

Experimental Observation of Casimir Forces in Tricritical and Liquid Crystalline Films

- KITP Nov. 2008 -

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PENNSTATE



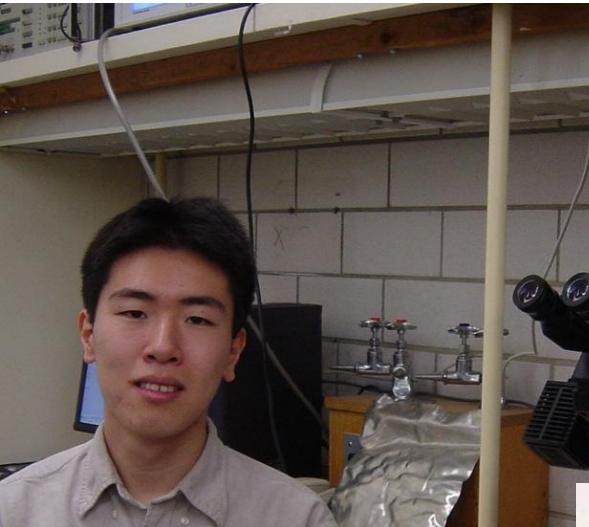
Also at Penn State



- Moses Chan
- Andrei Ganshin
- Sara Scheidemantel



Shinya Segawa



Robert Weiler



Ergys Subashi



Ryan Foltz



Ken Osborne



Cai Waegell

See also...

- Professor Chan, my principal collaborator in measuring Casimir forces in helium films has already given a KITP talk on this subject 9 Sept.
- Here I will only presented some major highlights on our experiments together, please see his talk for more details

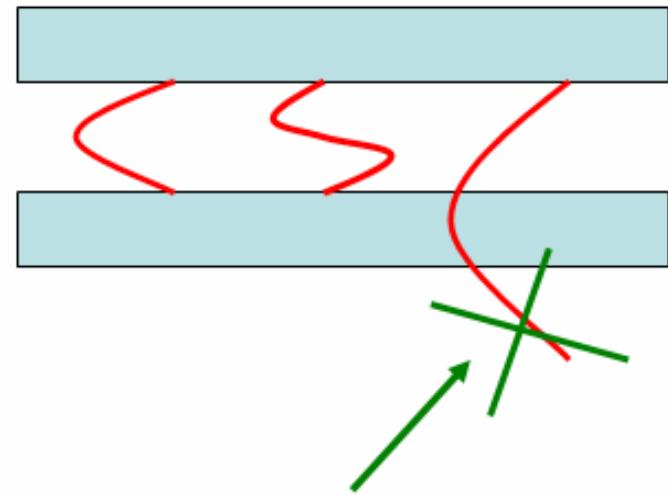
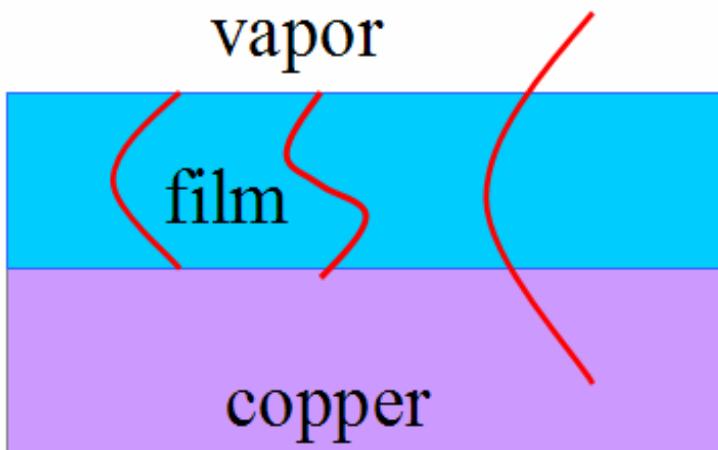
Suggested Open Questions:

- What is the precise relationship between boundary conditions and the sign of Casimir forces?
- Are Casimir forces observable in liquid crystalline films?
- Do Casimir forces cause wetting transitions?

Physics of Small

Thermal Fluctuation Casimir force

effect due to **confinement** of thermal fluctuations of fields

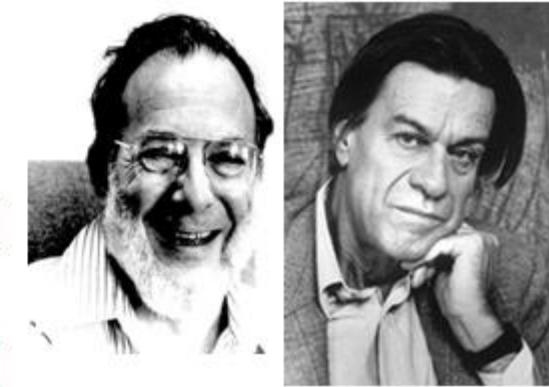
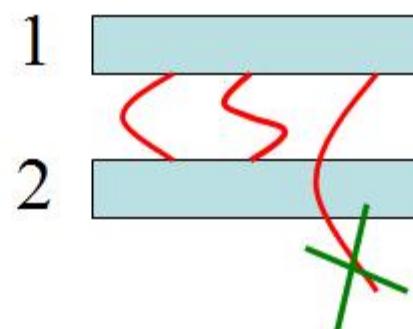


Not allowed because
 $E=0$ inside metal

Casimir forces in general–

Thermal fluctuation case

M.E. Fisher and P.-G. deGennes, C. R. Acad. Sci. Paris, Ser. B 287, 209 (1978).



$$\mathcal{F} = Vf_b + A\sigma_1 + A\sigma_2 + Af_{12}(d, \xi)$$

$$f_{12}(d, \xi) = \frac{\text{Fluctuation Energy}}{\text{Unit Area}} = \frac{k_B T_c}{d^2} \Theta_{12}(\frac{d}{\xi})$$

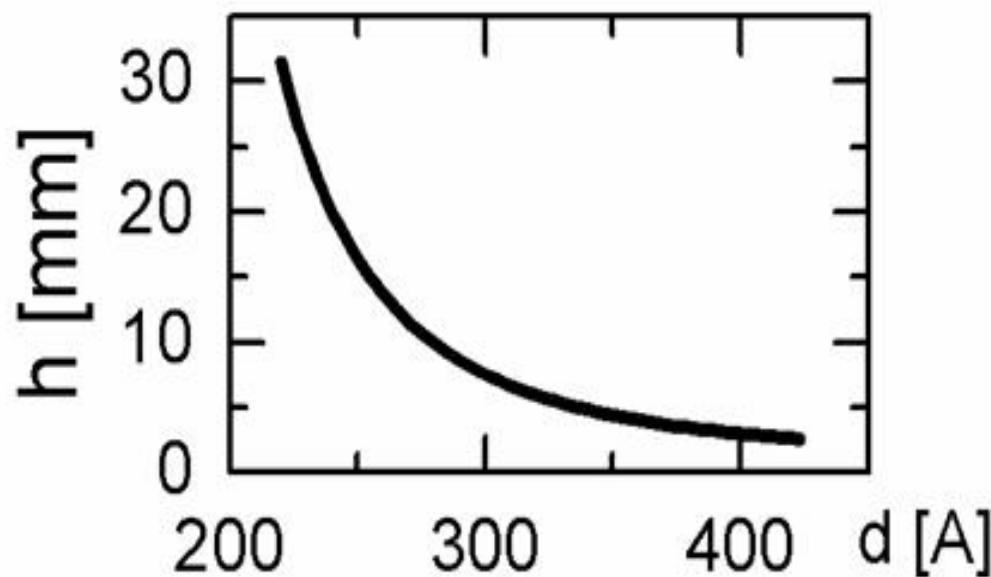
$$P_{\text{casimir}} = -\frac{\partial Af_{12}}{\partial V} = -\frac{\partial f_{12}}{\partial d} = \frac{k_B T_c}{d^3} \vartheta_{12}(\frac{d}{\xi})$$

$$V = Ad$$

Minimize free energy

$$F - \mu V = f_B V_B + \sigma A_B + f_B V_f + \sigma A_f + \frac{H}{2d^2} A_f + \rho g h d A_f - \mu(V_f + V_B)$$

$$\frac{\partial F}{\partial d} = 0 \Rightarrow \mu = f_B; \frac{H}{d^3} = \rho g h$$



If there is a force, there is also a correction to the chemical potential

M. P. Nightingale and J. O. Indekeu, PRL, 54
1824 (1985); J. O. Indekeu, J. Chem. Soc.
Faraday Transactions II 82, 1835 (1986).



Equilibrium film thickness at height h above bulk is determined by competition between van der Waals, gravity, and critical Casimir forces



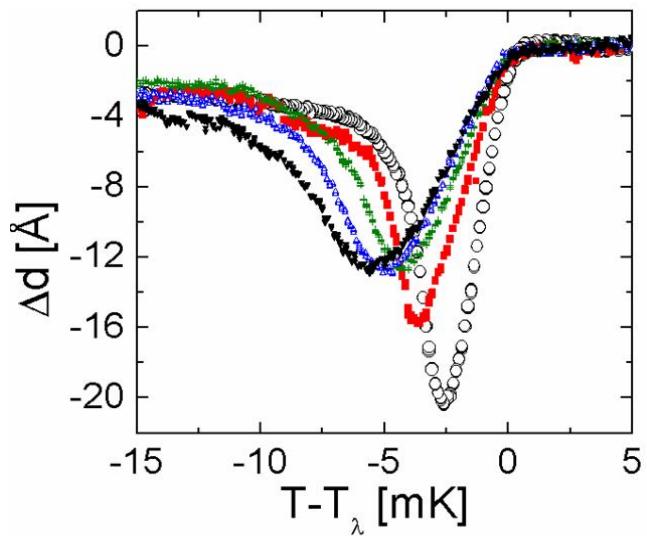
$$\frac{\gamma}{d^3(1+d/\lambda)} + \frac{k_B T_C \bar{V} \vartheta(d/\xi)}{d^3} = mgh$$

Van der Waals

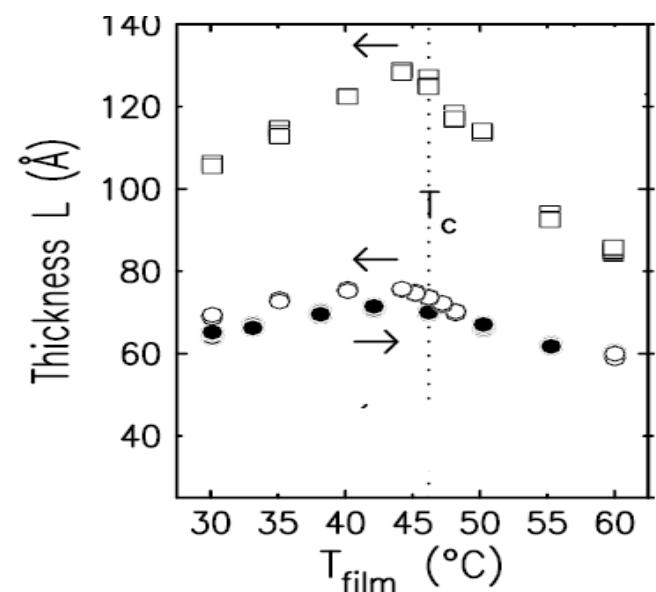
Critical Casimir

gravity

“Casimir forces”-due to thermal fluctuations



Helium films, R. Garcia and M. H. W. Chan *Phys. Rev. Lett.* **83**, 1187 (1999); A. Ganshin *et al.*, **97**, 075301 (2006).



Binary liquid mixture, M. Fukuto et al. *Phys. Rev. Lett.* **94**, 135702 (2005); C. Hertlein, *Nature* **451**, 172-175 (2008)

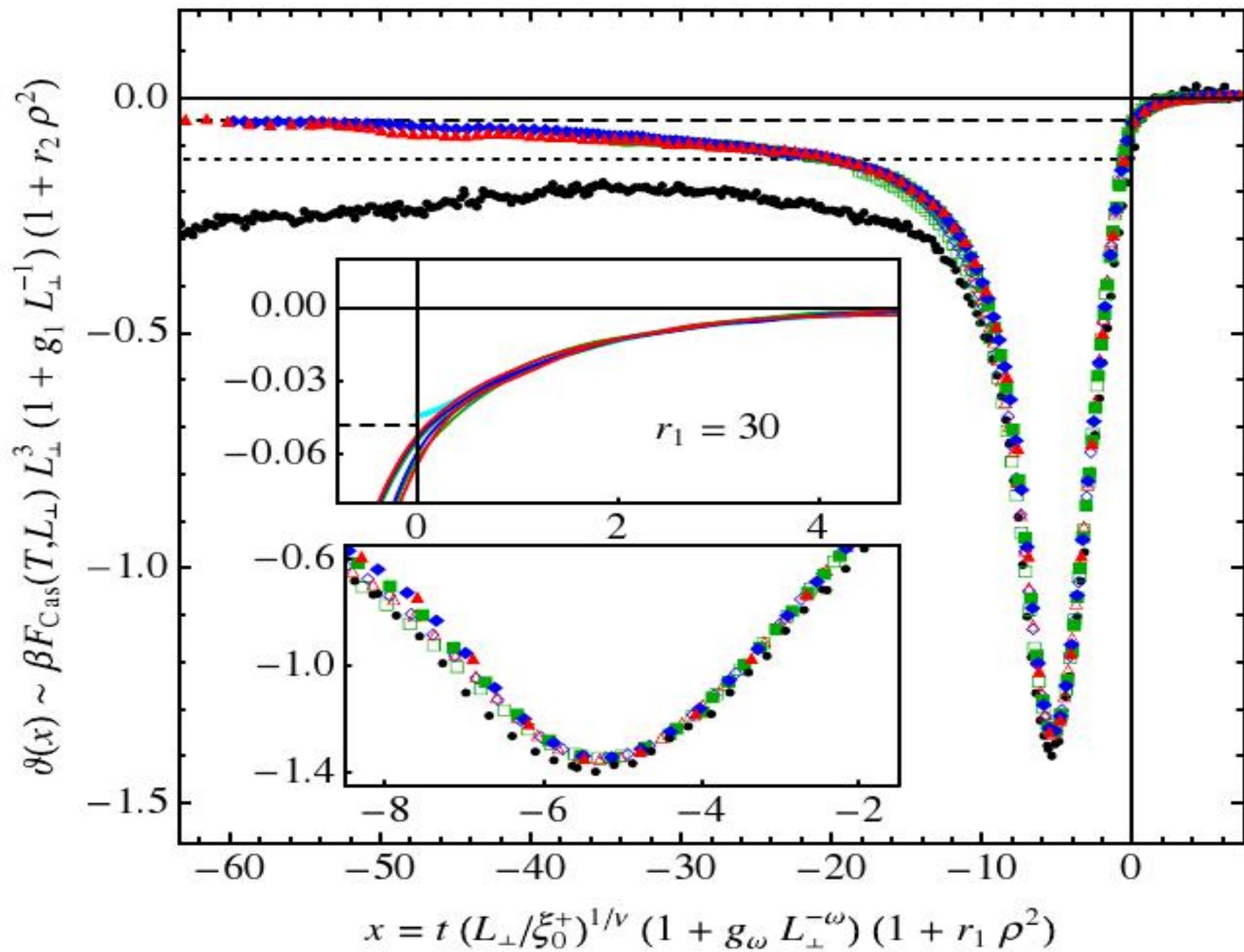
Theoretical Calculations

F. Hucht, Phys. Rev. Lett. 99, 185301 (2007).

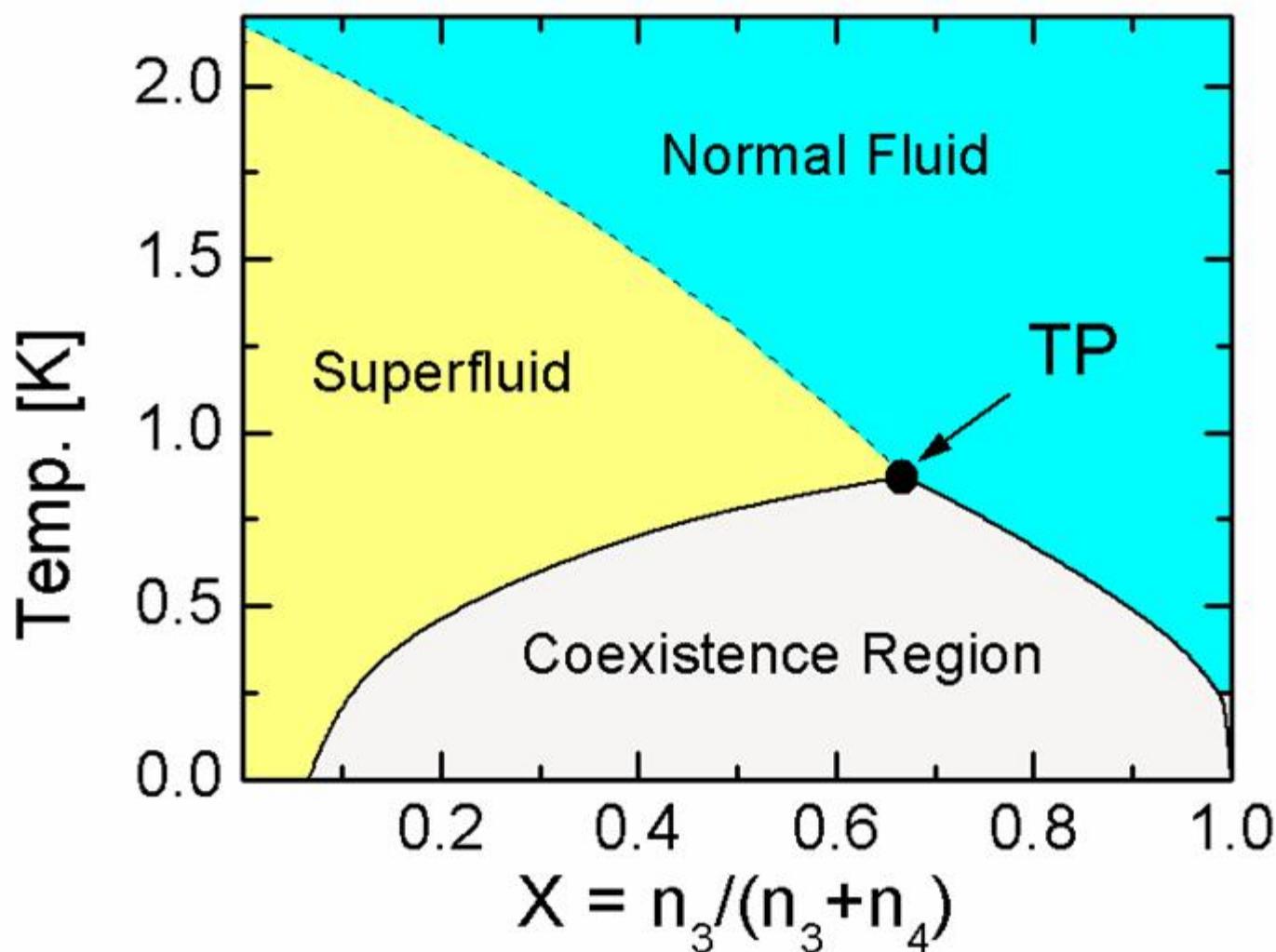
R. Zandi, Phys. Rev. E 76, 030601(R) (2007);

R. Zandi, et al. , Phys. Rev. Lett. 93, 155302 (2004).

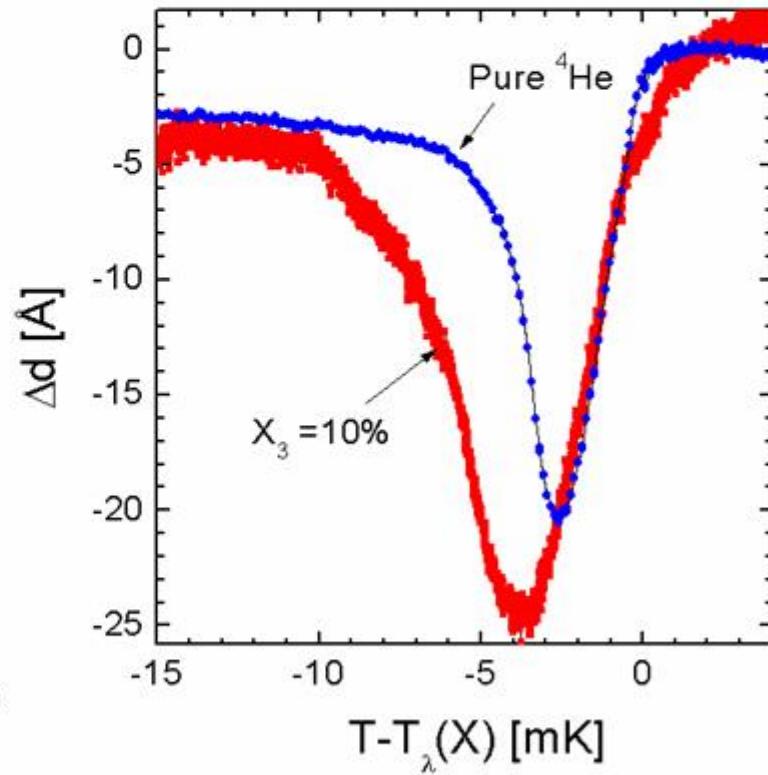
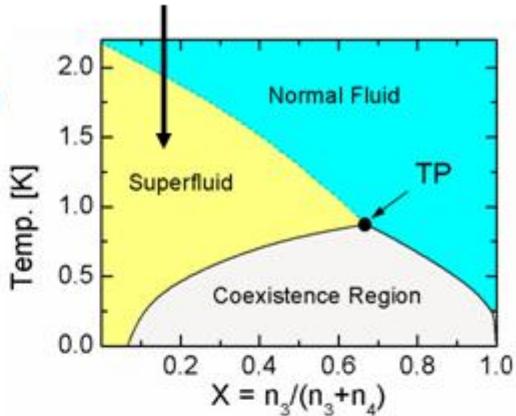
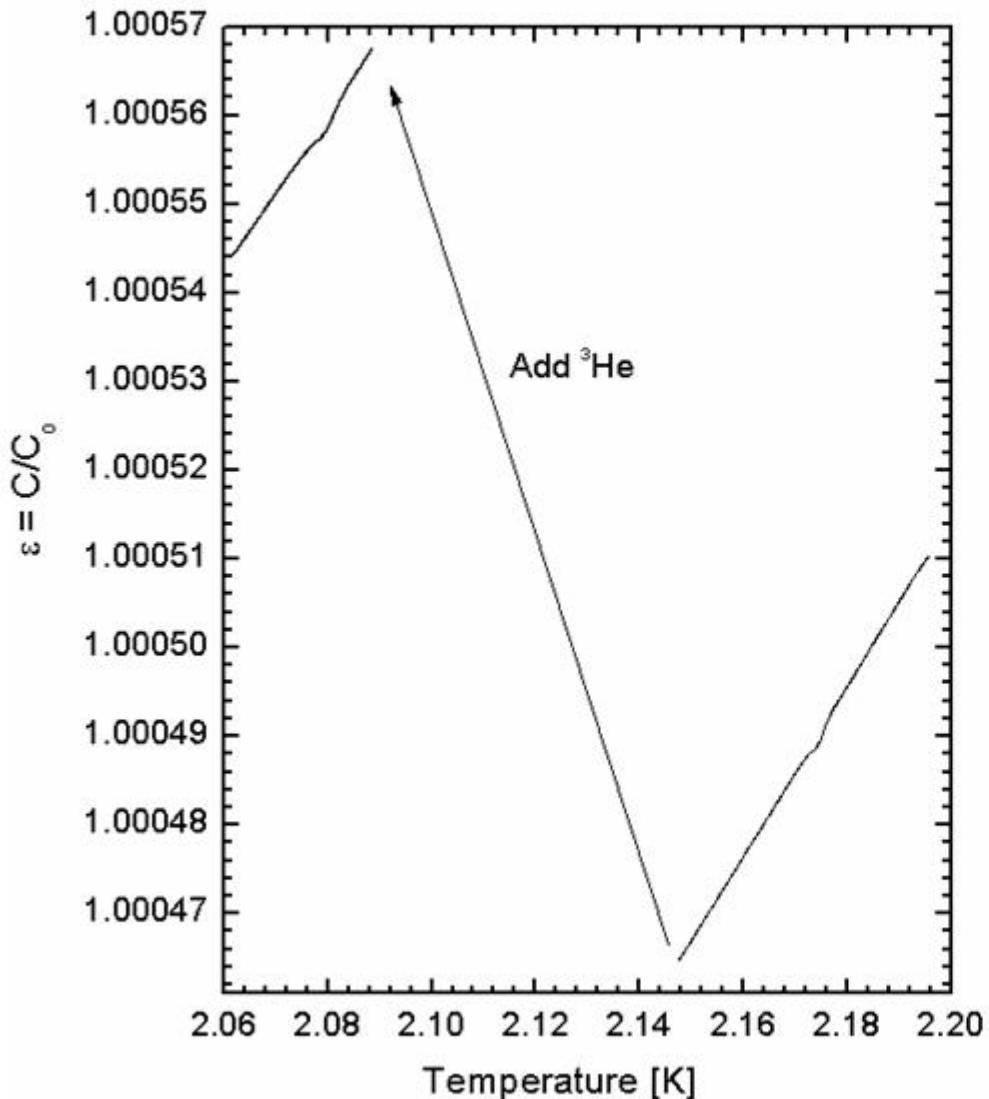
O. Vasilyev et al., Europhysics Letters 80, 60009 (2007) .



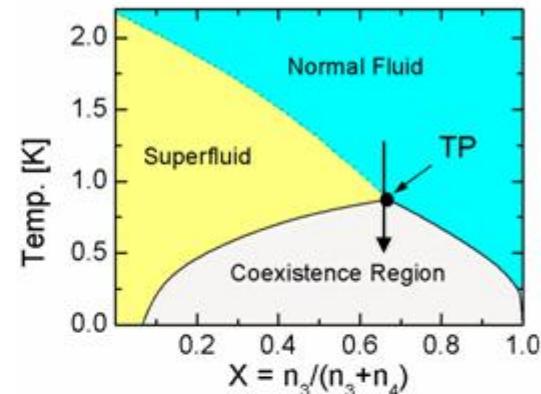
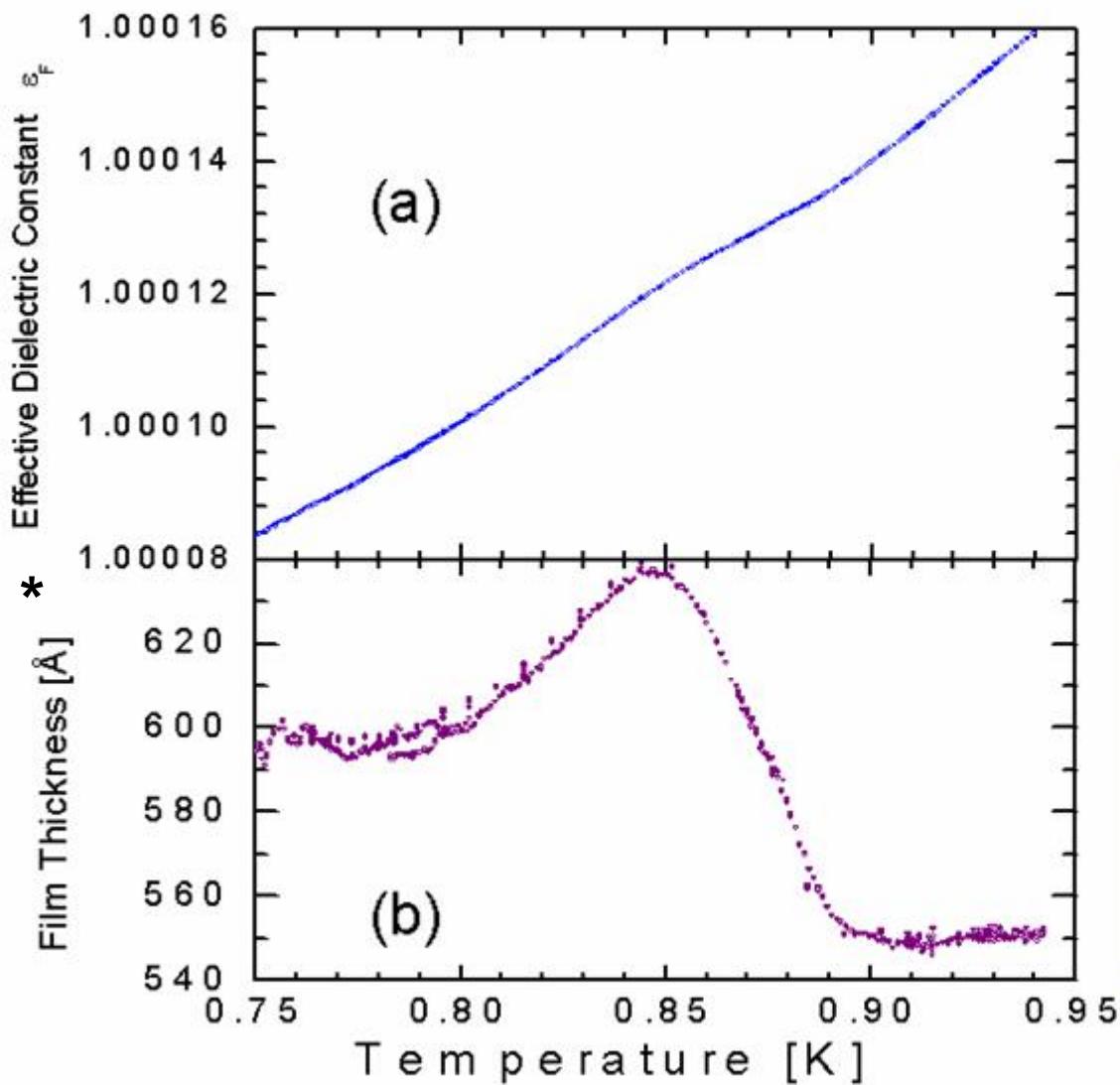
Phase Diagram of ^3He - ^4He Mixtures



Dilute Mixtures



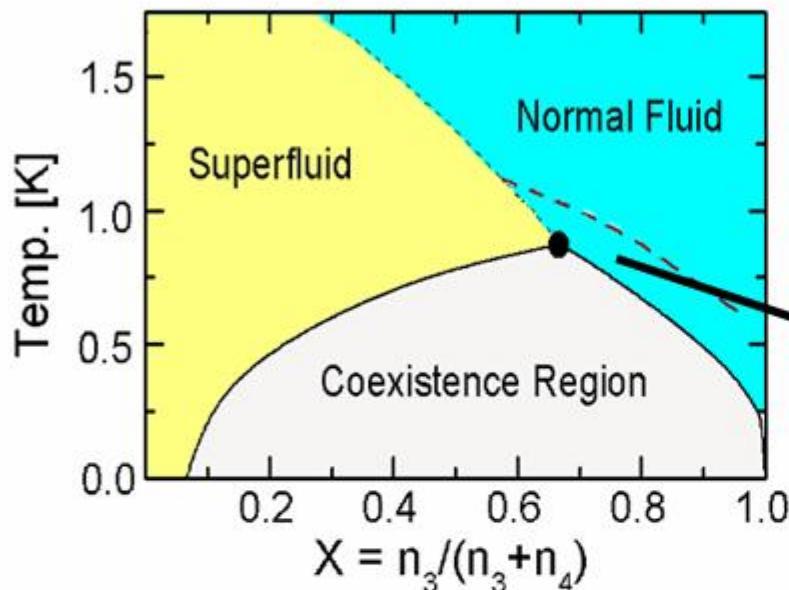
$\epsilon(T)$ and $d(T)$ close to tricritical point



The mixture film thickens as we approach TP!!

* Note: Uncorrected film thickness shown

The tricritical point in ^3He - ^4He mixtures

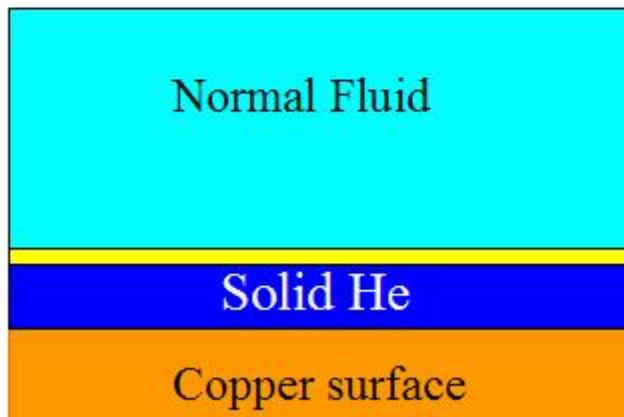


J.-P. Lahuerte et al., Phys. Rev. B 15, 4214 (1977)

Below this dotted line, a thin layer close to the substrate is superfluid !

This superfluid layer forces the O.P. in the fluid above it to assume a different B.C. close to the substrate

⇒ Repulsive critical Casimir force

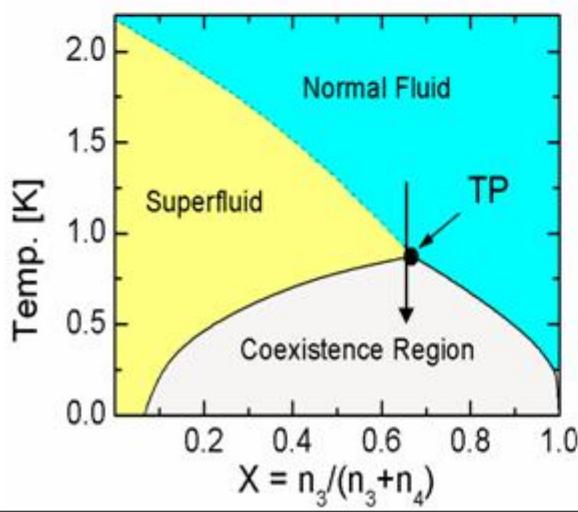
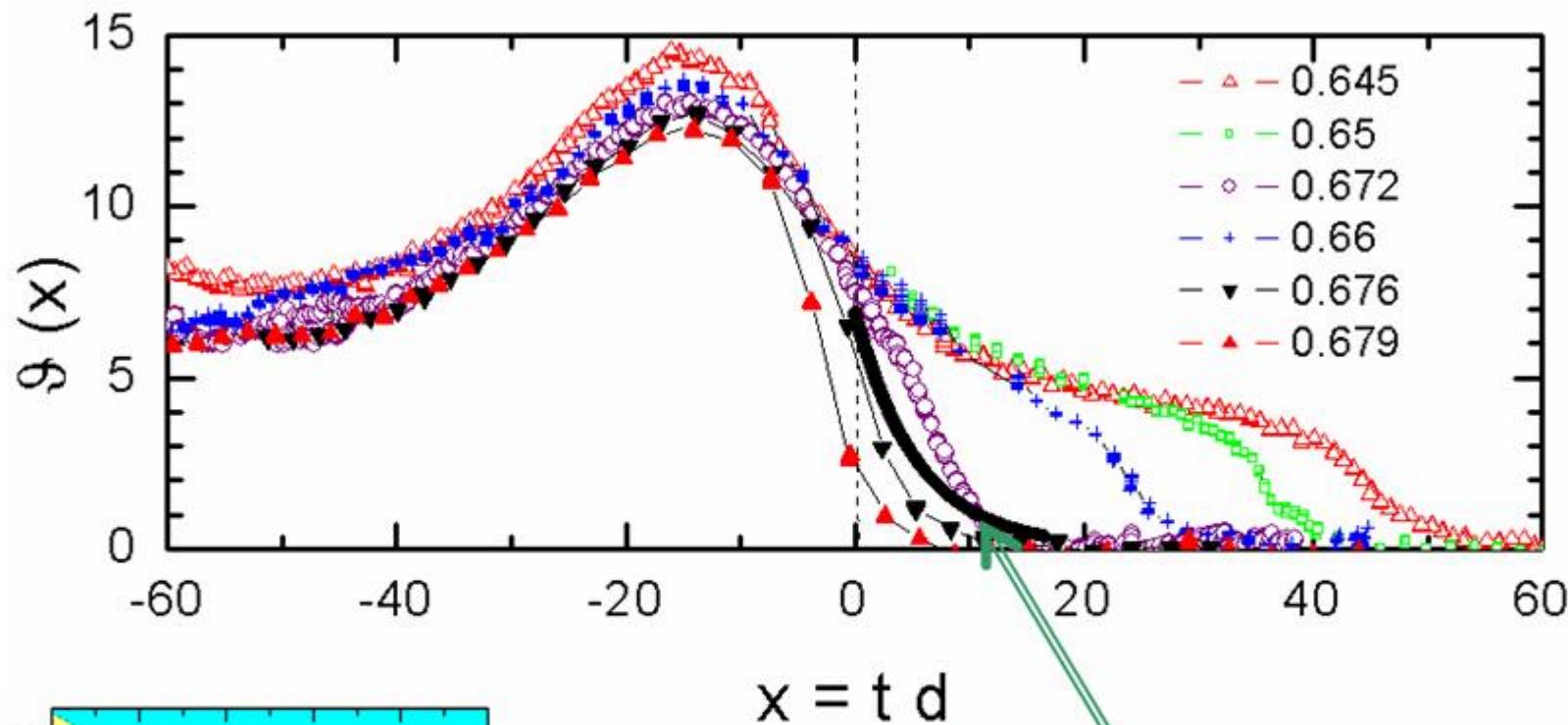


O. Indekeu, J. Chem. Soc. Faraday Transactions II 82, 1835 (1986)



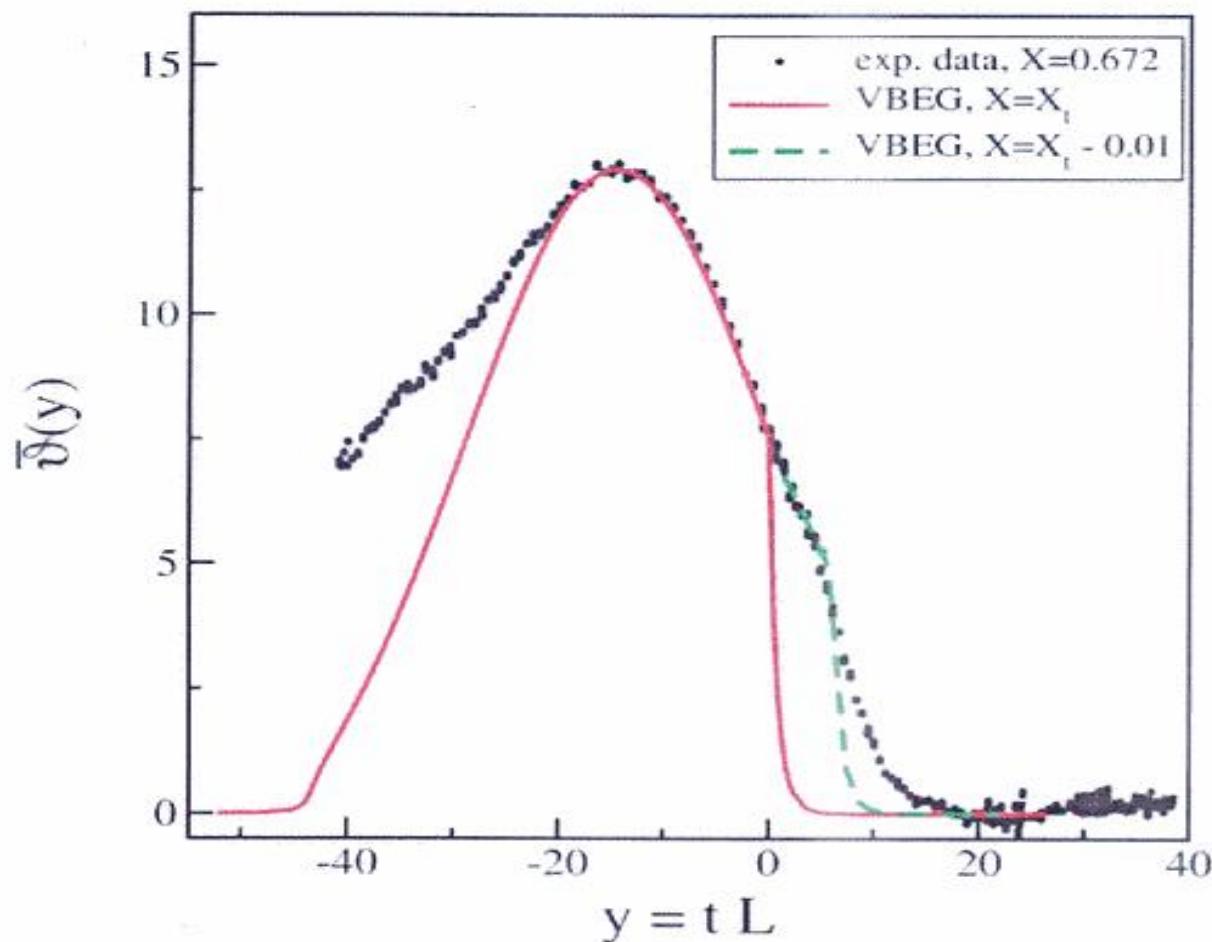
Scaling function $\vartheta(x)$

$$\frac{\gamma}{d^3(1+d/\lambda)} + \frac{k_B T_C \bar{V} \vartheta(d/\xi)}{d^3} = \bar{m}gh$$



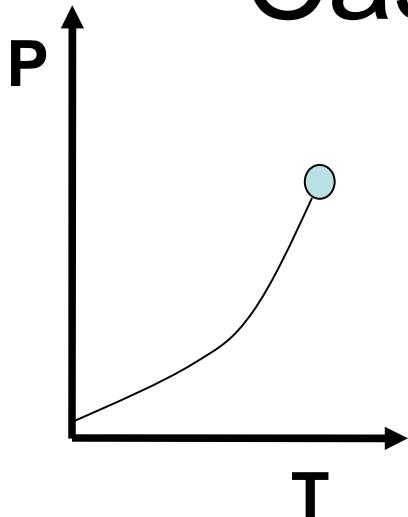
Solid curve is a theoretical calculation by M. Krech.

Agrees with theory, approximately



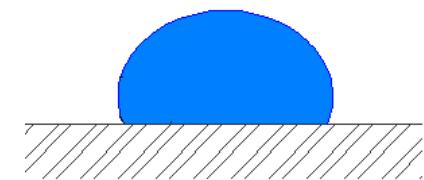
A. Maciolek, and S. Dietrich *Europhysics Letters* 74, 22-28 (2006); A. Maciolek, A. Gambassi, and S. Dietrich, *Physical Review E* 76, 031124, (2007).

Casimir-Induced Wetting Transitions?



Bulk Phase Transition

+



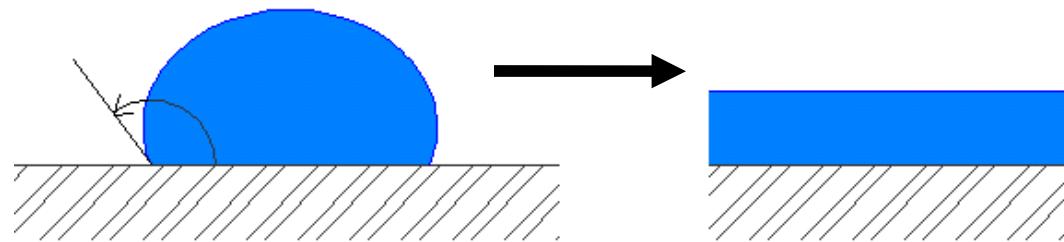
Confinement:Liquid Droplet on Surface

=

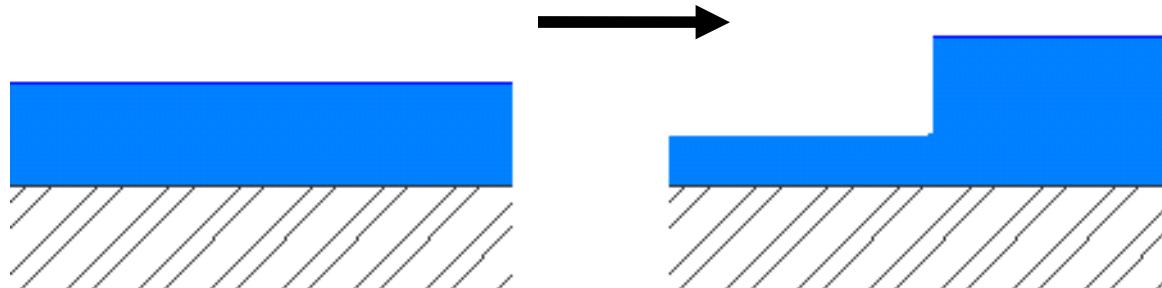
Surface Wetting Transition

Wetting transitions

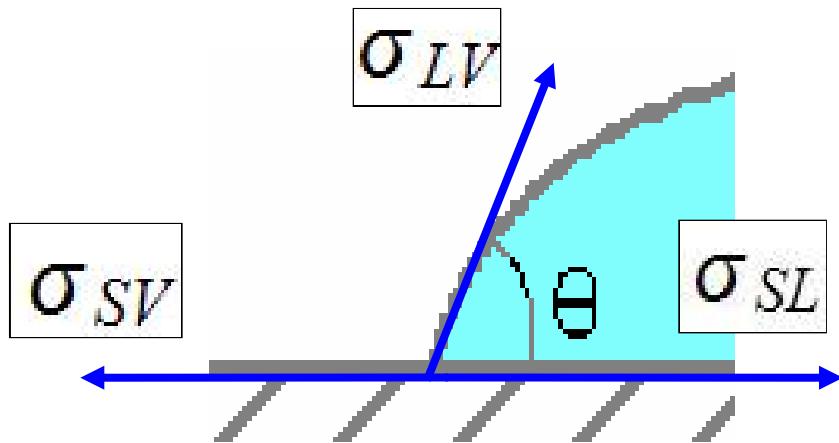
Classic Wetting Transition



Thick-Thin Coexistence Transition



The Wetting Angle Reflects Underlying Forces between Adsorbate atoms and the Solid Surface



Young's Equation

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cos \theta$$

Cheng, Cole, Saam Treiner Equation

$$\sigma_{SL} - \sigma_{SV} = \sigma_{LV} + \rho \int V dz$$

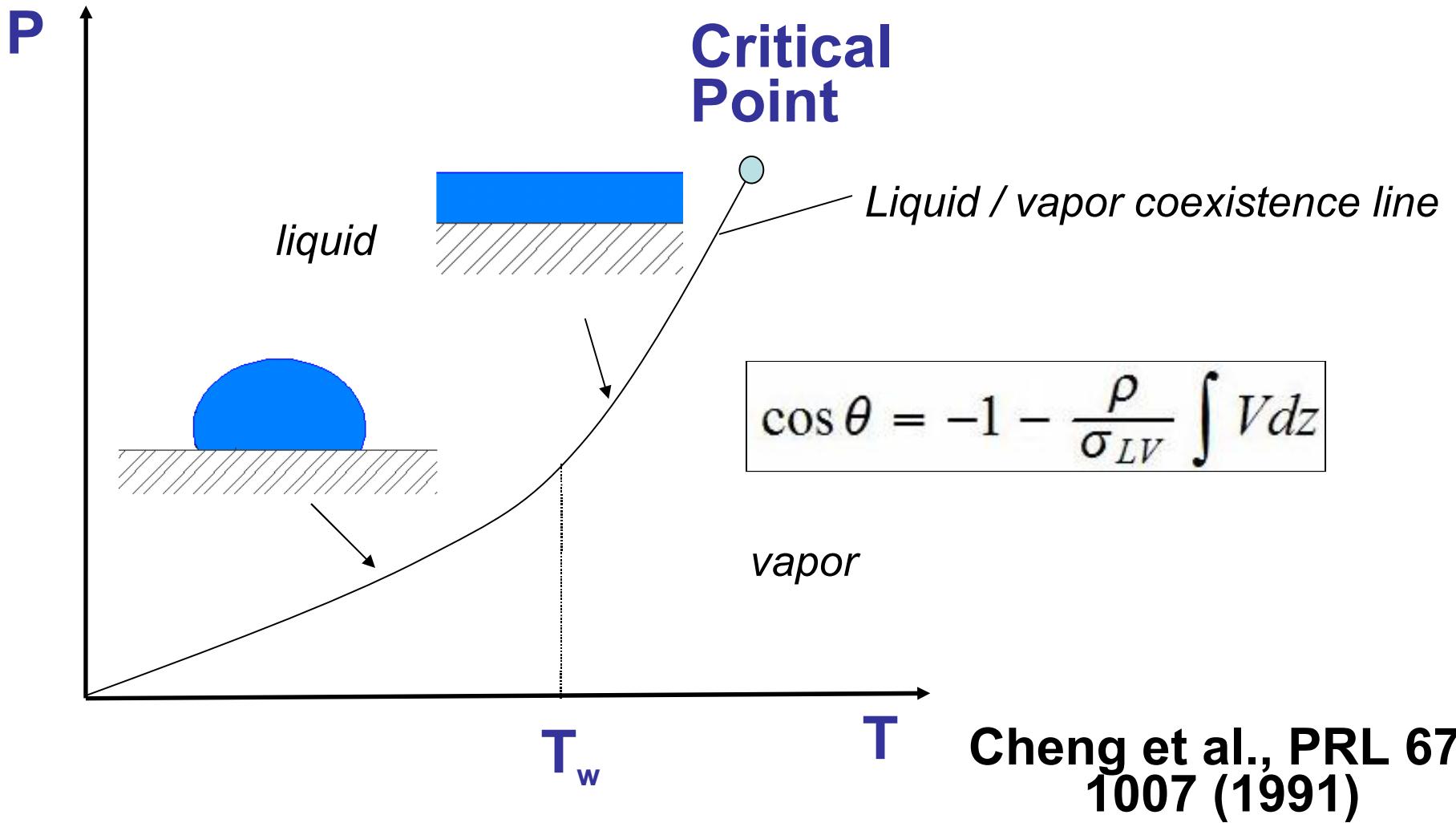


$$\cos \theta = -1 - \frac{\rho}{\sigma_{LV}} \int V dz$$

$$V = V_{Dispersion} + V_{Dipole} + V_{Thermal Fluctuation} + V_{electrostatic} +$$

Cheng et al., PRL 67,
1007 (1991)

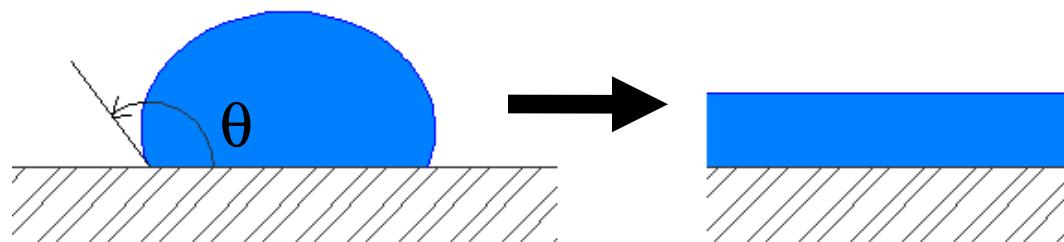
Phase Diagram of Generic Liquid



Cahn's General Theoretical Prediction:

Cahn, J. Phys. Chem., 66, 3667 (1977); Ebner, and Saam, PRL, 38, 1486 (1977); Cheng, Cole, Saam, and Treiner, PRL, 67, 1007 (1991); Cheng, Cole, Dupont-Roc, Saam, and Treiner, RMP, 65, 557 (1993).

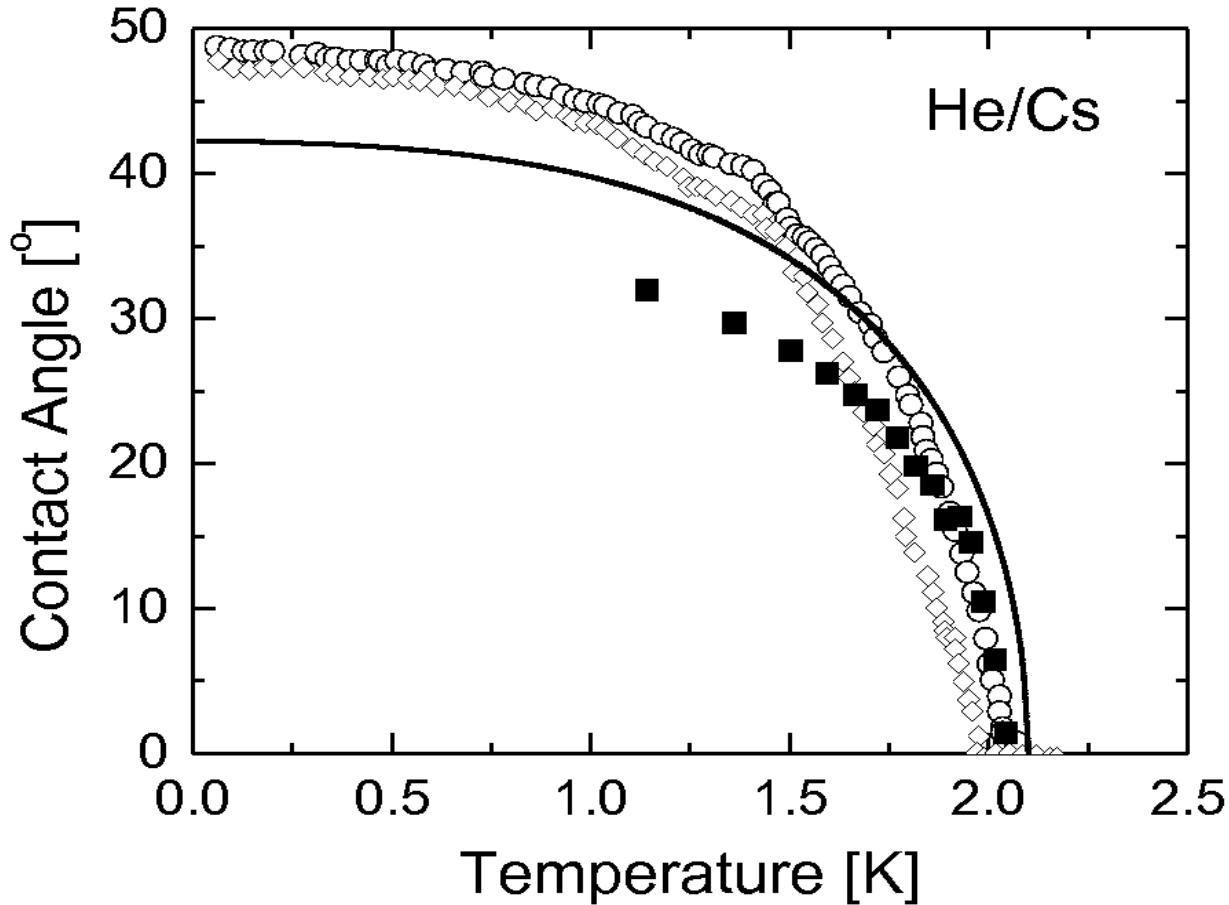
If a liquid does not wet a solid surface at low temperature, then eventually as we increase the temperature there will be a transition to complete wetting at a certain wetting temperature T_w .



All hydrophobic surfaces should become hydrophilic at sufficiently high temperature!

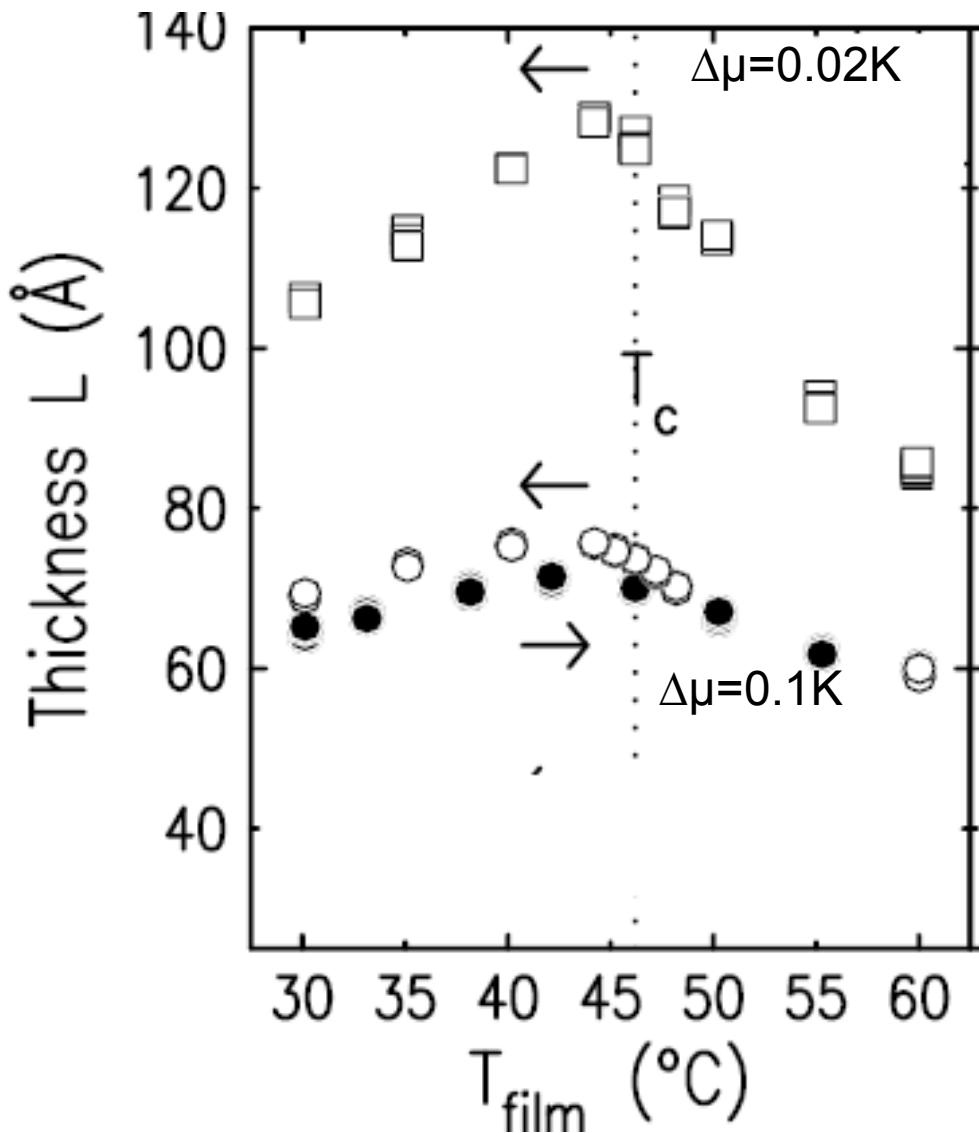
Formula agrees with experimental data

That exists for ${}^4\text{He}$ on Cs at low temp.

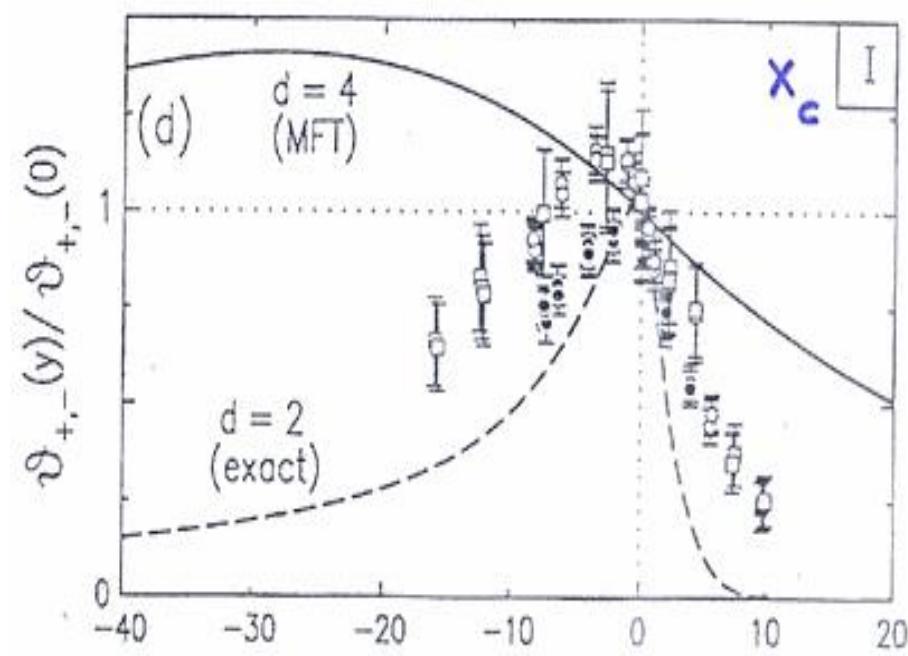
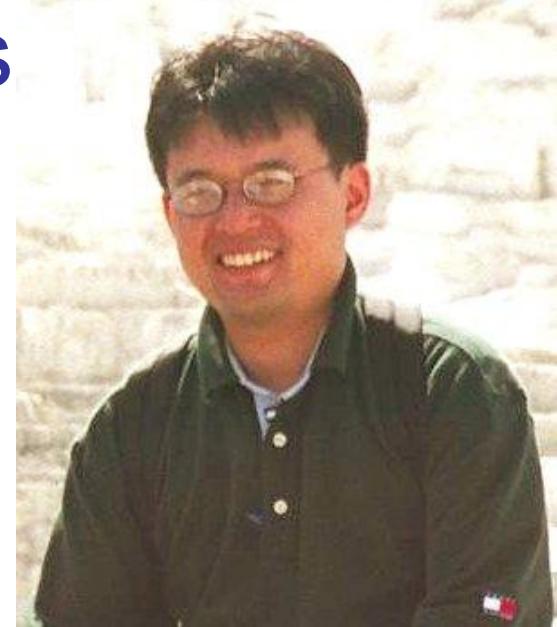


**Analysis of data
taken from D.
Ross et al., JLTP
111, 1 (1988); and
Klier et al., PRL
75, 3709 (1995).**

Cas. in Binary Mix. Films

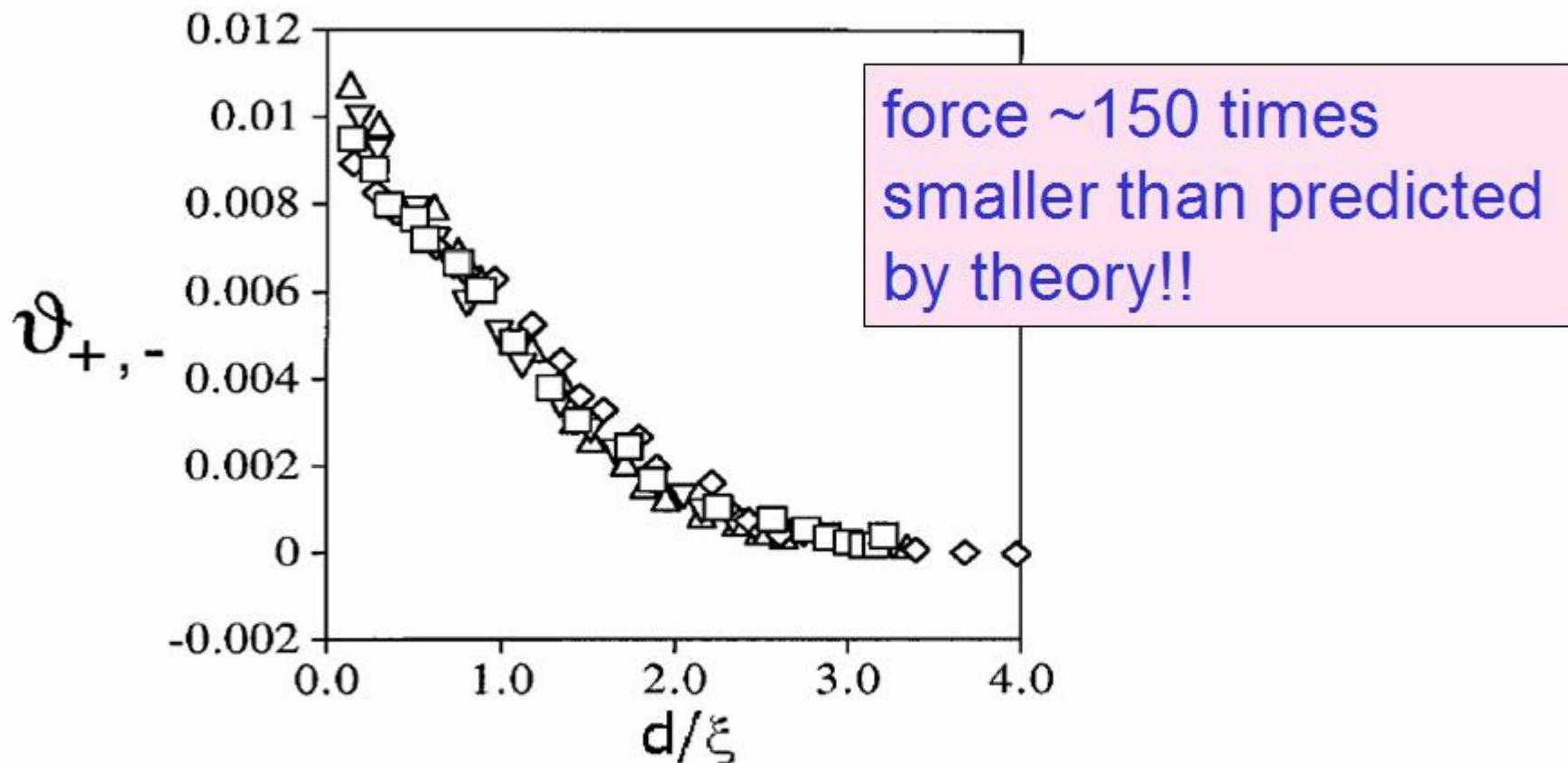


M. Fukuto et al.
Phys. Rev. Lett.
94, 135702
(2005), C.
Hertlein, *Nature*
451, 172 (2008).



O. Vasilyev et al EPL **80**, 60009 (2007) $y = \pm(L/\xi^+)^{1/\nu} = t(L/\xi_0^+)^{1/\nu}$

Cas. force measured in methanol-hexane mixture films

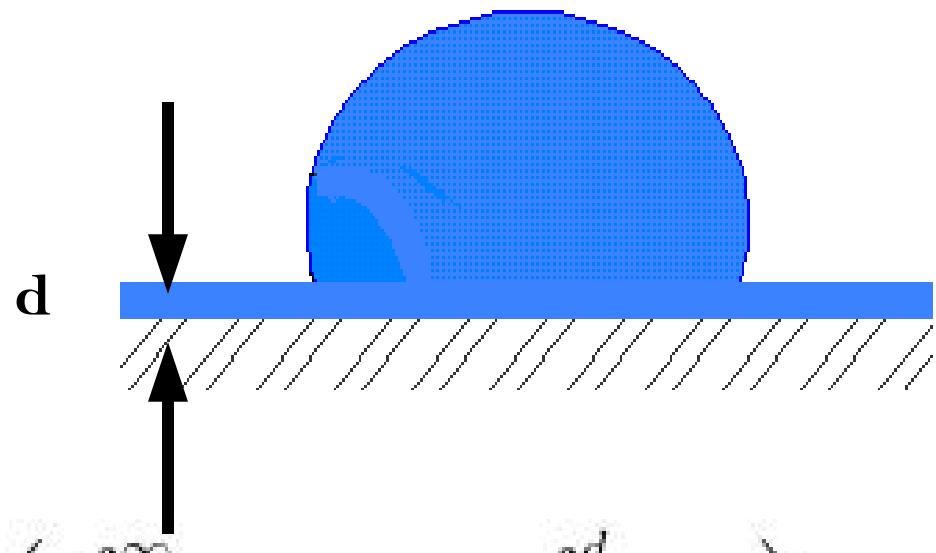


A. Mukopadhyay and B. M. Law, *Phys. Rev. Lett.* 83, 772 (1999).

Hypothesis:

- Perhaps the discrepancy between the Law experiment and theory is due to an underlying wetting transition!

More General Expression for Non-negligible Non-wetting Film Thicknesses



$$\cos\theta = -1 - \frac{\Delta\rho}{\sigma_{lg}} \left(\int_{z_{min}+d}^{\infty} V dz - \int_0^d V_l dz \right)$$

Lothar Schimmele, R. Garcia, S. Dietrich, and Kenneth Osborne, Private Communication

Can we observe Casimir forces
in liquid crystalline films?



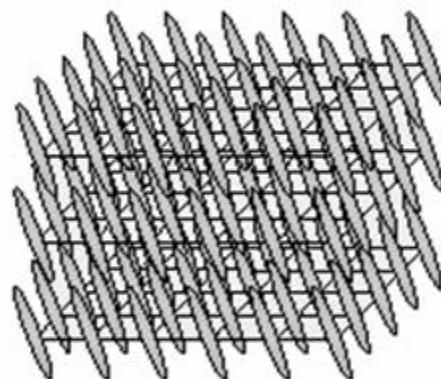
WPI

WPI Experimental Condensed Matter Research

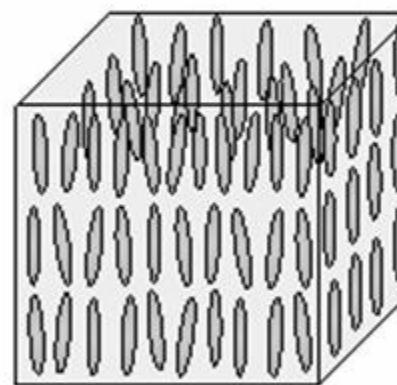
Phases of Cigar-shaped Liquid Crystals

temperature

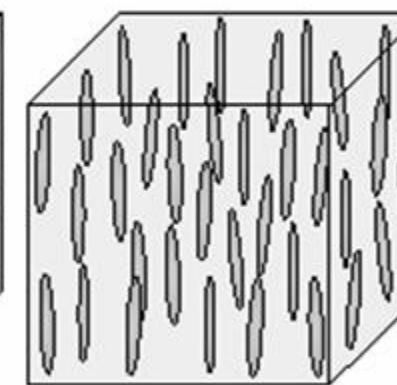
crystal



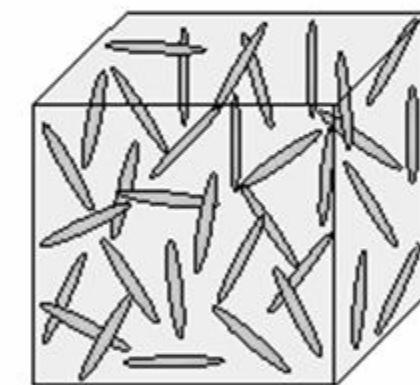
smectic



nematic



isotropic



- 3-D lattice
- orientation
- solid

- 1- (2-)D lattice
- orientation
- fluid

- no lattice
- orientation
- fluid

- no lattice
- no orientation
- fluid

**F. Vandenbrouck, M. P. Valignat, and A. M. Cazabat,
Phys. Rev. Lett. 82, 2693 (1999)**

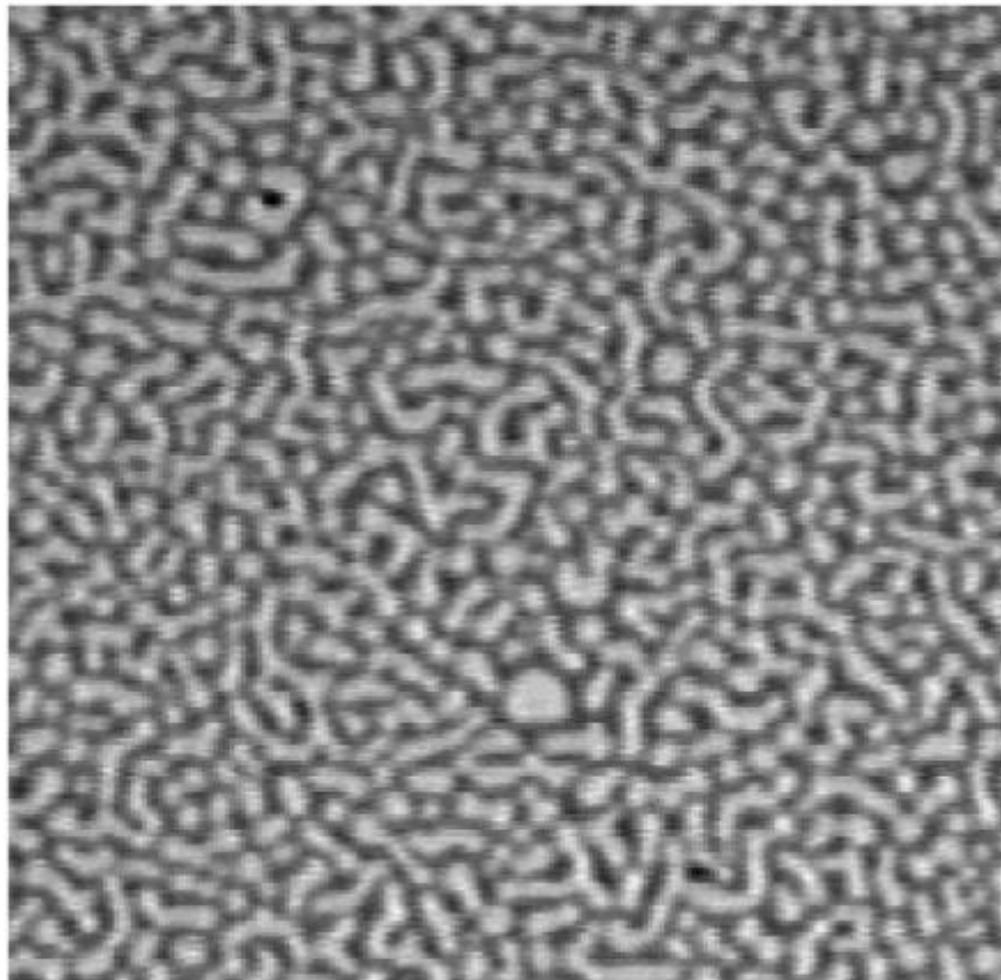
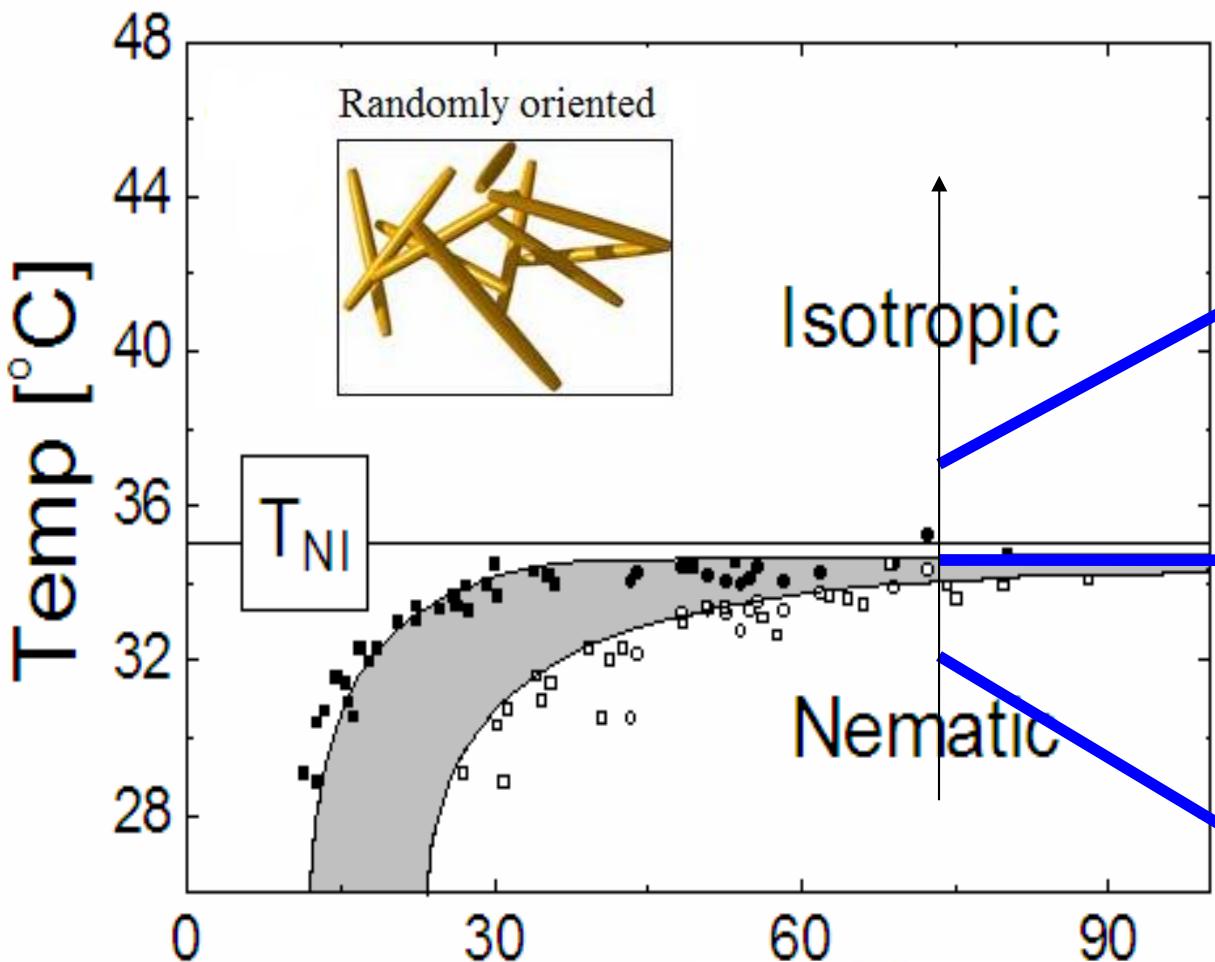
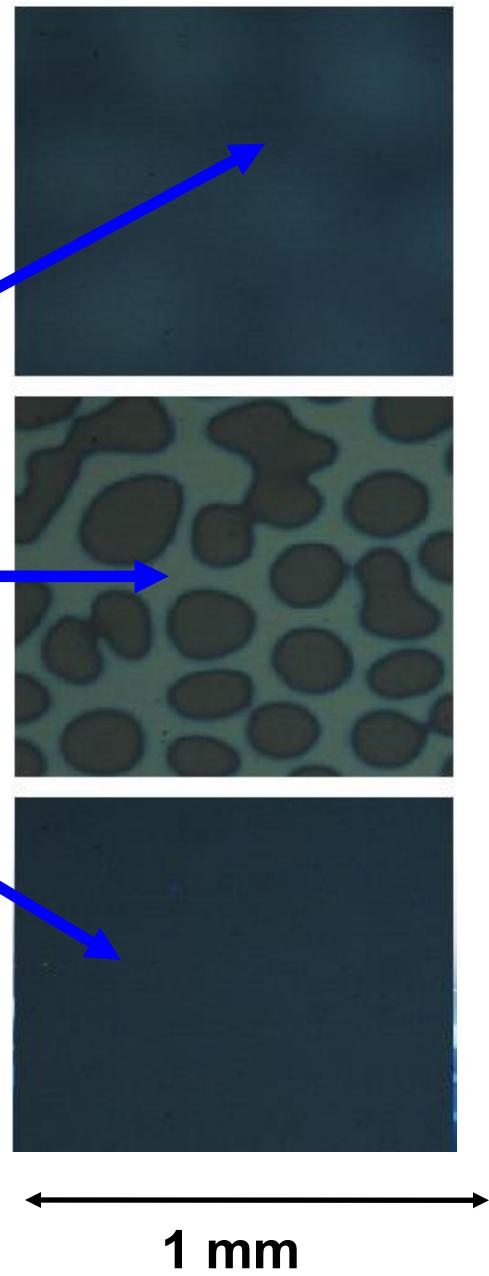


FIG. 1. View of spinodal dewetting of a 42.8-nm-thick film ($T = 33.5 \pm 0.5$ °C). This pattern is reminiscent of those observed in spinodal decomposition studies. The image size is $460 \mu\text{m} \times 460 \mu\text{m}$.



D. van Effenterre et al.,
Phys. Rev. Lett. 87,
125701 (2001)

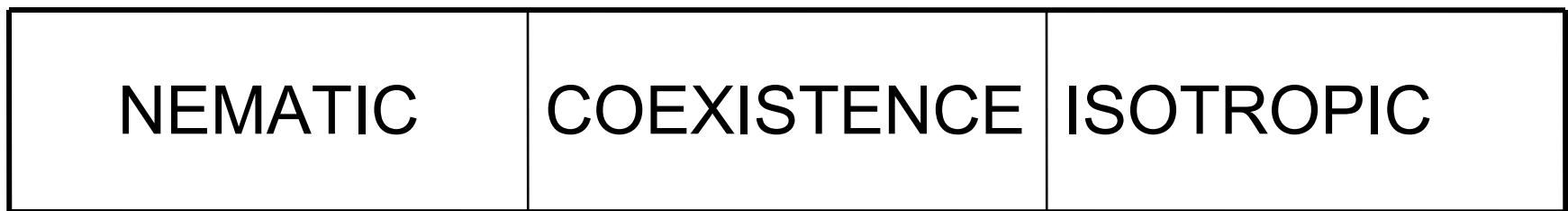
Aligned along a direction



Coexistence Region ($d \sim 60\text{nm}$)

33.558 C

5CB Transition Behavior for films ~20-100nm



Temperature

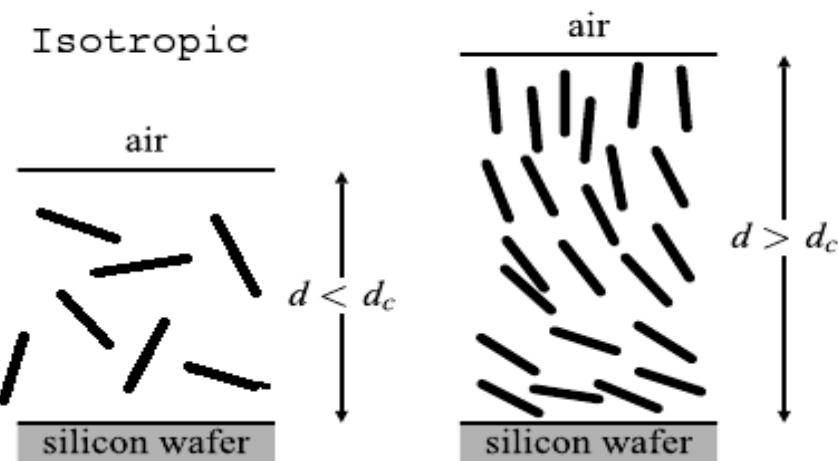
Proposed Explanation

$$F - \mu V = f_1 V_1 + \sigma_1 A_1 + \frac{H}{2d_1^2} A_1 + f_2 V_2 + \sigma_2 A_2 + \frac{H}{2d_2^2} A_2 + \frac{K\Delta\theta^2}{2d_2} A_2 - \mu(V_f + V_B)$$

$$\frac{\partial F}{\partial d} = 0$$

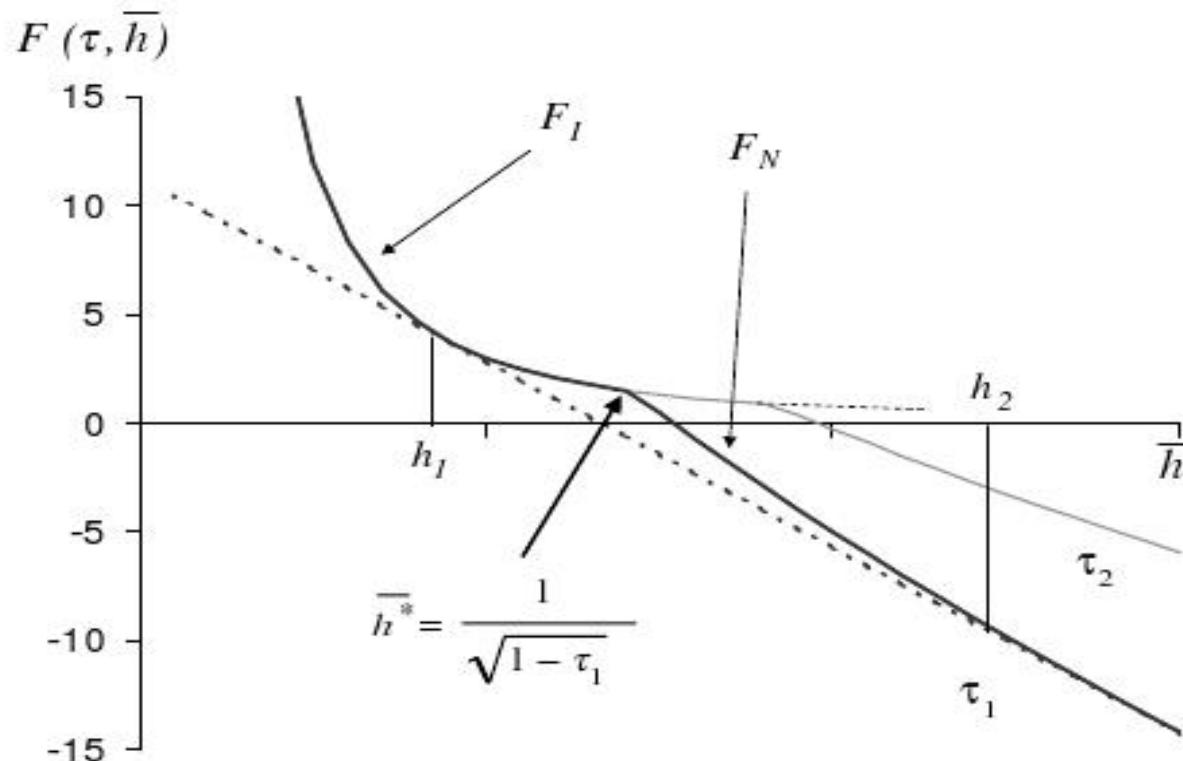
$$\Rightarrow \frac{H}{d_1^3} - \frac{H}{d_2^3} = (f_1 - f_2) + \frac{K\Delta\theta^2}{2d_2^2}$$

Nematic

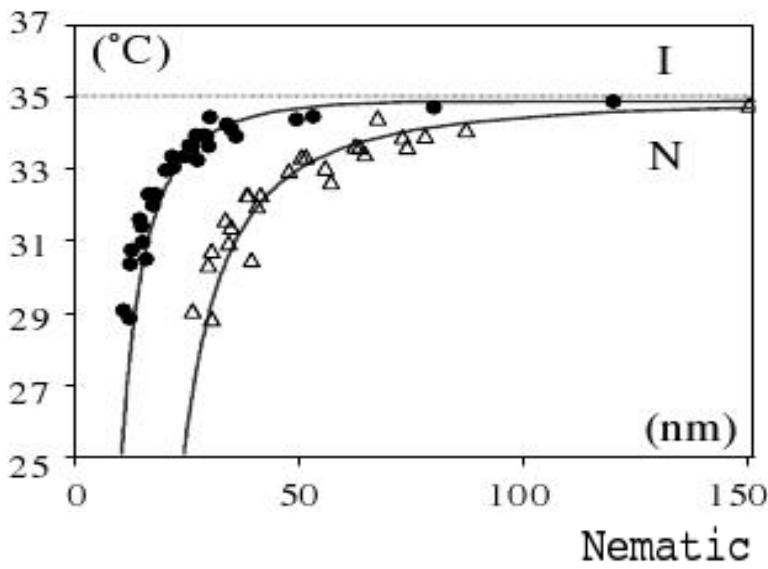


Proposed Explanation

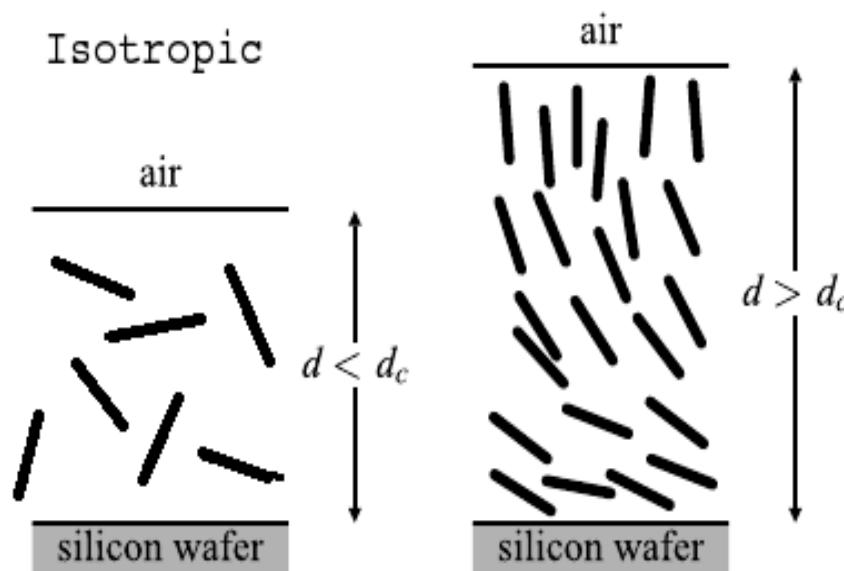
$$F - \mu V = f_1 V_1 + \sigma_1 A_1 + \frac{H}{2d_1^2} A_1 + f_2 V_2 + \sigma_2 A_2 + \frac{H}{2d_2^2} A_2 + \frac{K\Delta\theta^2}{2d_2} A_2 - \mu(V_f + V_B)$$



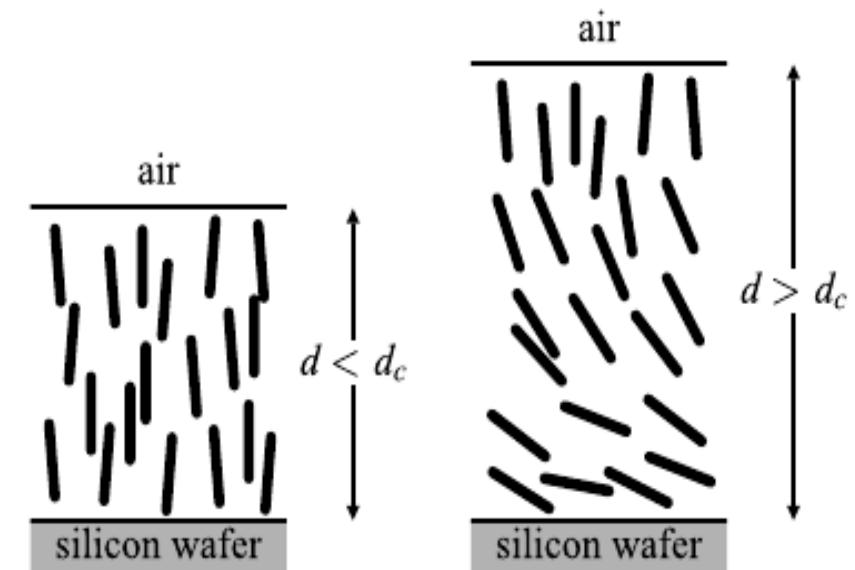
D. van Effenterre and M. P. Valignat
Eur. Phys. Lett. 62, 526 (2003)



Controversy



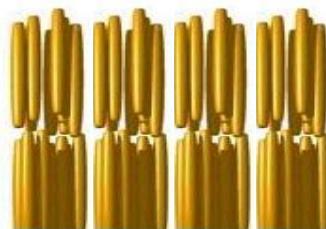
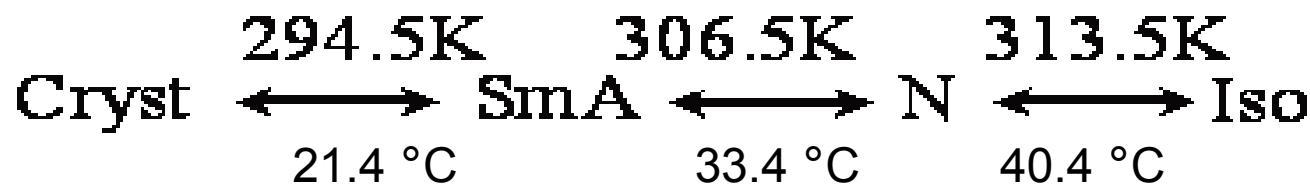
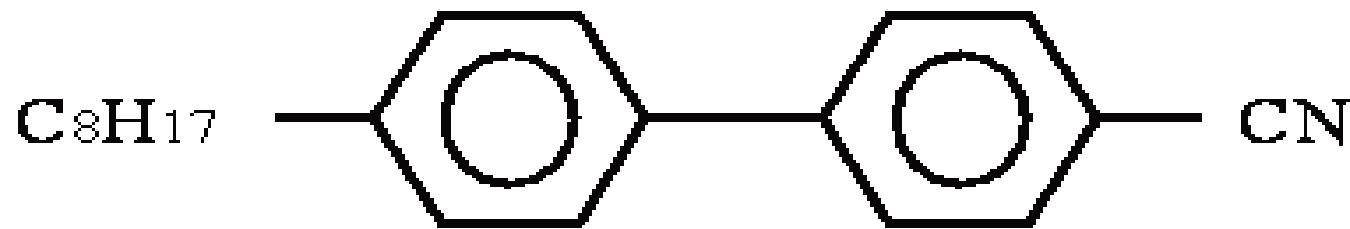
D. van Effenterre and M. P.
Valignat, Eur. Phys. Lett. 62,
526 (2003)



P. Ziherl and S. Zumer, Eur.
Phys. J. E., 12, 61 (2003)

Liquid Crystal 8CB

4-cyano-4'-octylbiphenyl



SmecticA

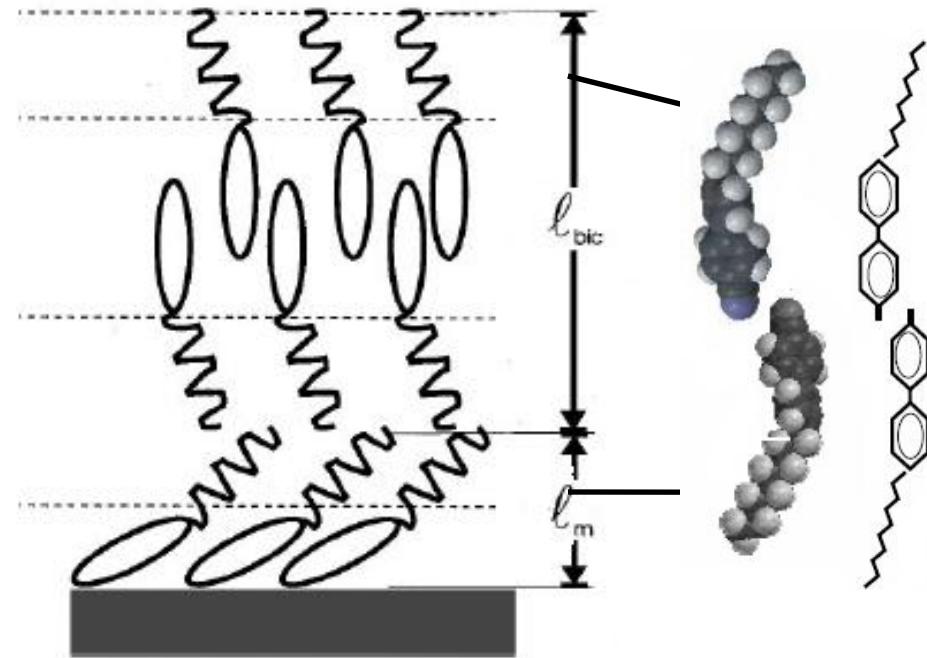
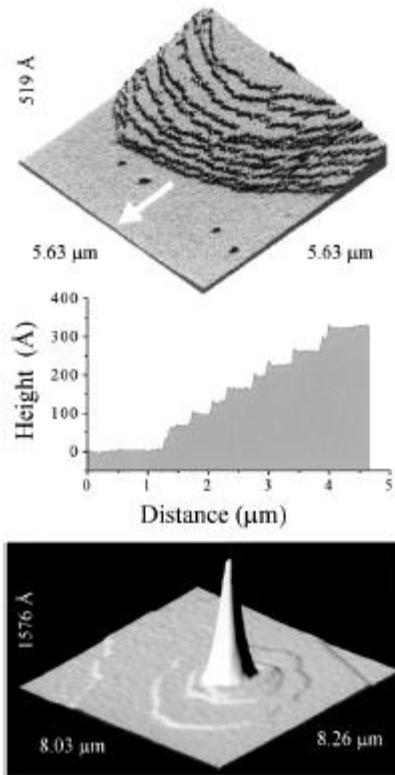


Nematic



Isotropic

8CB on Silicon Surfaces



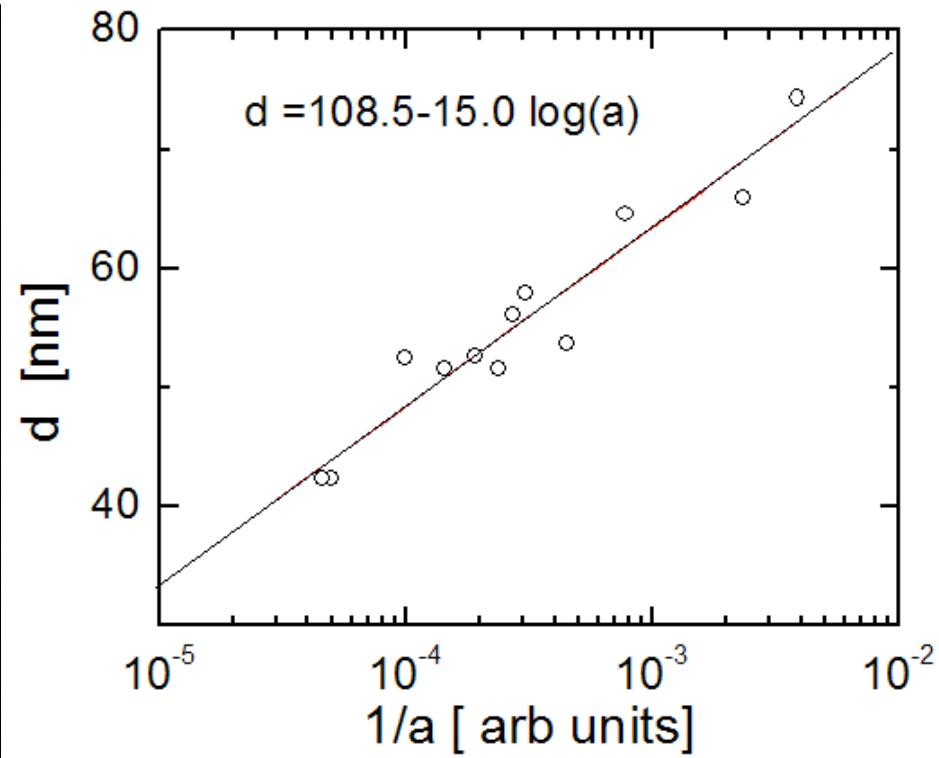
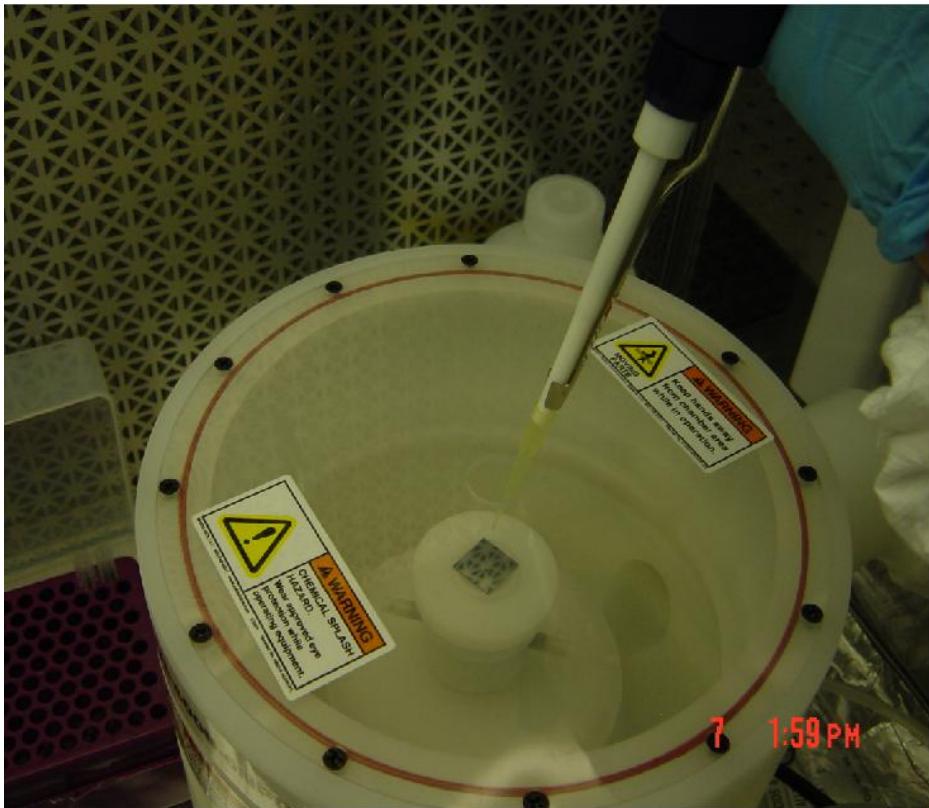
→Layer-by-layer spreading
-2 nm/sec
-32 Å

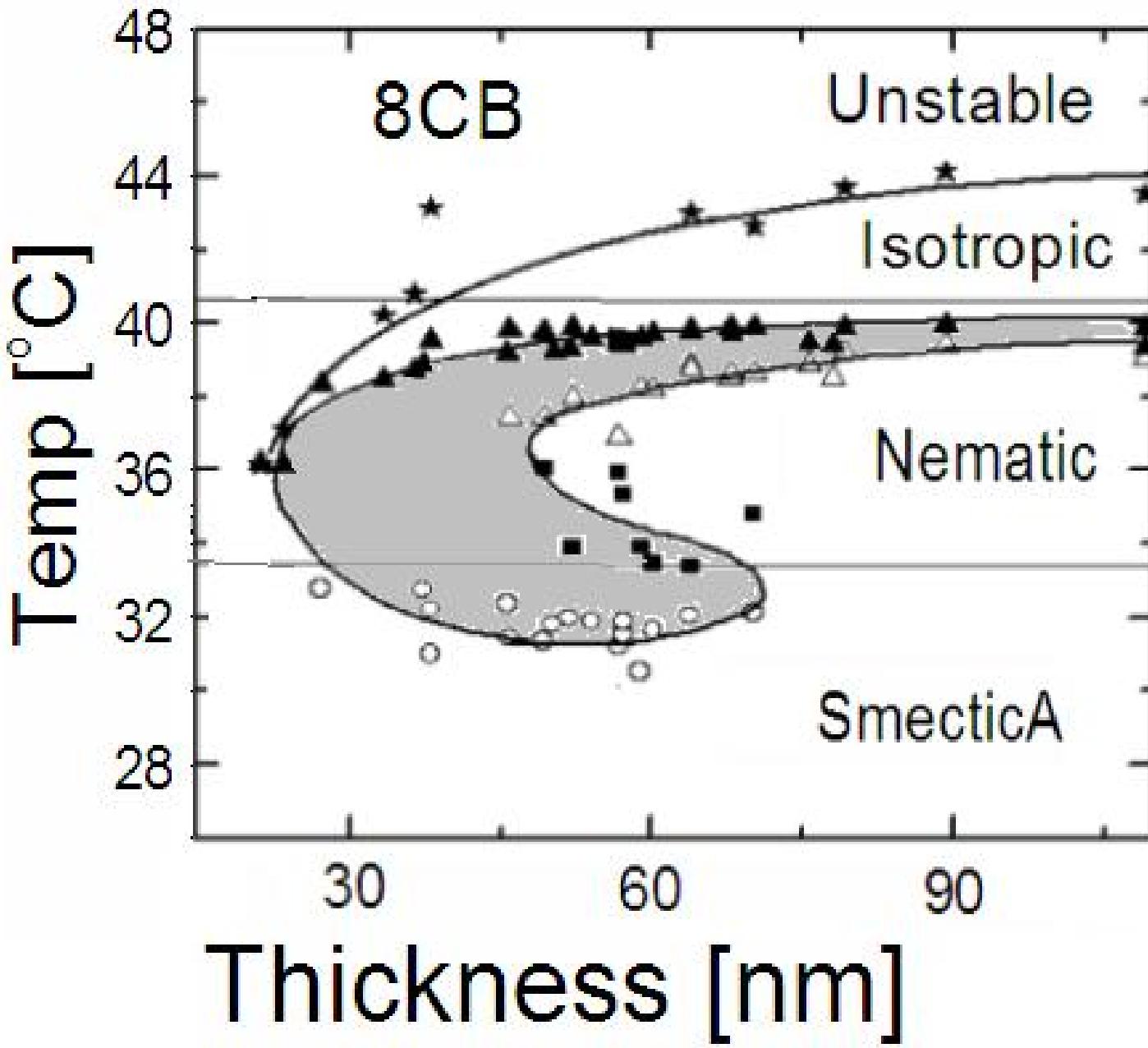
L. Xu, M. Salmeron, S. Bardon
Phys. Rev. Lett. **84**, 1519 (2000)

→Trilayer ordering
-Monomer
-Dimer

-S.Bardon, et. al. Phys. Rev. E. **59**, 6808 (1999)
-M.Salmeron, *Workshop on Mesoscopic and Nanoscopic Science Using X-Ray Techniques* (2004).

Films were spun cast from a Chloroform solution, where we found the film thickness was determined by the acceleration of the spinner.

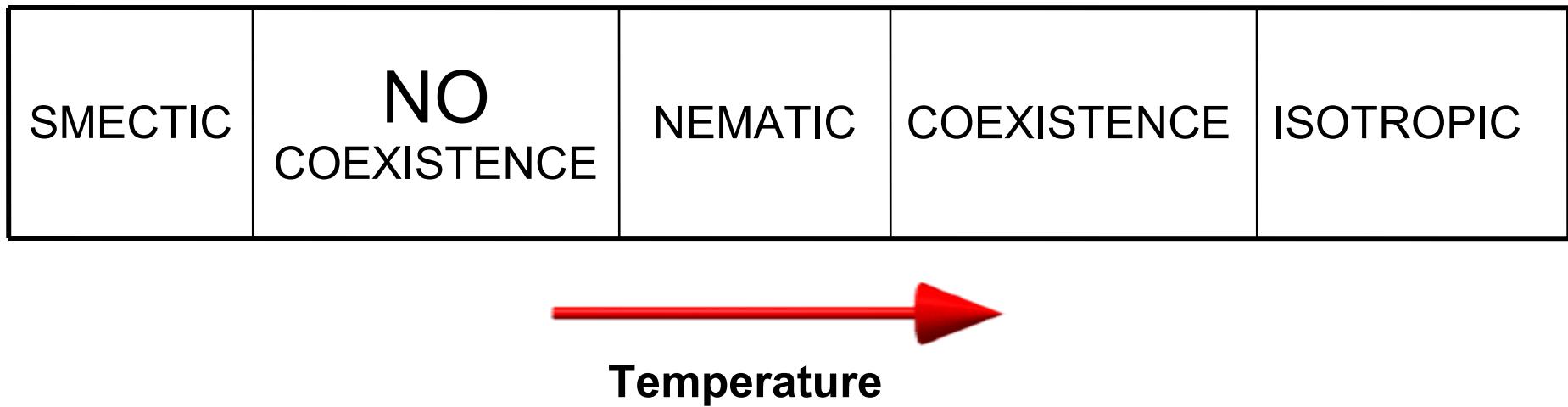




8CB film (thick d~80nm)

28.111C

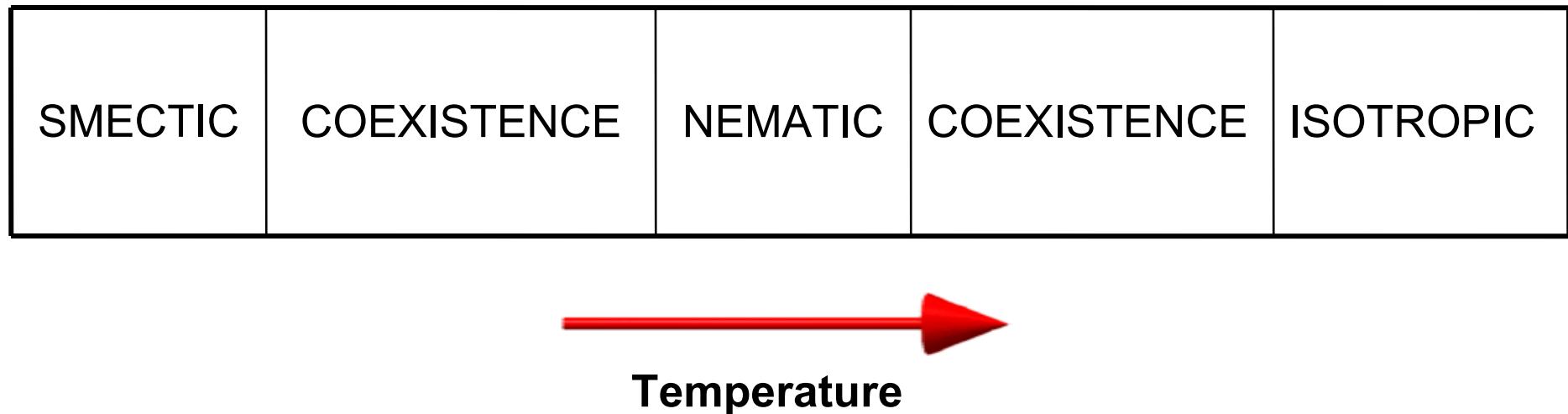
8CB Transition (~80nm)



8CB film (thinner d~50nm)

27.562C

8CB Transition (~50nm)



8CB film (very thin d~30nm)

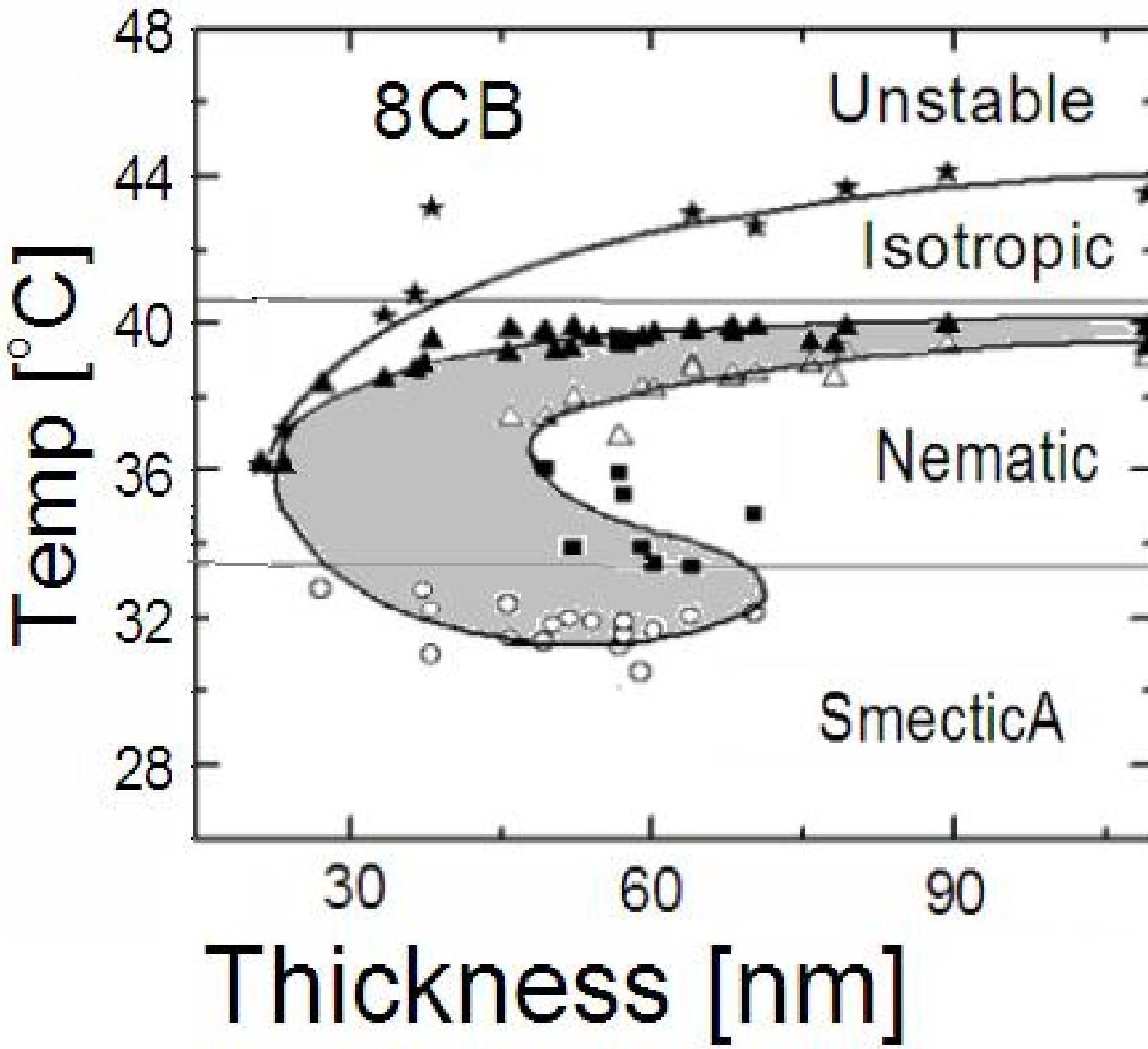
27.716C

8CB Transition (~30nm)

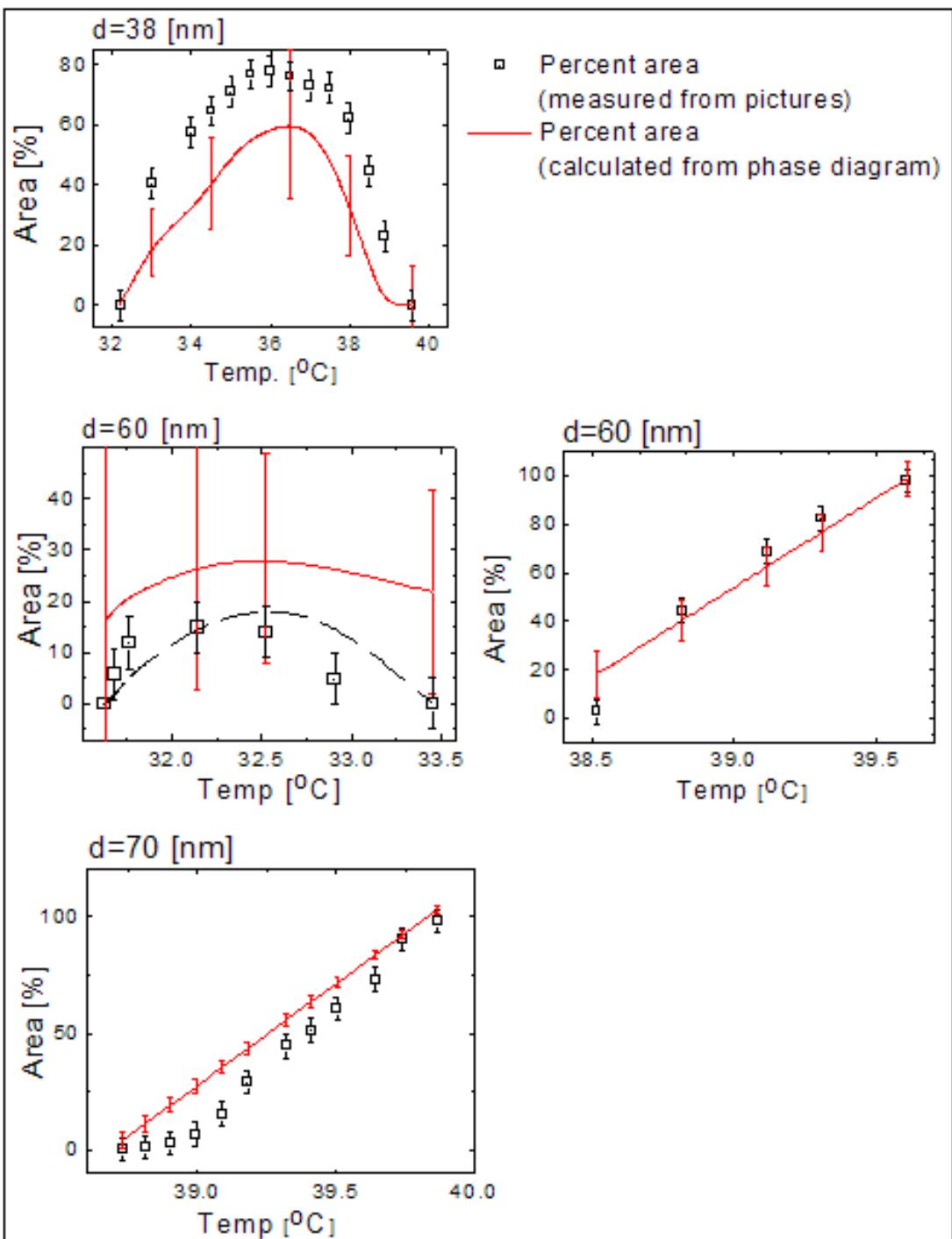
SMECTIC	COEXISTENCE	COEXISTENCE	COEXISTENCE	ISOTROPIC
---------	-------------	-------------	-------------	-----------

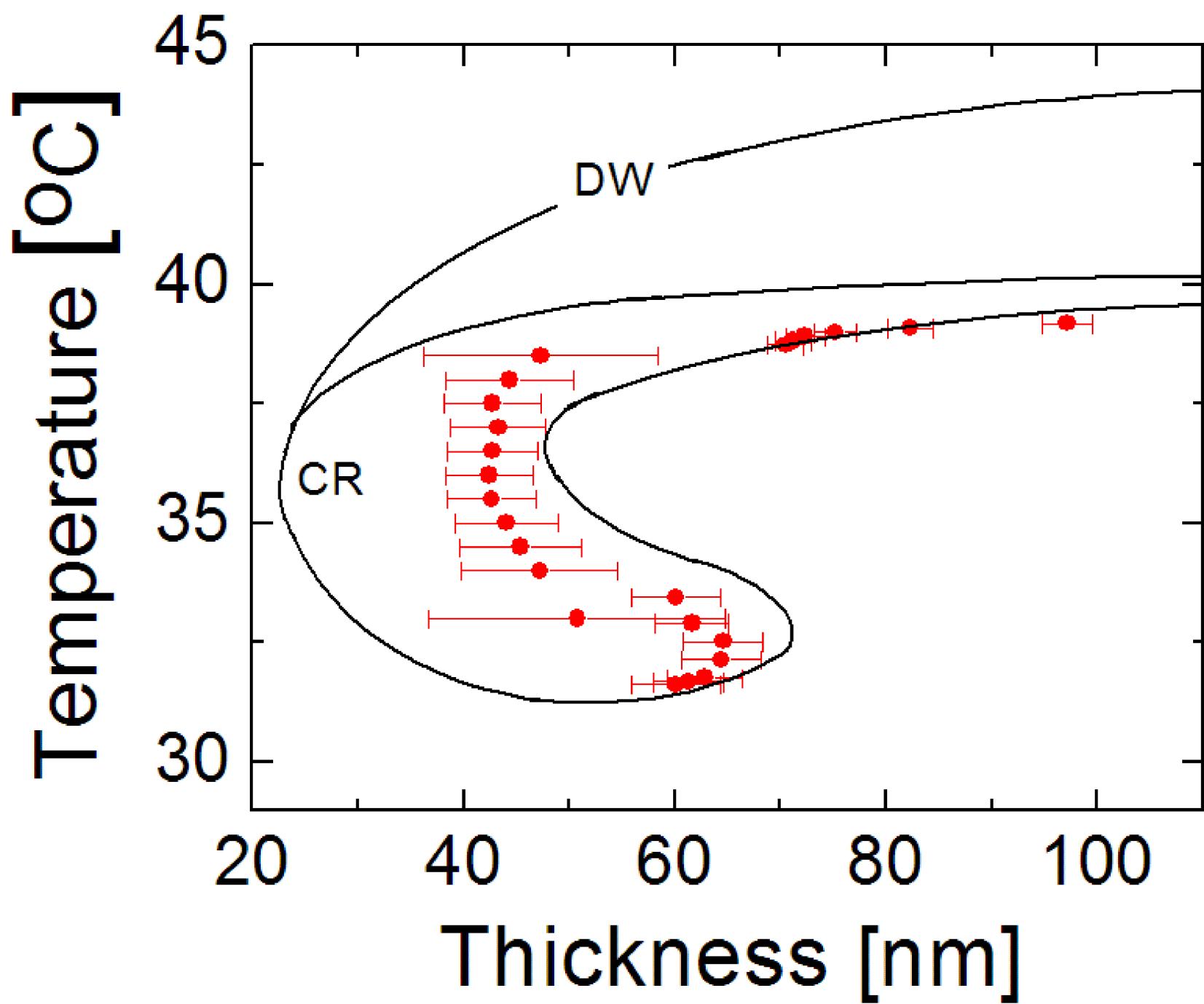


Temperature

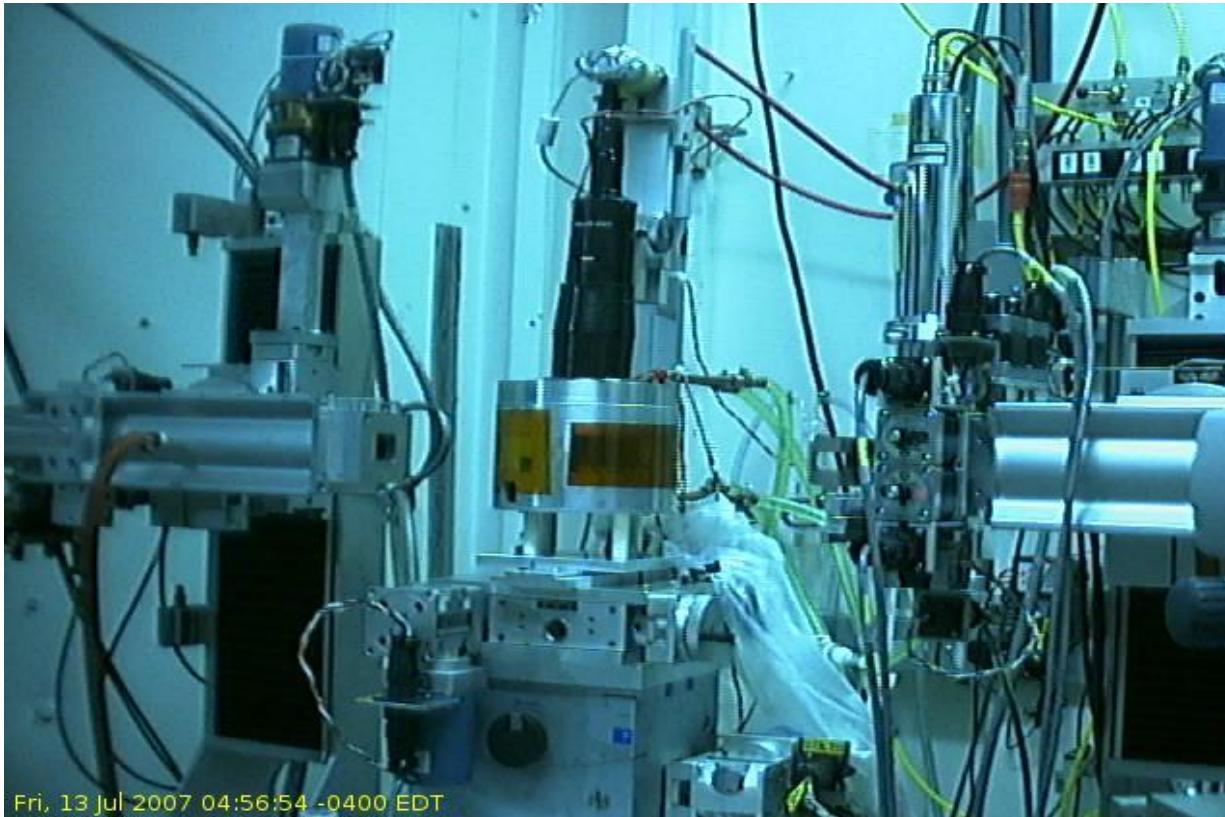


$$d_{\text{avg}} = d_{\text{low}} f_{\text{low}} + d_{\text{high}} f_{\text{high}}$$





Beamline X-22B

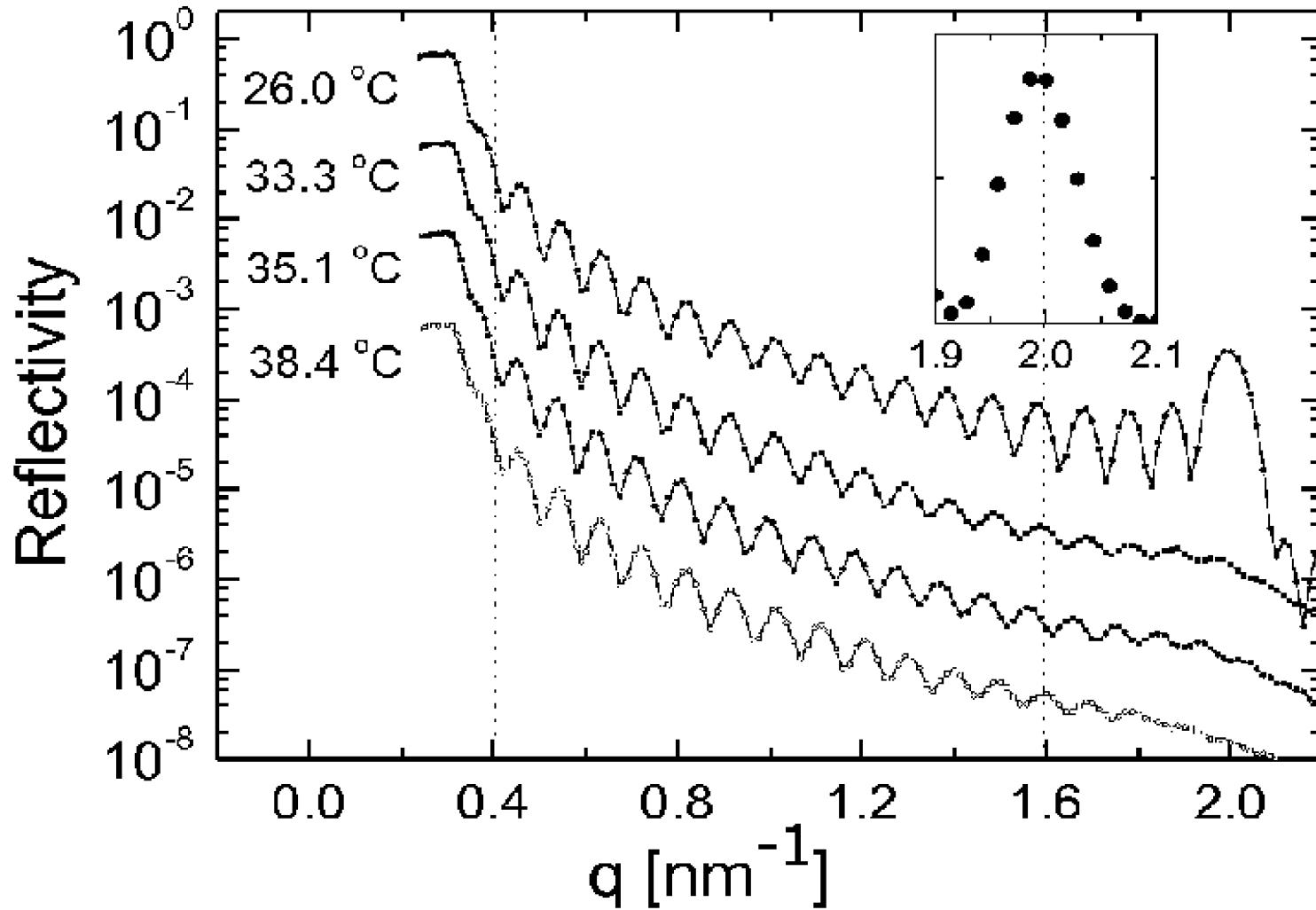


- Optimized for studies of liquid films
- Temperature control, optical window and CCD camera to view film.

Sample X-ray data

Bragg peak
due to smectic
layering

$$d = 2 \pi / \Delta q$$



Work in progress



Conclusions:

- 1. The Nematic to Smectic transition in 8CB has a coexistence region which is not similar to that which had been previously observed near the Isotropic to Nematic transition in 5CB: is it due to Casimir forces?**
- 2. For 8CB films thinner than a critical thickness (~45 nm) there is no uniform nematic phase: coexistence extends from NA to IN temperatures.**
- 3. X-ray measurements will be used to determine the structure and phase of the film at different temperatures.**