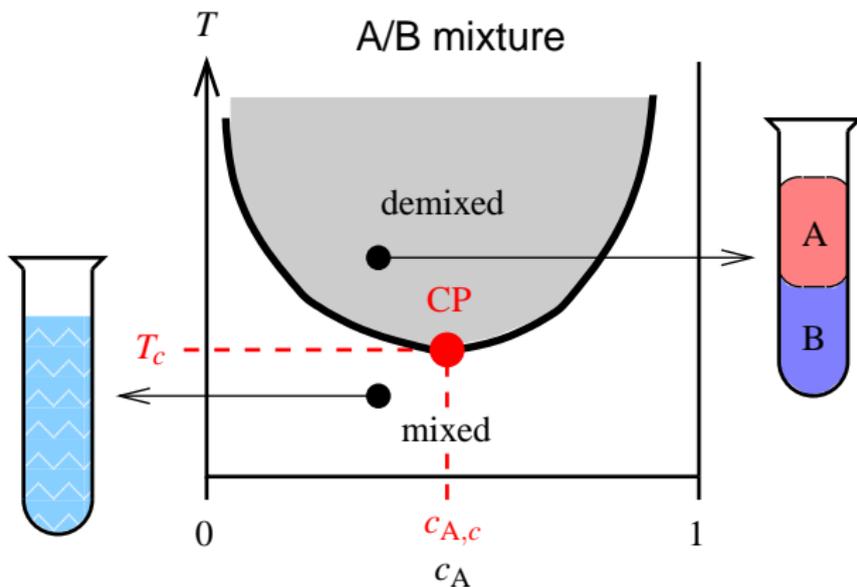
“Phenomena at the walls in a critical binary mixture”

C. R. Acad. Sc. Paris **B287**, 207 (1978)

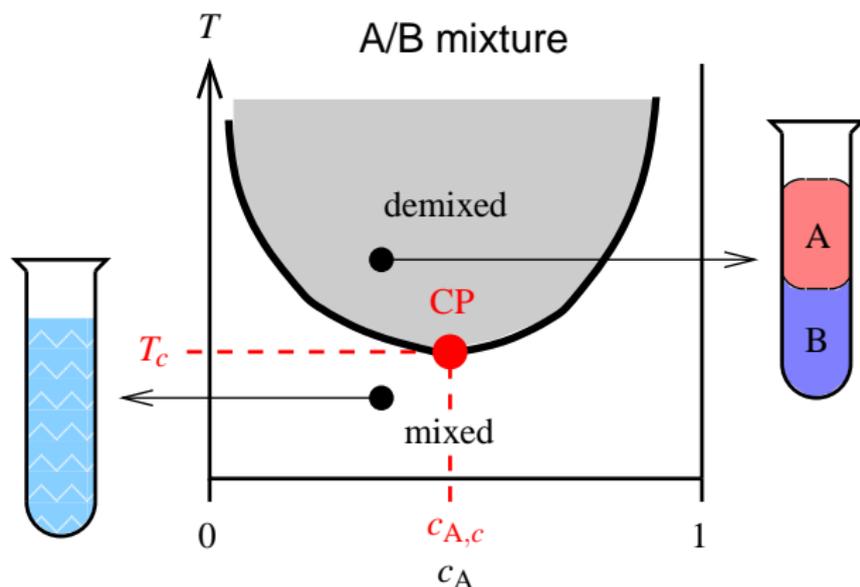


↪ **Casimir-like effect in Stat Phys**

Binary mixtures & Critical points (reminder)



Binary mixtures & Critical points (reminder)



Order param. $\phi(\mathbf{x}) \equiv c_A(\mathbf{x}) - c_{A,c}$: $\langle \phi(\mathbf{x})\phi(\mathbf{y}) \rangle \sim e^{-|\mathbf{x}-\mathbf{y}|/\xi}$

CP: $\xi \nearrow \infty$ for $(T, c_A) \rightarrow (T_c, c_{A,c})$

QED

fluctuating quant.:

E, B

excitation:

Quantum
 $\hbar\mathbf{c} (T = 0)$

range of fluct.:

∞



Confinement

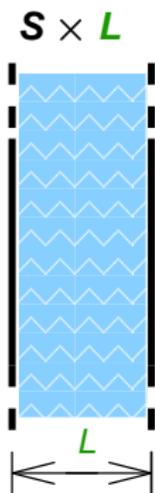


Long-range force

Casimir: QED vs. Stat Phys

	QED	Stat Phys
fluctuating quant.:	E, B	Order param. ϕ
excitation:	Quantum $\hbar\mathbf{c}$ ($T = 0$)	Thermal (classical) $k_B T$ ($\hbar = 0$)
range of fluct.:	∞	finite: ξ $\xi \nearrow \infty$ at CP!
	⇓	⇓
	<div style="border: 1px solid green; padding: 5px; display: inline-block;">Confinement</div>	
	⇓	⇓
	Long-range force	Range: ξ Long-range at CP!

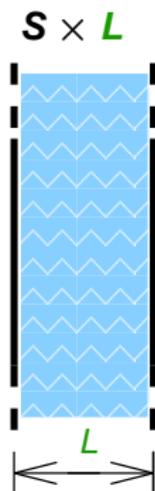
Critical Phenomena: Confined systems



: *critical medium*:

- ^4He , $^4\text{He}/^3\text{He}$
- binary liquid mixt.
- Bose gas
- liquid crystals
-

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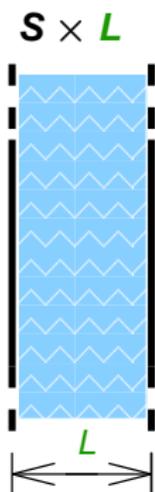
–

$$c_A = c_{A,c}; \quad L, \xi \gg l_{\text{micr}}$$

$$\xi \sim \xi_0 |(T - T_c)/T_c|^{-\nu} \nearrow \infty$$

$$\mathcal{F} = \mathcal{F}_{\text{bulk}} + \mathcal{F}_{\text{surf}}^{(L+R)} + S \frac{k_B T}{L^2} \Theta_{\parallel} (L/\xi) + \dots$$

Critical Phenomena: Confined systems



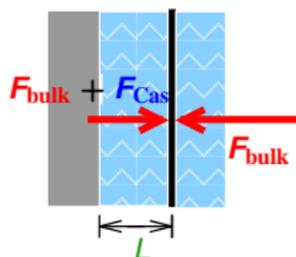
: critical medium: – ${}^4\text{He}$, ${}^4\text{He}/{}^3\text{He}$

- binary liquid mixt.
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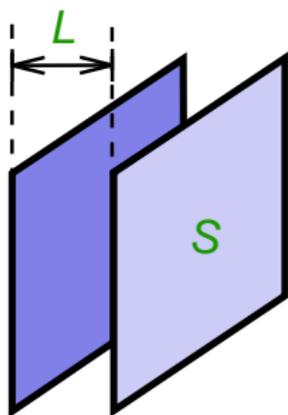


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gross features \implies Universality!

How large is the Casimir force?



$$\begin{aligned} S &= 1 \text{ cm}^2 \\ L &= 1 \text{ } \mu\text{m} \end{aligned}$$

QED

$$T = 0$$

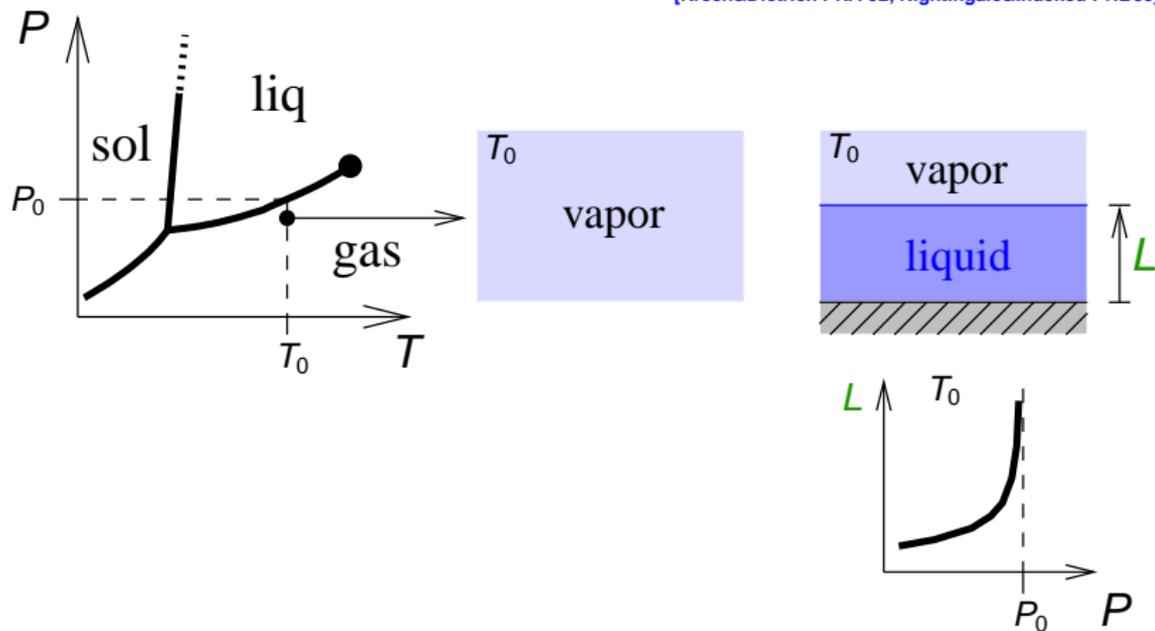
$$\text{force} \sim \hbar c / L^4 \sim 10^{-7} \text{ N}$$

Stat Phys

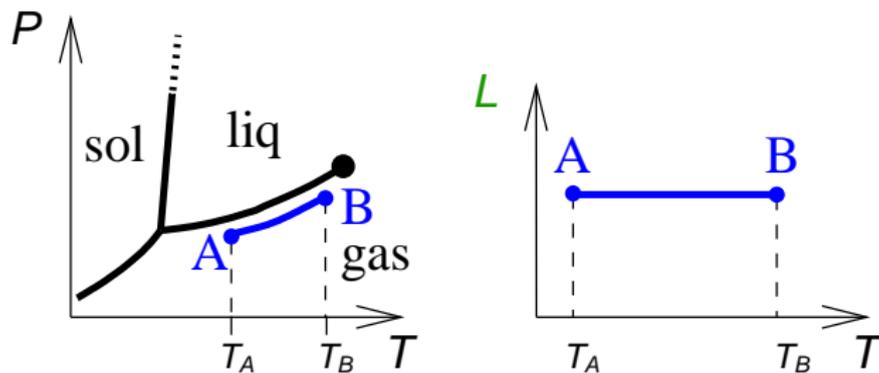
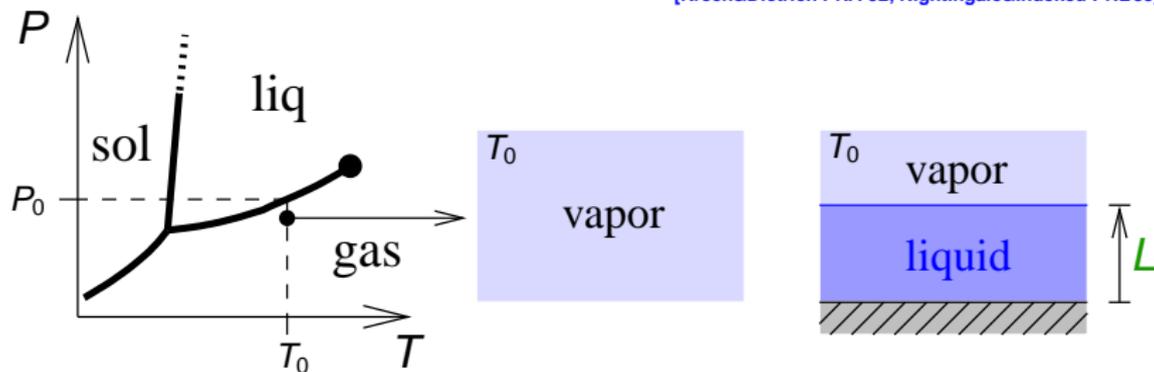
$$T \simeq 300 \text{ K}$$

$$\text{force} \sim k_B T / L^3 \sim 0.2 \cdot 10^{-7} \text{ N}$$

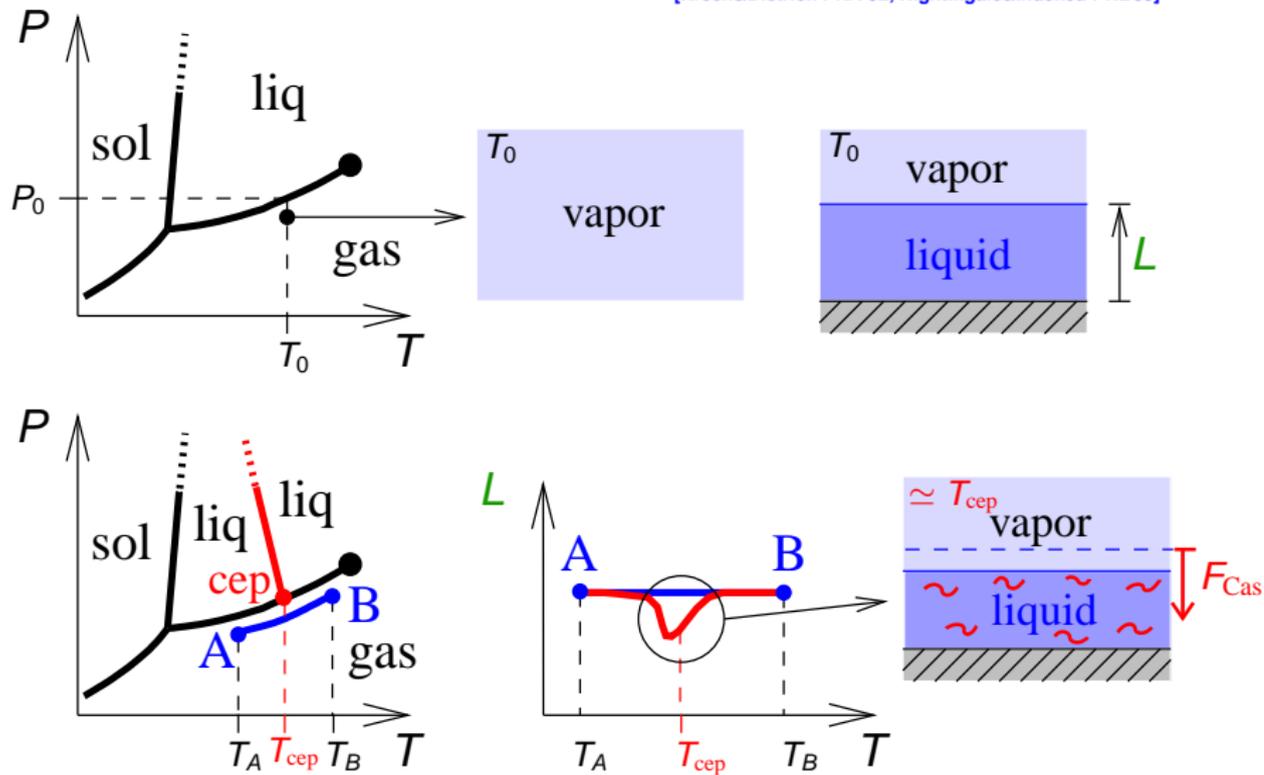
[Krech&Dietrich PRA'92; Nightingale&Indekeu PRL'85]

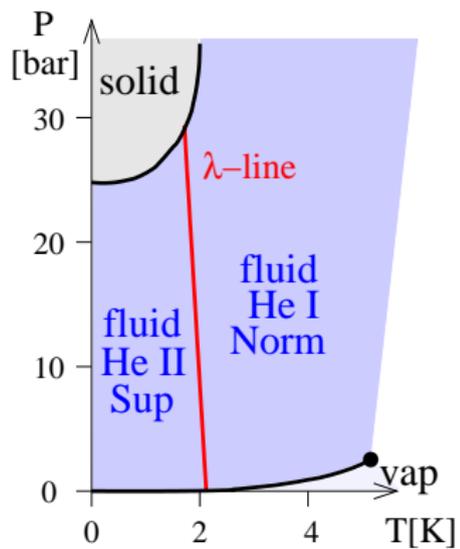


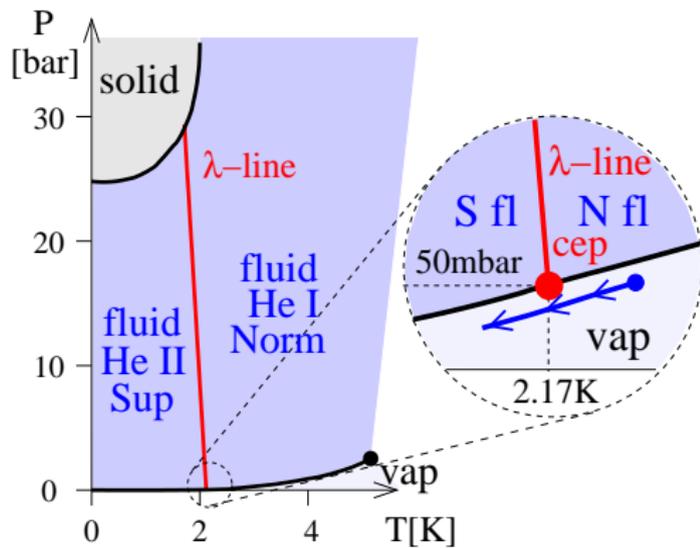
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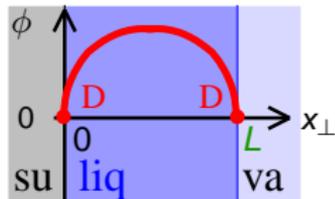






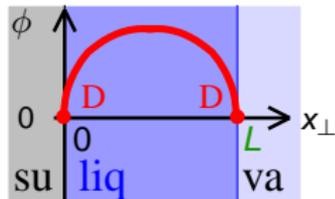
^4He films & XY univ. class

norm/superfl $\xleftrightarrow{\text{universality}}$ XY Model



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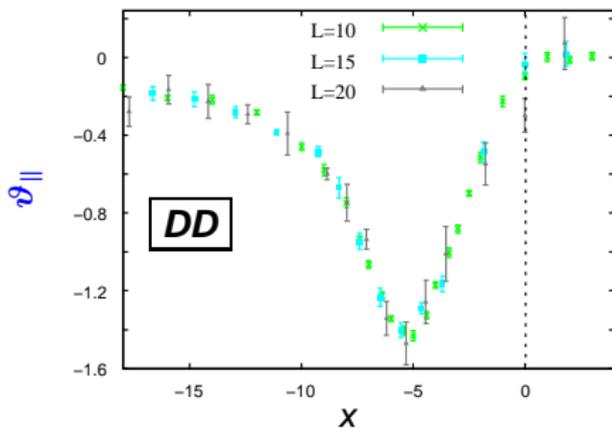


Monte Carlo sim.:

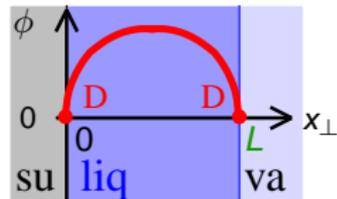
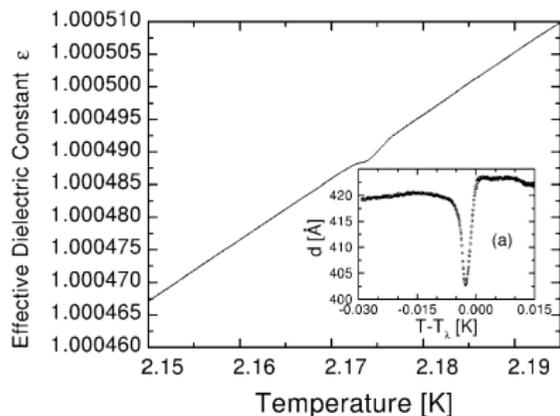
$$x = (T/T_\lambda - 1)(L/\xi_0)^{1/\nu} \quad \nu \simeq 0.66$$

[Vasilyev, Gambassi, Maciolek & Dietrich EPL'07; PRE'09]

[Hucht PRL'07; Hasenbusch > '09]



^4He films & XY univ. class



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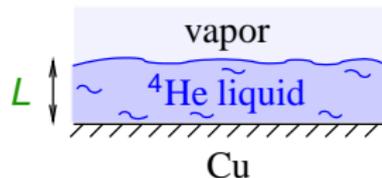
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exp:

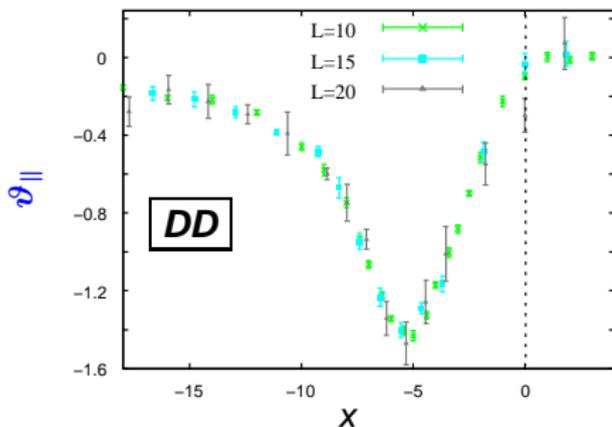
[Garcia & Chan PRL'99]

[Ganshin, Scheidemantel, Garcia & Chan PRL'06]

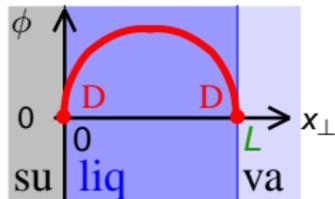
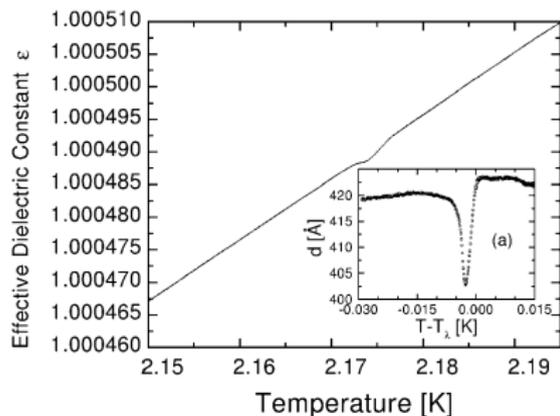
$T_\lambda = 2.18\text{K}$
 $L \simeq 200 \dots 300\text{\AA}$



Features: shape [Zandi, Shackell, Rudnick, Kardar, Chayes, PRE'07]
[Maciolek, Gambassi & Dietrich PRE'07]
low-T plateau [Zandi, Rudnick, Kardar PRL'04]



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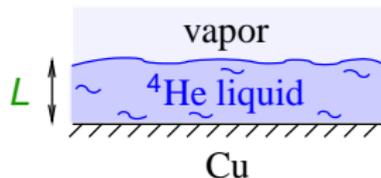
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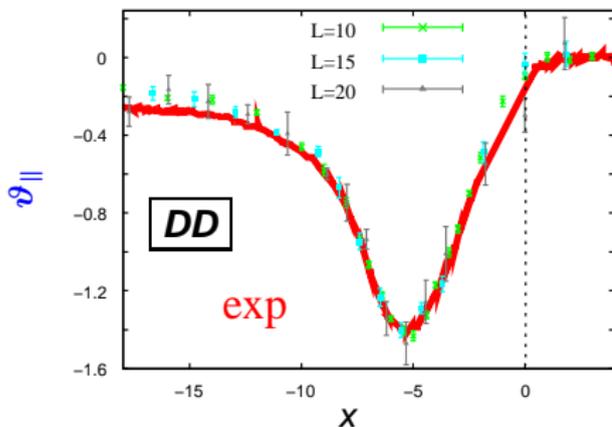
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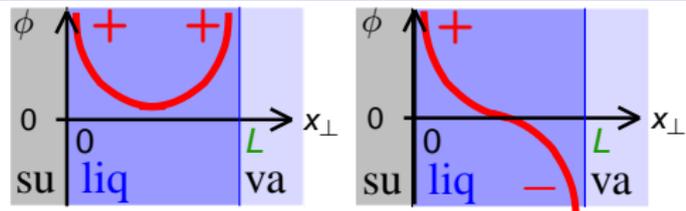


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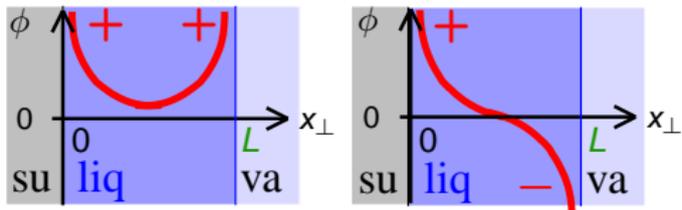
Binary liquid mixtures & Ising univ. class

mixing trans. $\xleftrightarrow{\text{universality}}$ Ising model



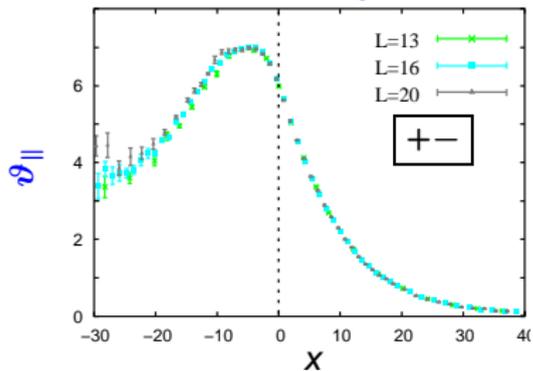
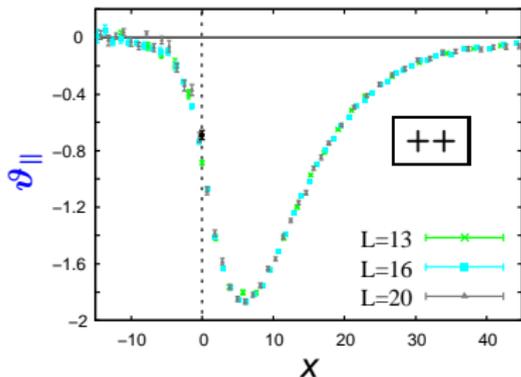
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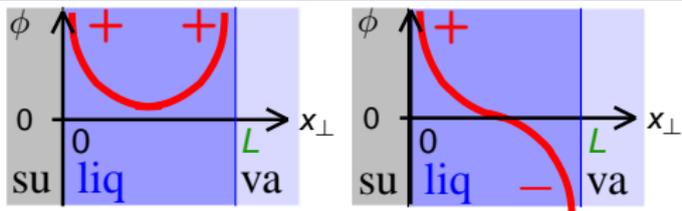
MC sim.: $x = (1 - T/T_c)(L/\xi_0)^{1/\nu}$, $\nu \simeq 0.63$

[Vasilyev, Gambassi, Maciolek & Dietrich EPL'07; PRE'09]
[Hasenbusch '09,'10]



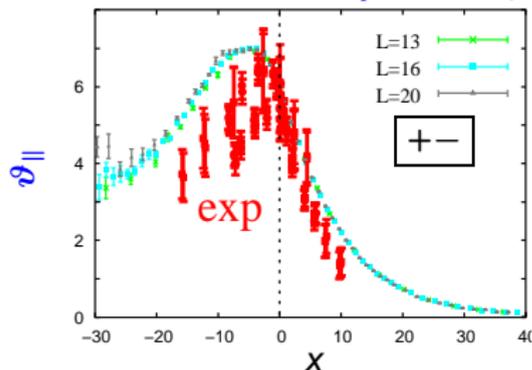
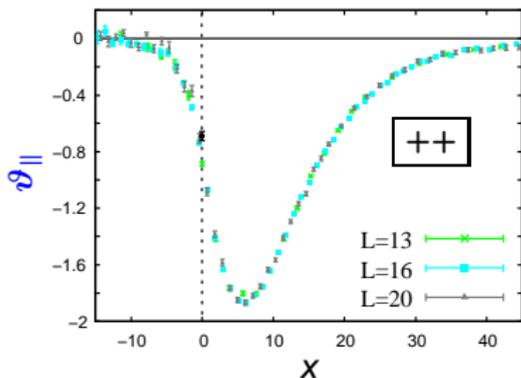
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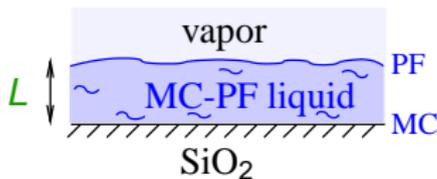
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exp: [Rafai, Bonn & Meunier Physica A'07]

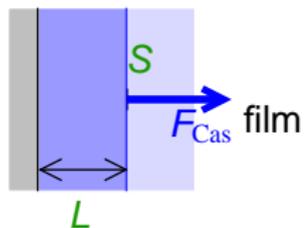
Si substr.
[++] nonane-methanol
[+-] heptane-methanol



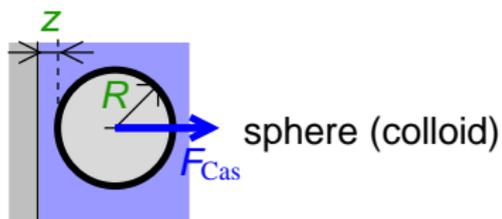
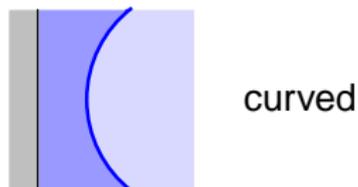
exp: [Fukuto, Yano & Pershan PRL'05]

MC = methylcyclohexane
PF = perfluoroMC
 $T_c = 42.6^\circ\text{C}$
 $x_c(\text{PF}) = 0.36$ molar fr.
 $L \simeq 100\text{\AA}$

From films to colloids...



$$F_{\text{Cas}} = k_B T \frac{S}{L^3} \vartheta_{\parallel}(L/\xi)$$



$$R \gg z:$$

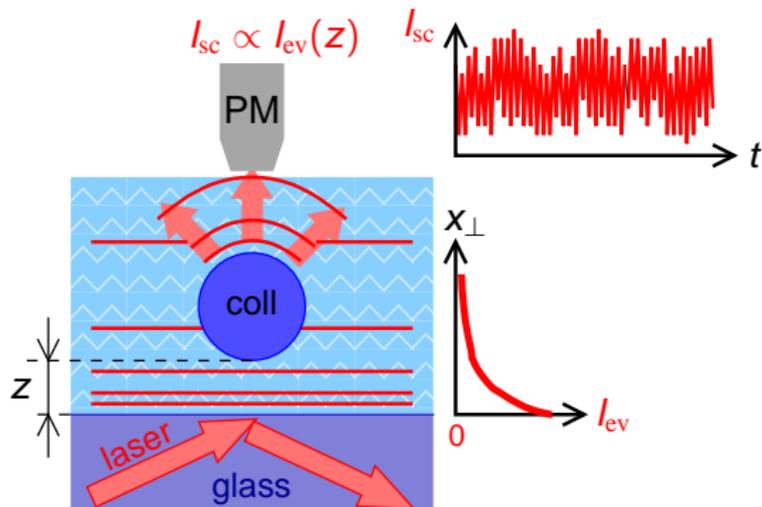
$$F_{\text{Cas}} = k_B T \frac{R}{z^2} \vartheta_{\parallel 0}(z/\xi)$$

$$\vartheta_{\parallel} \rightsquigarrow \vartheta_{\parallel 0}$$

fN dynamometer: TIRM

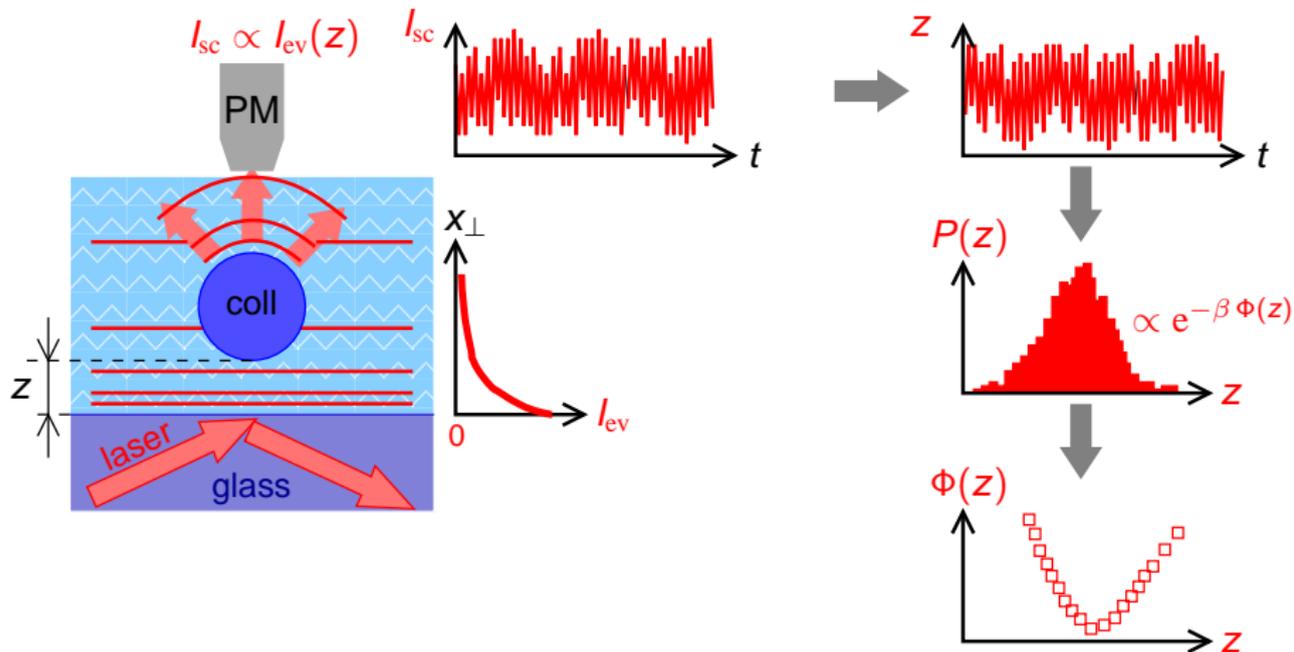
Total Internal Reflection Microscopy (1 fN = 10^{-15} N):

Cavendish $\simeq 1.4 \cdot 10^{-7}$ N
AFM $\simeq 10^{-12}$ N

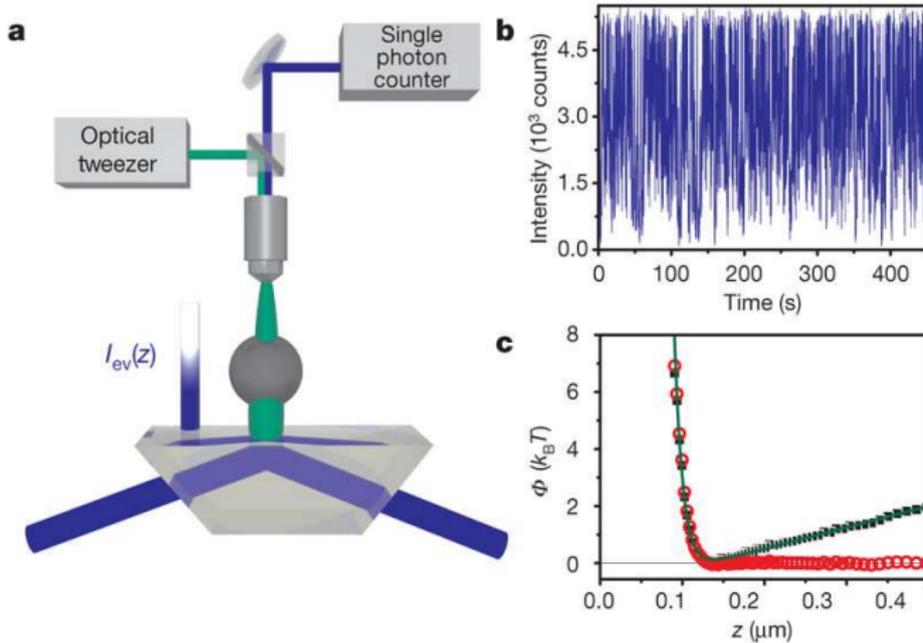


fN dynamometer: TIRM

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Experimental setup

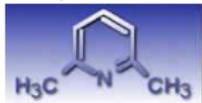


C.Hertlein, L.Helden, A.Gambassi, S.Dietrich, and C.Bechinger,
Nature **451**, 172 (2008)

Casimir force on a colloid

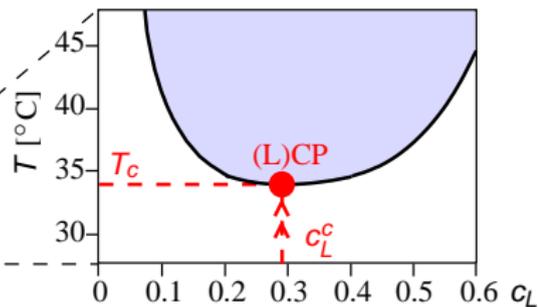
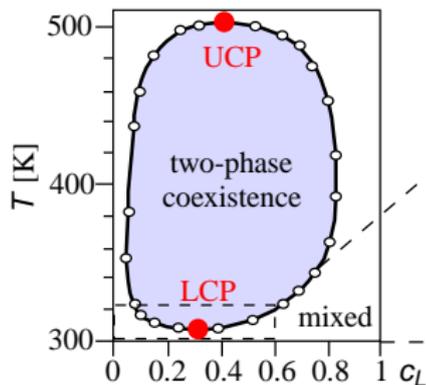
direct!

water + 2,6-lutidine



c_L mass fract.

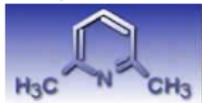
$$\phi(\mathbf{x}) \equiv c_L(\mathbf{x}) - c_L^c$$



Casimir force on a colloid

direct!

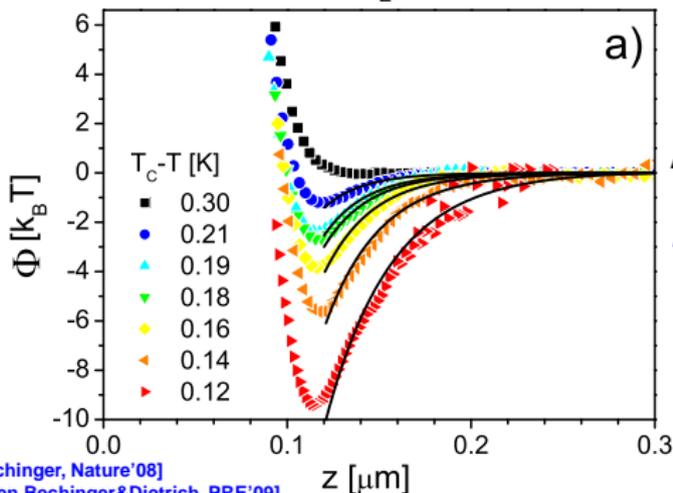
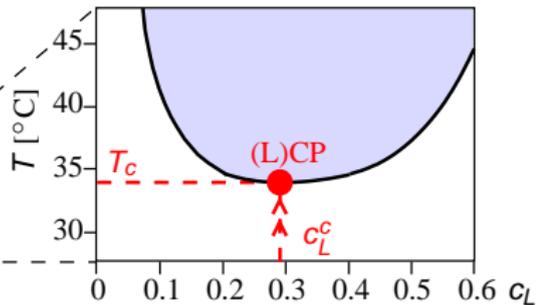
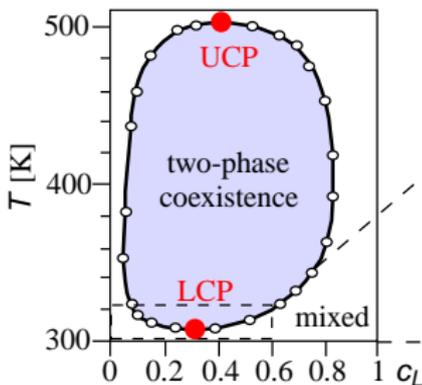
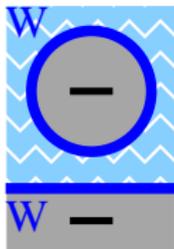
water + 2,6-lutidine



c_L mass fract.

$$\phi(x) \equiv c_L(x) - c_L^c$$

$R = 1.2 \mu\text{m}$



ATTRACTIVE

$$F_{\text{Cas}} \simeq 600 \text{ fN}$$

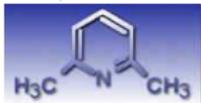
[Hertlein, Helden, Gambassi, Dietrich & Bechinger, Nature '08]

[Gambassi, Maciołek, Hertlein, Nellen, Helden, Bechinger & Dietrich, PRE '09]

Casimir force on a colloid

direct!

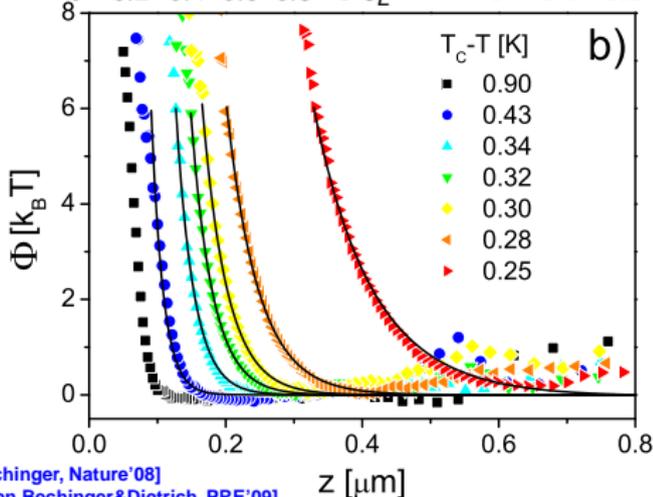
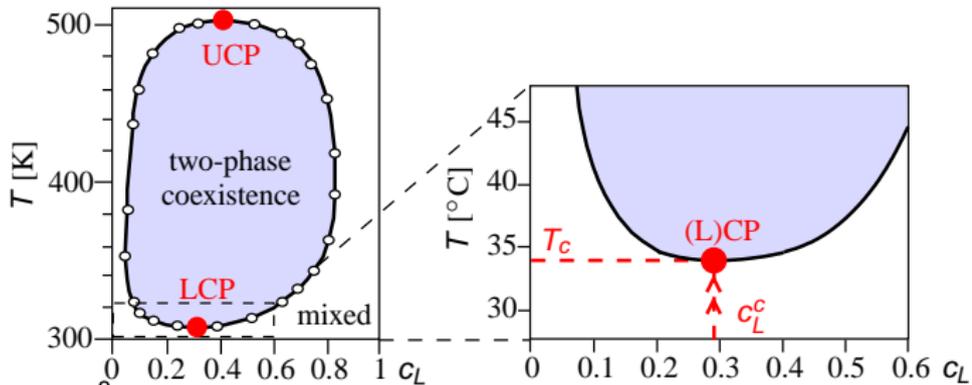
water + 2,6-lutidine



c_L mass fract.

$$\phi(x) \equiv c_L(x) - c_L^c$$

$R = 1.8 \mu\text{m}$



REPULSIVE

[Hertlein, Helden, Gambassi, Dietrich & Bechinger, Nature '08]

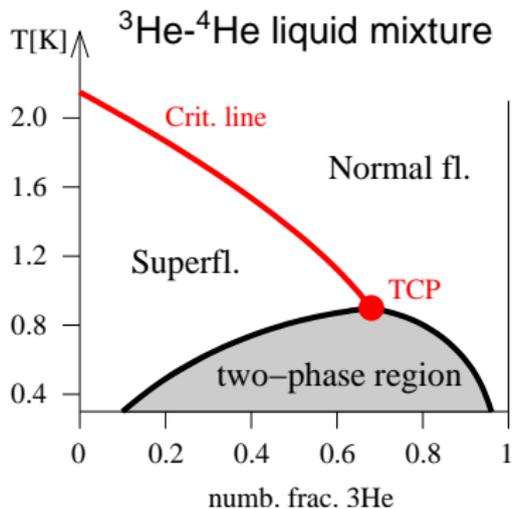
[Gambassi, Maciołek, Hertlein, Nellen, Helden, Bechinger & Dietrich, PRE '09]

Tricritical Casimir effect

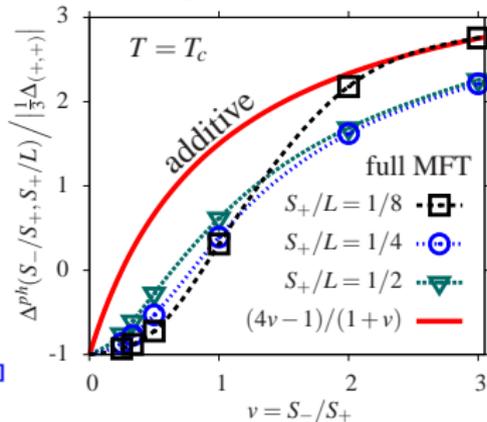
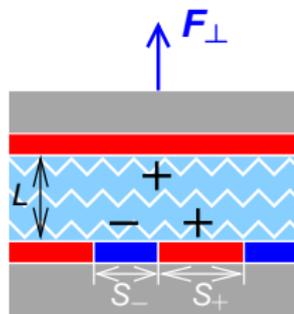
EXP: [Garcia&Chan PRL'02]

TH: [Maciołek&Dietrich EPL'06]

TH: [Maciołek,Gambassi&Dietrich PRE'07]

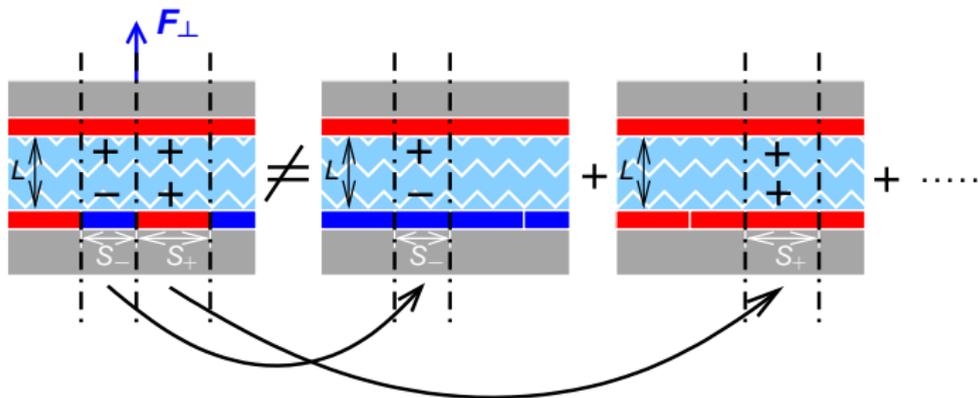


» Inhomogeneous surf.s (chem/topog)

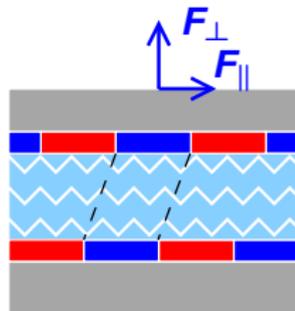
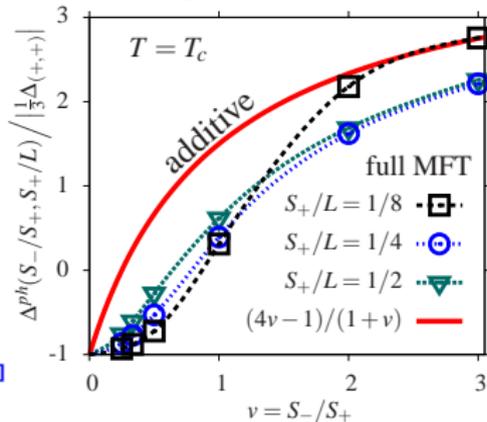
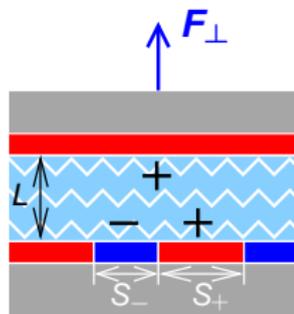


MFT: [Sprenger, Schlesener & Dietrich JCP '06]

MC: [Parisen Toldin & Dietrich '10]

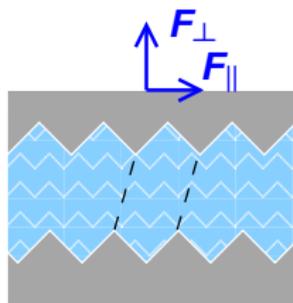


» Inhomogeneous surf.s (chem/topog)

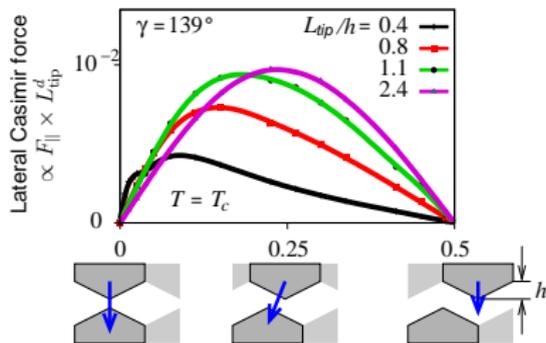


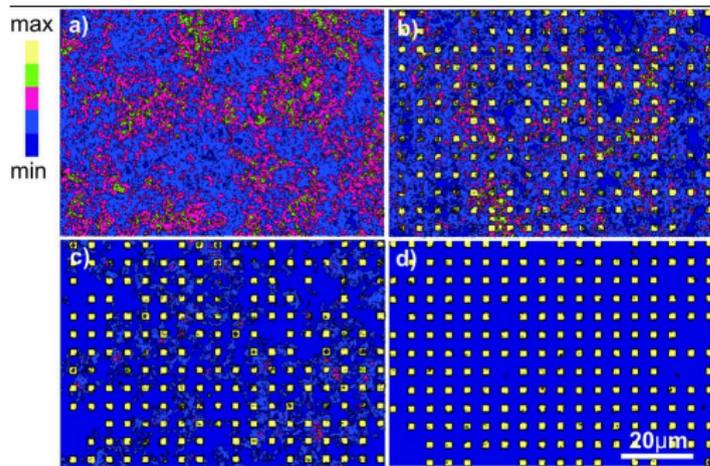
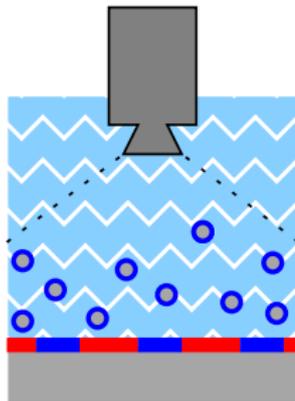
MFT: [Sprenger, Schlesener & Dietrich JCP '06]

MC: [Parisen Toldin & Dietrich '10]

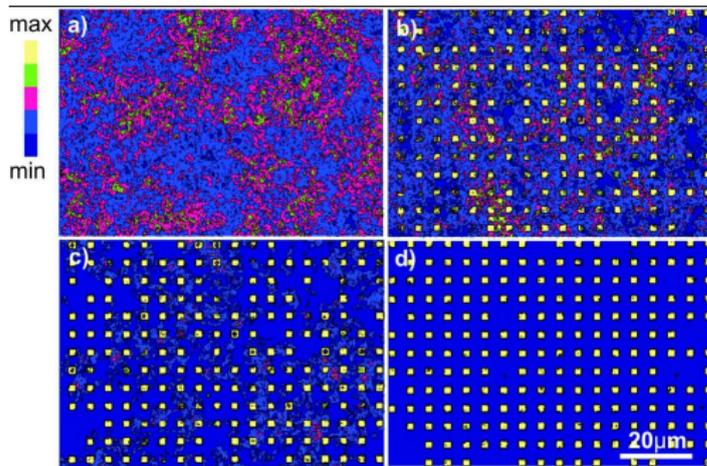
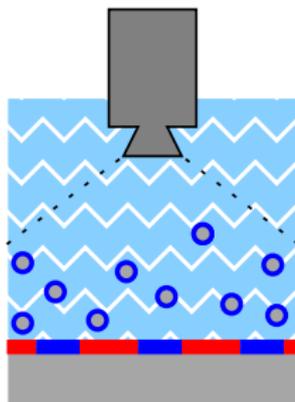


MFT: [Tröndle, Harnau & Dietrich JCP '08]

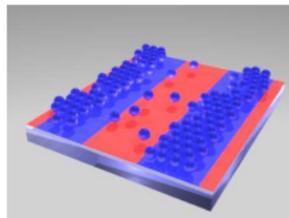




[Soyka,Zvyagolskaya,Hertlein,Helden&Bechinger PRL'08]



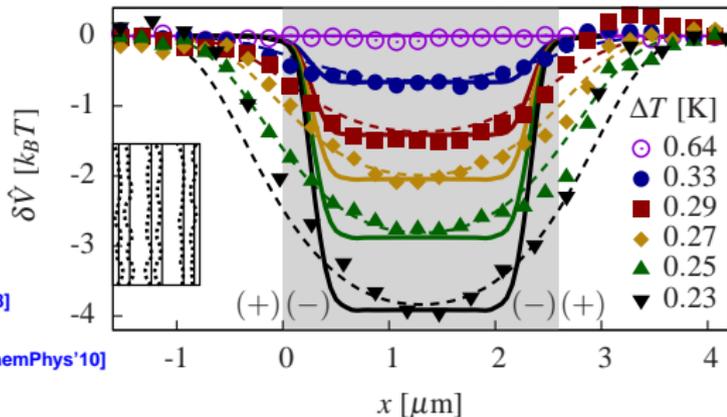
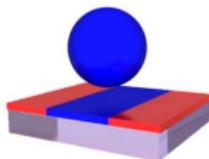
[Soyka,Zvyagolskaya,Hertlein,Helden&Bechinger PRL'08]

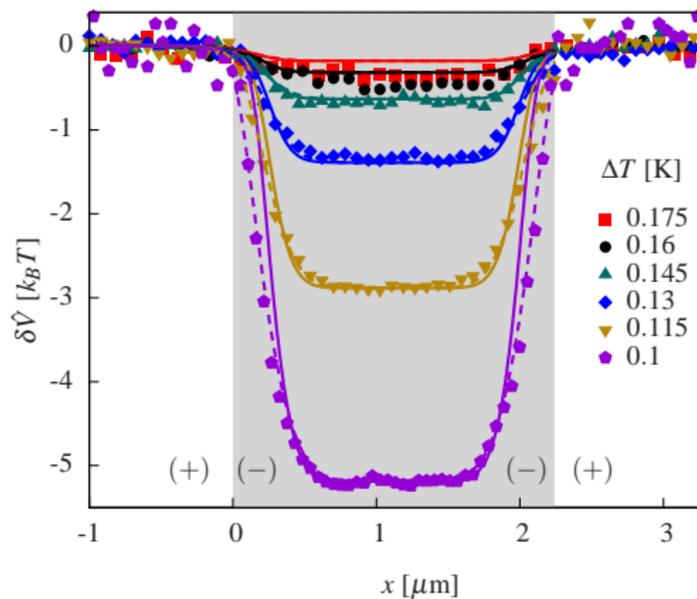


$$\rho(x) \propto \exp(-\hat{V}(x))$$

EXP: [Soyka,Zvyagolskaya,Hertlein,Helden,Bechinger PRL'08]
(focused ion beam)

TH: [Tröndle,Kondrat,Gambassi,Harnau&Dietrich EPL'09,JChemPhys'10]





» Critical Casimir levitation

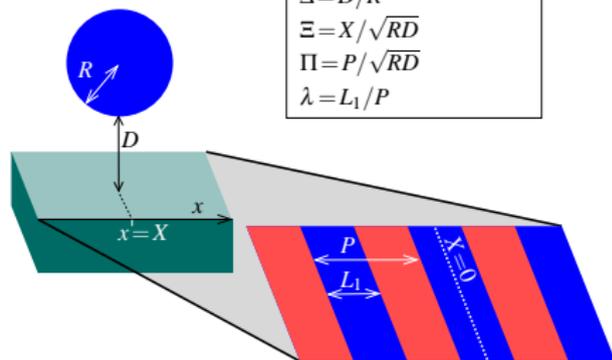
$$\Theta = \text{sign}(t)D/\xi_{\pm}$$

$$\Delta = D/R$$

$$\Xi = X/\sqrt{RD}$$

$$\Pi = P/\sqrt{RD}$$

$$\lambda = L_1/P$$



- lateral equilib.: $X = 0$

» Critical Casimir levitation

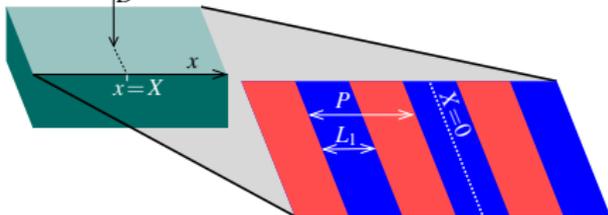
$$\Theta = \text{sign}(r)D/\xi_{\pm}$$

$$\Delta = D/R$$

$$\Xi = X/\sqrt{RD}$$

$$\Pi = P/\sqrt{RD}$$

$$\lambda = L_1/P$$



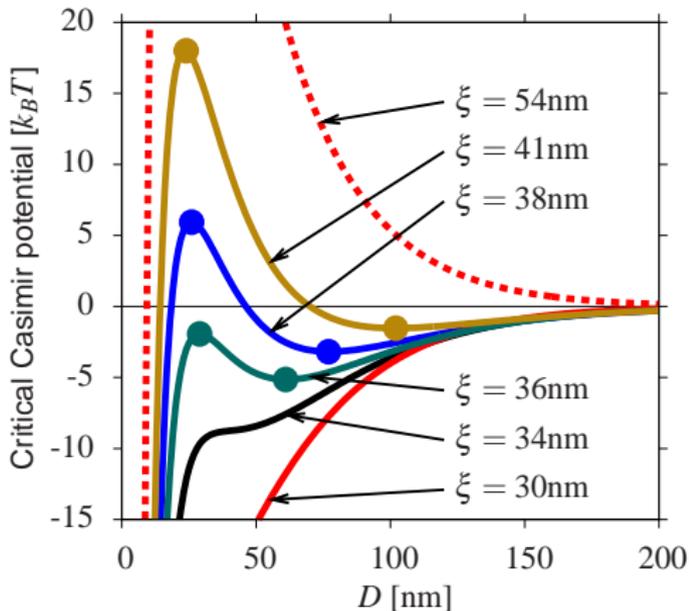
- lateral equilib.: $X = 0$

[Tröndle, Kondrat, Gambassi, Harnau & Dietrich JCP'10]

Mini-review: [Gambassi & Dietrich, Soft Matter'11]

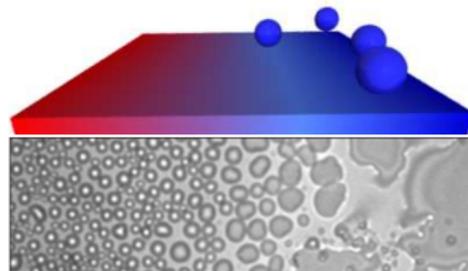
- $T = T_c$: no stable levitation
- $\delta D_{\min}/\delta T > 200 \text{ nm/K}$

$$R = 1.35 \mu\text{m}, P = 1 \mu\text{m}, \lambda = 0.4$$



» Crossover / adsorption gradient

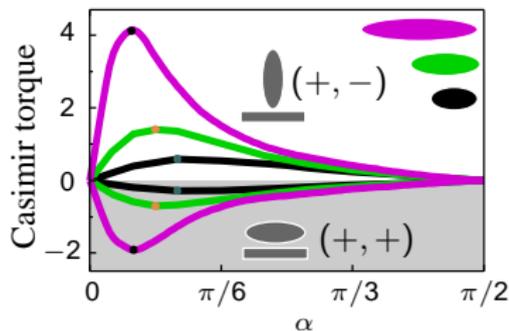
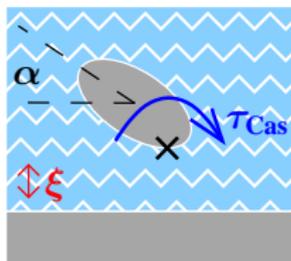
EXP: [Nellen,Helden,Bechinger EPL'09]



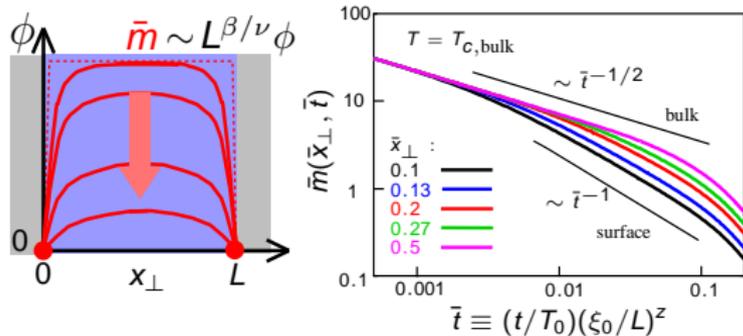
hydrophobic \longrightarrow hydrophilic

» Critical Casimir torque

MFT:[Kondrat,Harnau&Dietrich JCP'09]

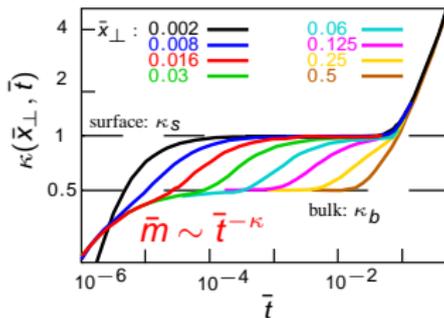


» Eq./Non-eq. dynamics



[Gambassi&Dietrich JSP'06]

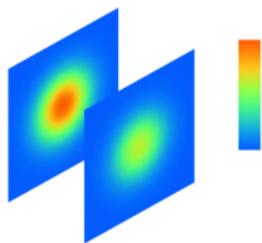
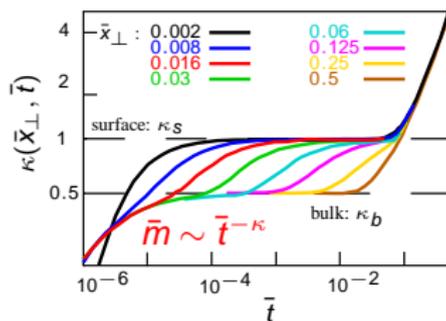
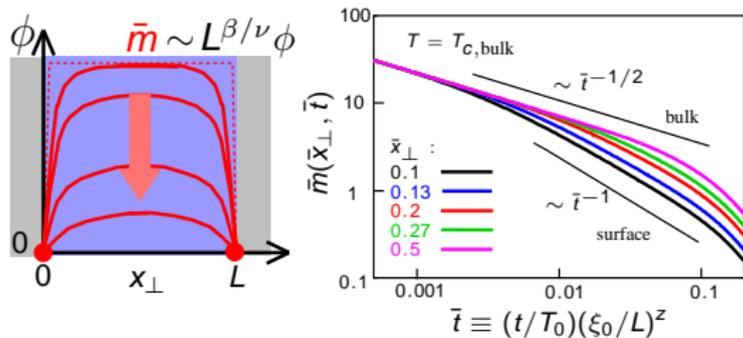
[Gambassi EPJB'08]



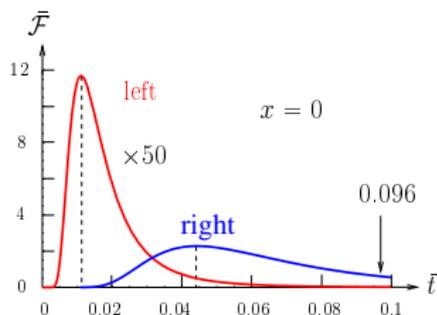
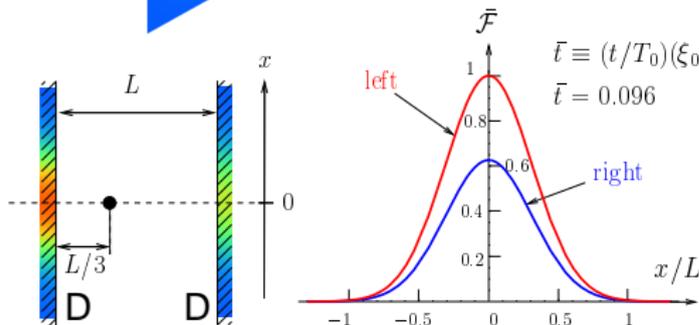
» Eq./Non-eq. dynamics

[Gambassi&Dietrich JSP'06]

[Gambassi EPJB'08]

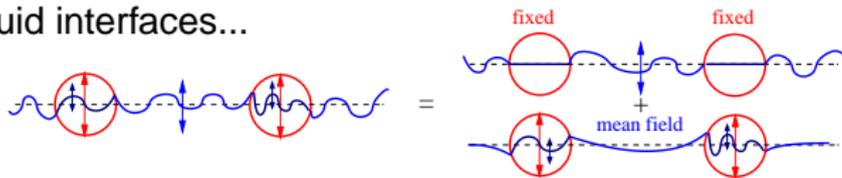


Model A, $T = T_{c,bulk}$, Gauss, $\bar{\mathcal{F}} \equiv L^d F_{Cas}/(S k_B T) \propto h_{ext}^2$



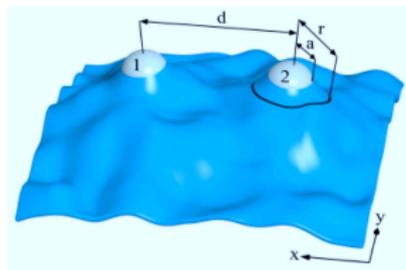
Different fluctuating media....

» Fluid interfaces...



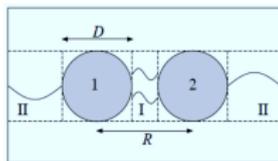
[Oettel et al. > '05]

» Membranes...



[Fournier et al. > '03]

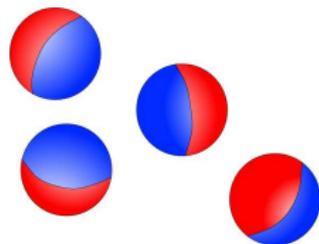
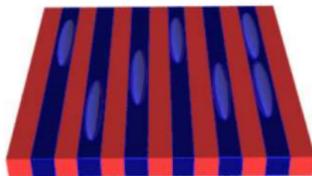
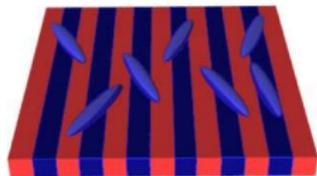
» Granular media...



[Brito et al. > '06]

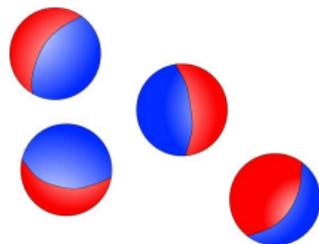
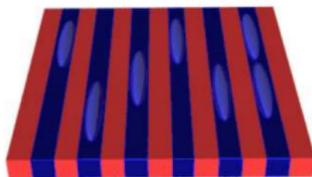
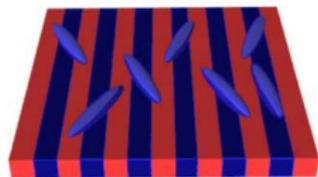
Agenda

» Complex colloids

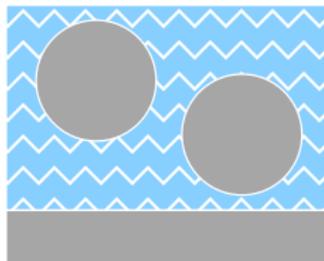


Agenda

» Complex colloids



» Many-body effects

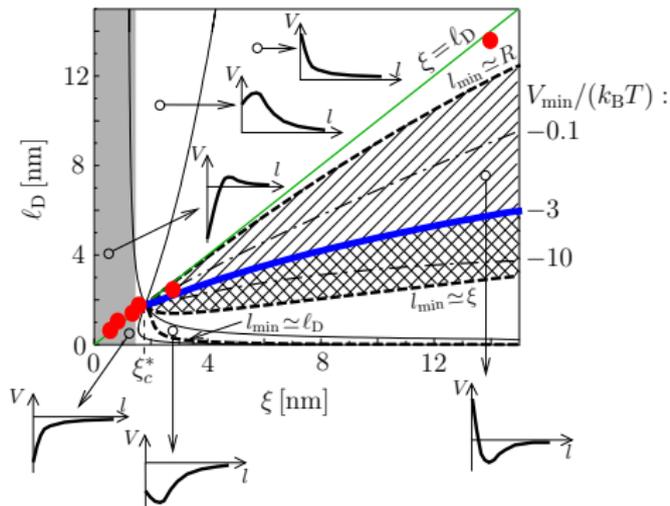
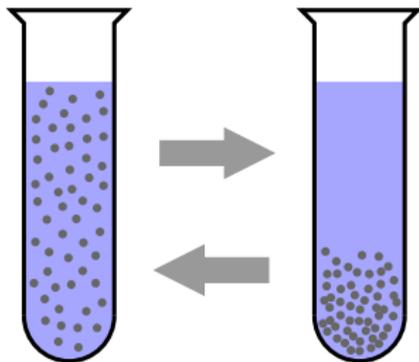


» Flocculation/aggregation

[Beysens et al > '85]

[Gallagher, Maher et al > '92]

[Narayanan, Wegdam et al '08]



EXP: [Bonn et al PRL'09]

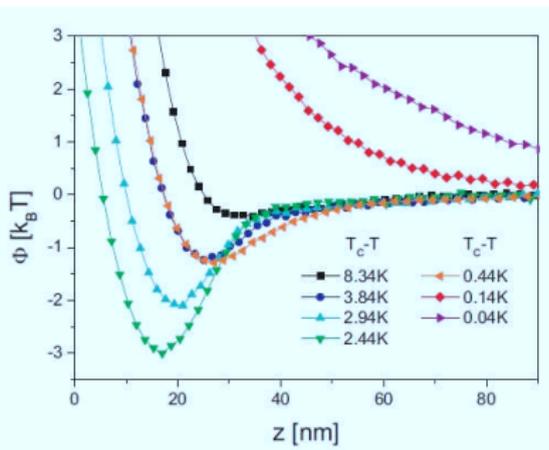
TH: [Gambassi&Dietrich,'10]

Binary mixture \mapsto solvent + surfactant
(depletion)

EXP+TH [Buzzaccaro,Colombo,Parola&Piazza,PRL'10]

Salt-induced changes of colloidal interactions in critical mixtures

Ursula Nellen,^{*a} Julian Dietrich,^a Laurent Helden,^a Shirish Chodankar,^b Kim Nygård,^b J. Friso van der Veen,^{bc} and Clemens Bechinger^{ad}

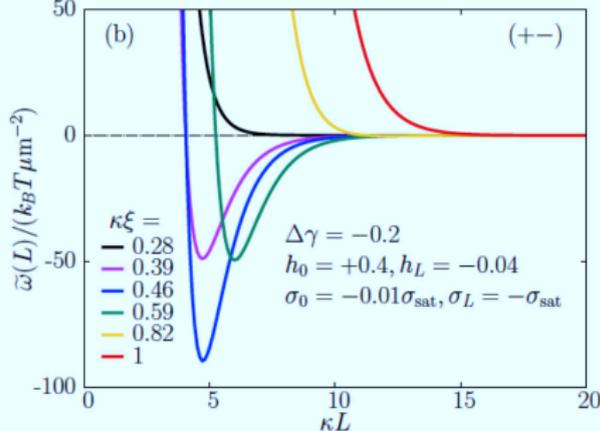
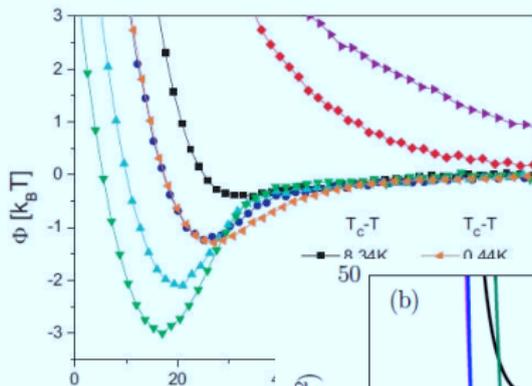


$\boxed{+-}$: attraction!

[Maciolek & Ciach, PRE'10]
 [Bier,Gambassi,Oettel&Dietrich EPL'11]
 [Pousaneh & Ciach, JPCM'11; Samin & Tsori'12]

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Theory

S. Dietrich

S. Kondrat

A. Maciołek

M. Tröndle

O. Vasilyev

L. Harnau

T. Mohry

M. Oettel

D. Dantchev

M. Bier

Experiments

C. Bechinger

C. Hertlein

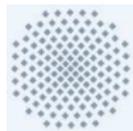
L. Helden

U. Nellen

F. Soyka

O. Zvyagolskaya

T. Vogt



2. Physikalisches Institut
Universität Stuttgart



International School

"Physics of Complex Systems"

where: Trieste, Italy

when: May 13th - June 8th 2012

for: Master - junior PhD students

more info: gambassi@sissa.it