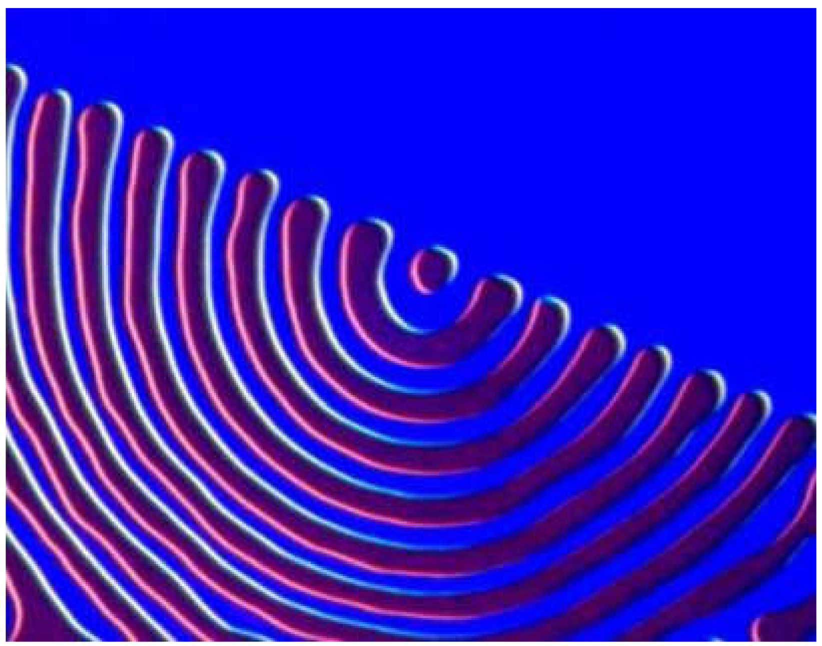
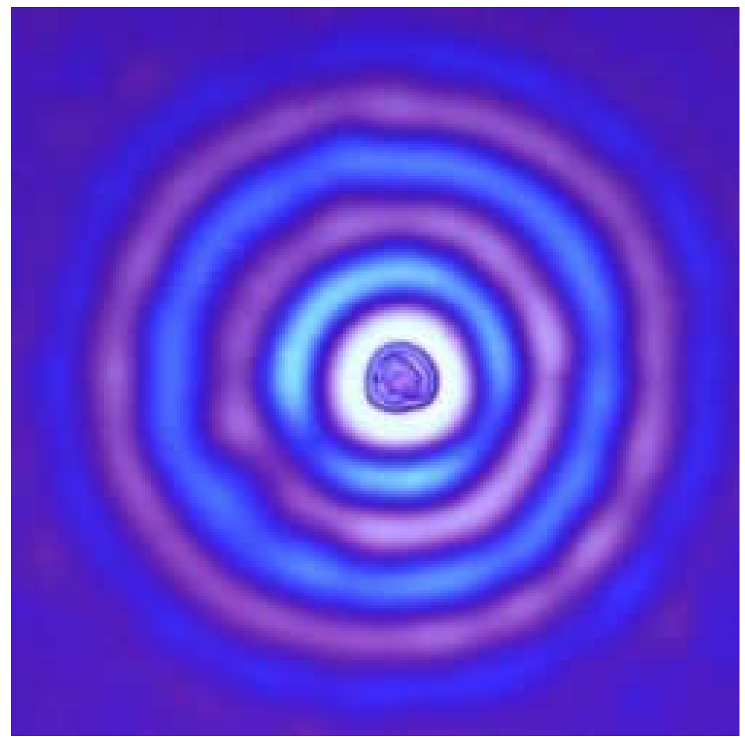
Controlled Pattern Formation In Thin Polymer Films





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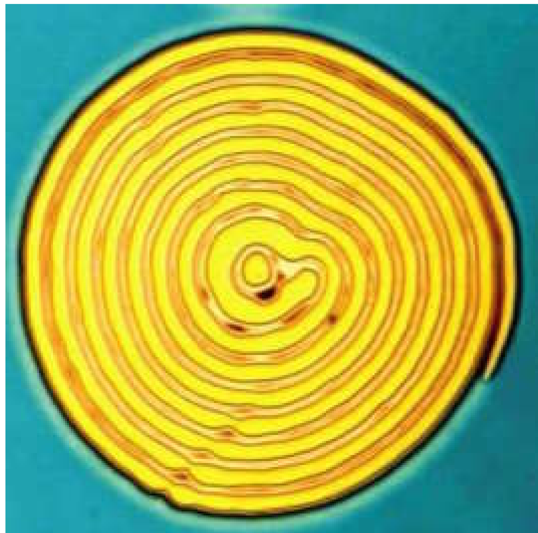
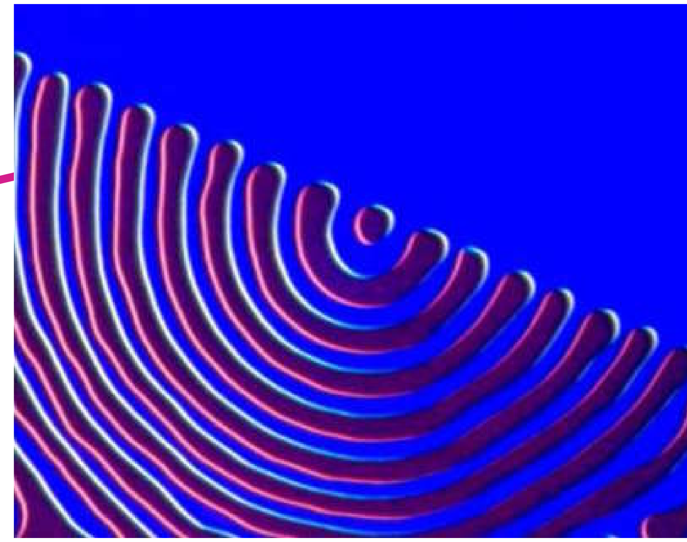
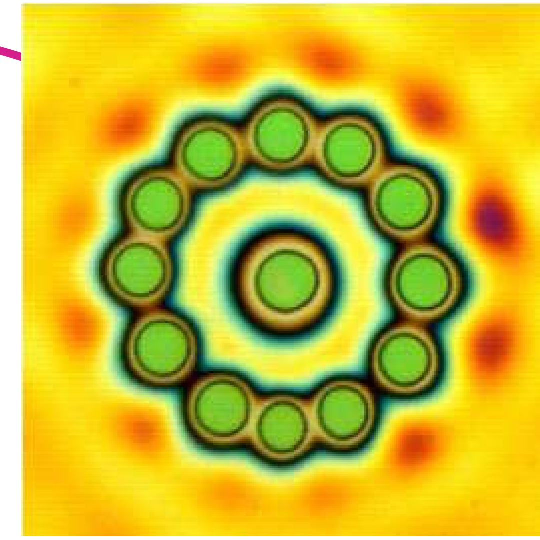
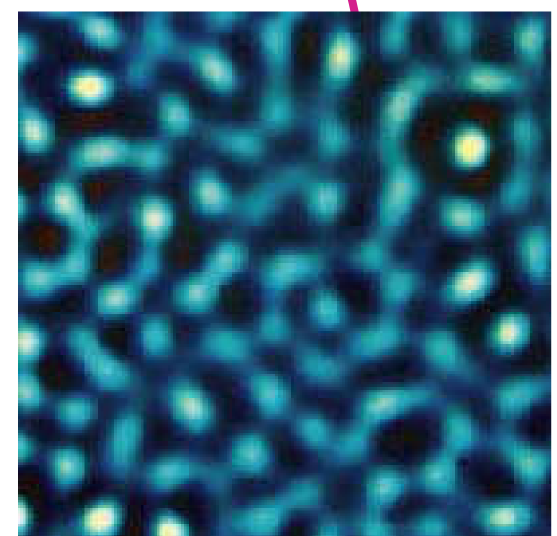
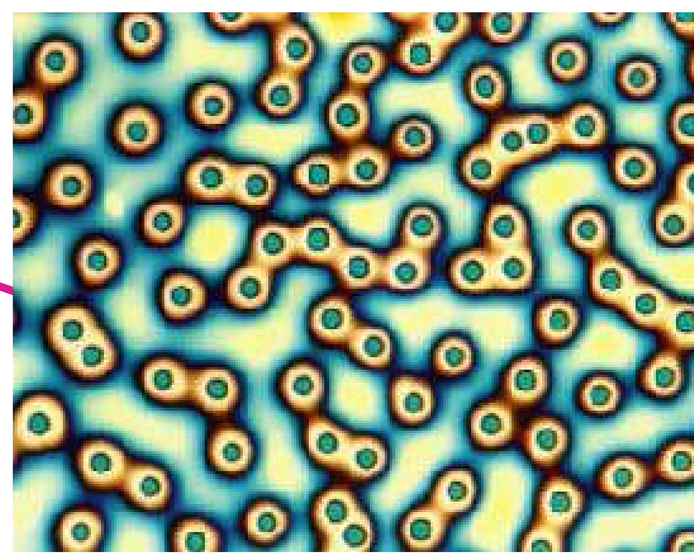


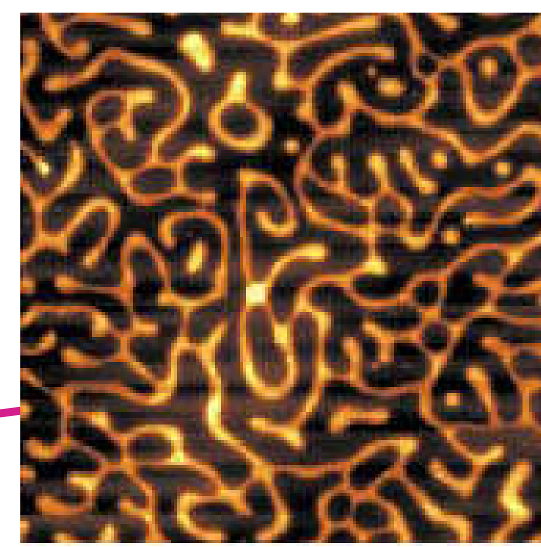




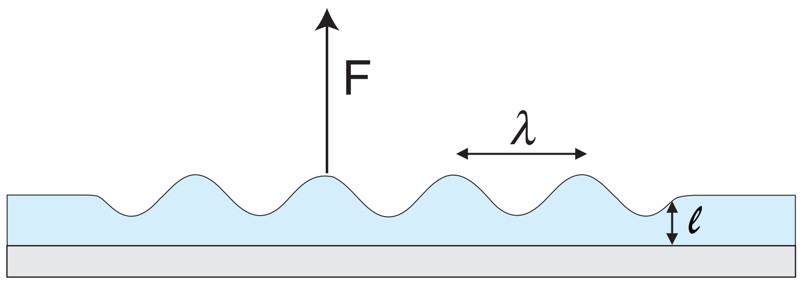
Capillary Instabilities
reflect interfacial forces







Film Instabilities



Fundamental Aspects

- Film Instabilities as "measurement device" for interfacial forces

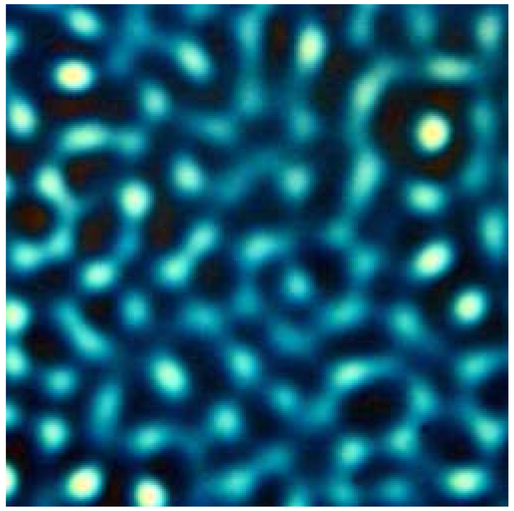
Applied Aspects

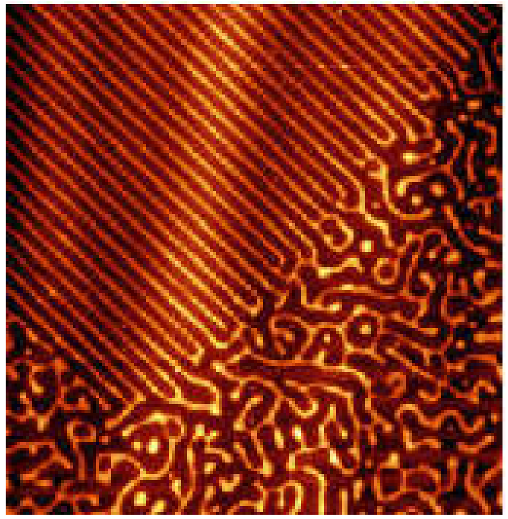
- Pattern Replication
- "Functional" Films:
  - plastic LEDs, electronics, photovoltaics
  - optical layers: anti-reflective coatings, super-opaque coatings, optical band-gap materials
  - Adhesive Surfaces: Gecko Effect
  - Super-hydrophobic surfaces: Lotus Effect

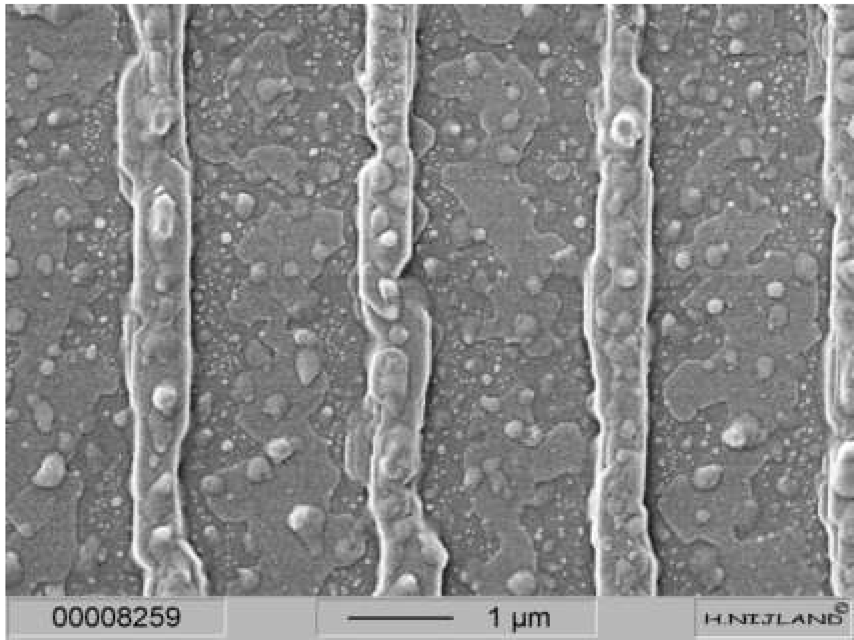
Films: Confined Geometry: small potentials, high fields (1 V over 1 μm = 1 MV/m)

Outline

1. Capillary Instabilities
2. Electrohydrodynamic Instabilities
3. Confinement Induced Forces
4. Film Instabilities Caused by Thermal Noise
5. Temperature Gradients
6. Control of Pattern Formation
7. Polymer Based Ceramics



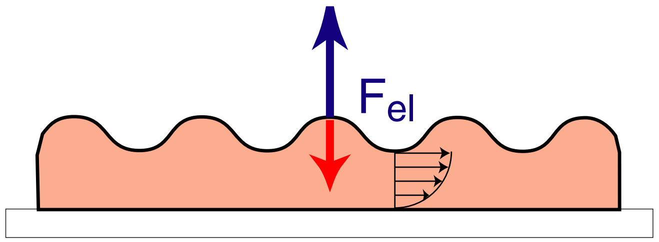




Theory: Linear Stability Analysis

Is a film stable with respect to pertubations (capillary waves)?

- Laplace pressure (surface tension) always stabilizes the film
- An additional force is needed to destabilize the film



1. Sinusoidial Pertubation:

$$h(x,t) = h_0 + u e^{iqx + \frac{t}{\tau}}$$

2. Hydrodynamic Response (Poiseulle Flow):

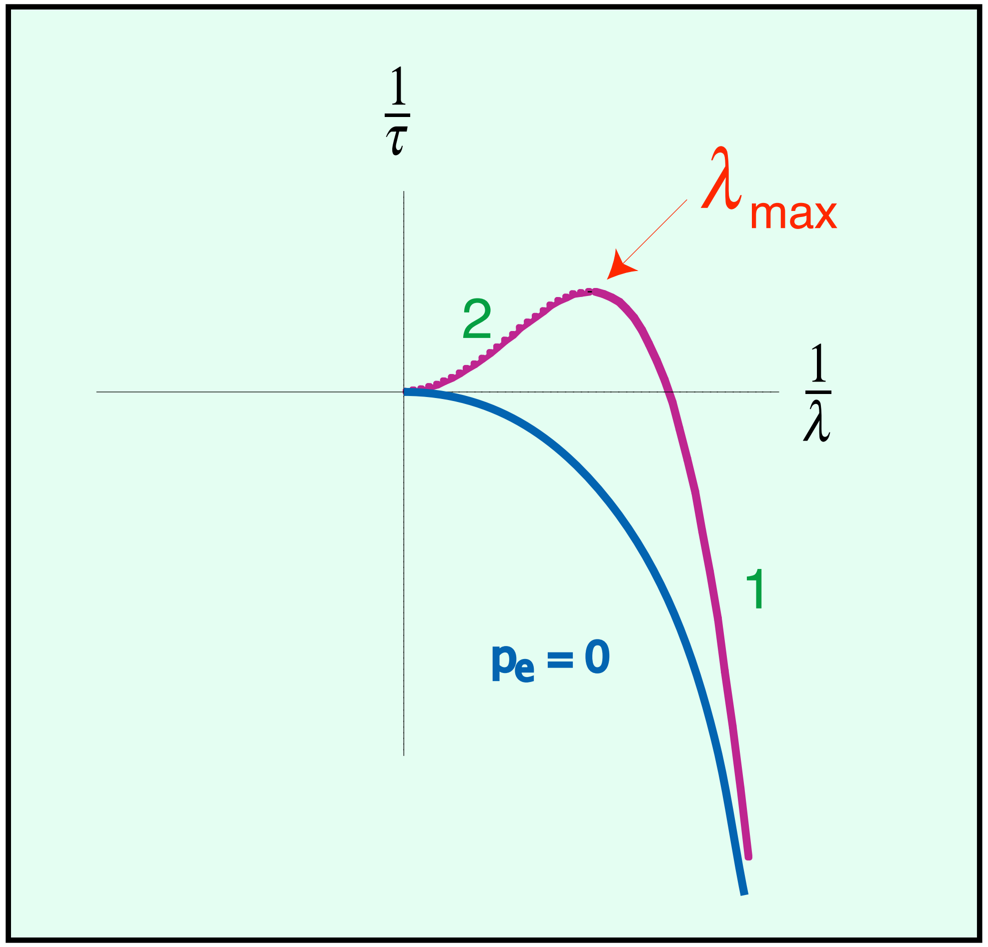
$$j = \frac{h^3}{3\eta}\left(-\frac{\partial p}{\partial x}\right)$$

3. Continuity Equation (Mass conservation):

$$\frac{\partial j}{\partial x} + \frac{\partial h}{\partial t} = 0$$

1. + 2. + 3. –> Differential equation for the hydrodynamic response of a film to an applied force

Linear Stability Analysis



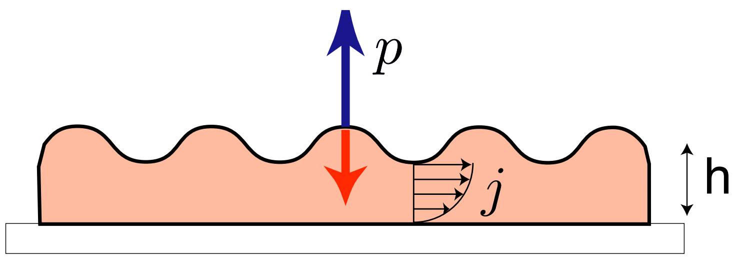
1. short wavelength perturbations: damped by surface tension

2. long wavelength perturbations: slow: viscous damping

λ_{max}: fastest growing mode: compromise between 1 and 2

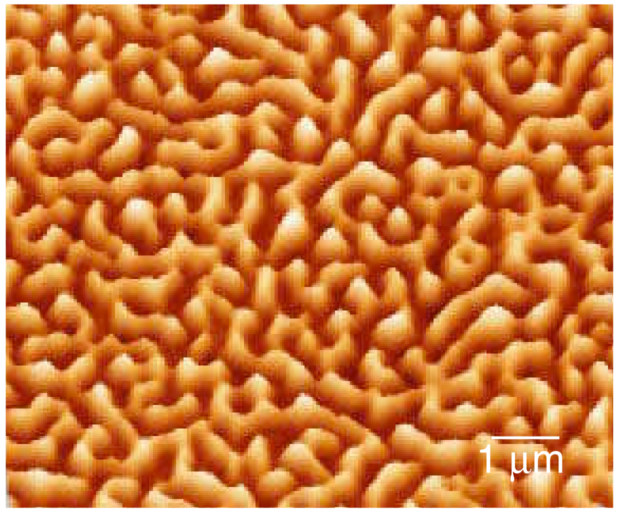
Generic Equation for any pressure p_e:

$$\lambda = 2\pi \sqrt{2\gamma \left(\frac{\partial p_e}{\partial h} \right)^{-1}}$$

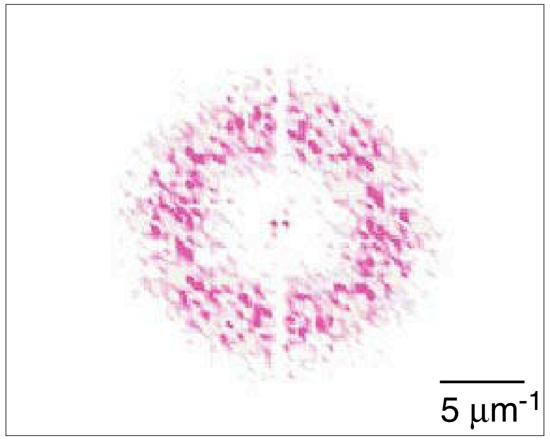


Capillary Instabilities: the Experiment

Capillary Instability



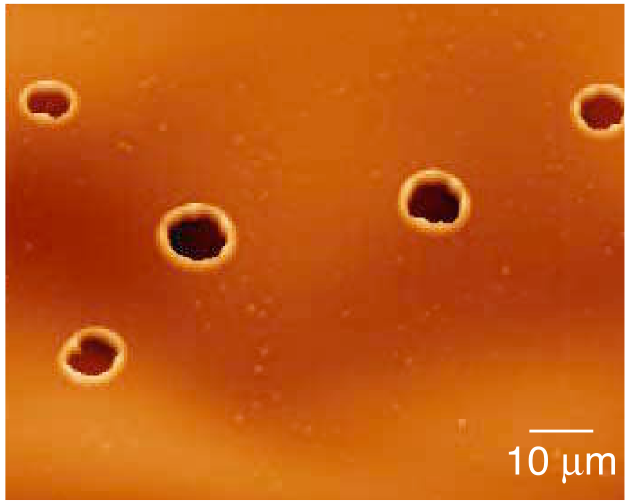
- characteristic wave-pattern
- signature of (a) destabilizing force(s)
- force sensor



$$\lambda = 2\pi\sqrt{2\gamma\left(\frac{\partial p_e}{\partial h}\right)^{-1}}$$

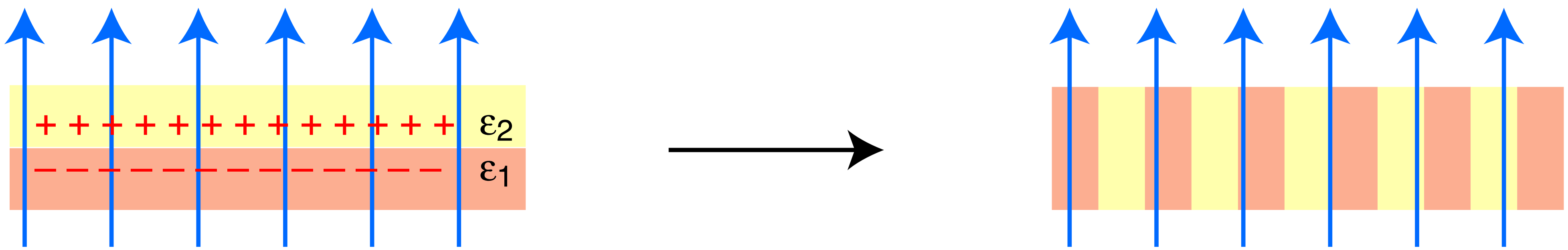
or

Heterogeneous Nucleation



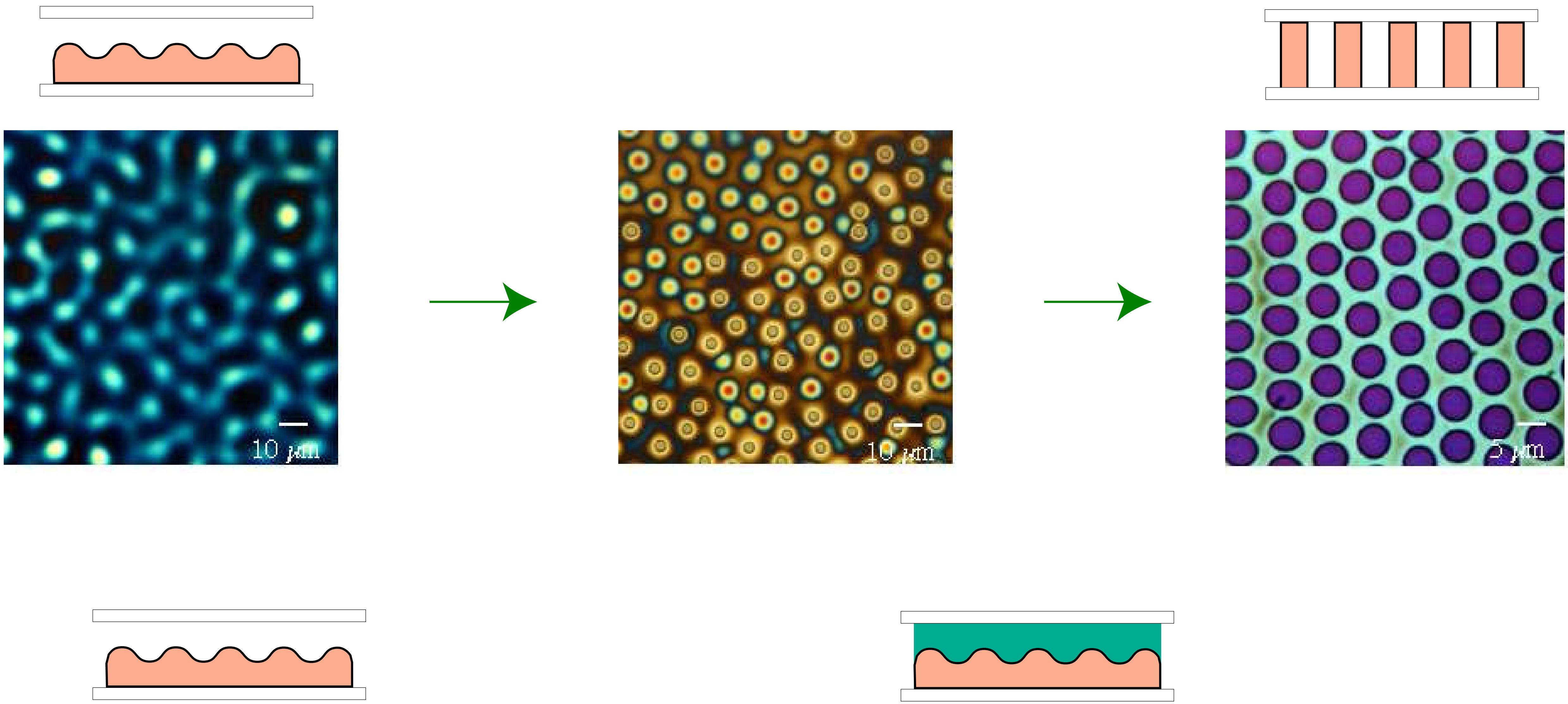
- isolated holes
- causes not fully understood
- difficult to control

Electrically Induced Instability of the Interface



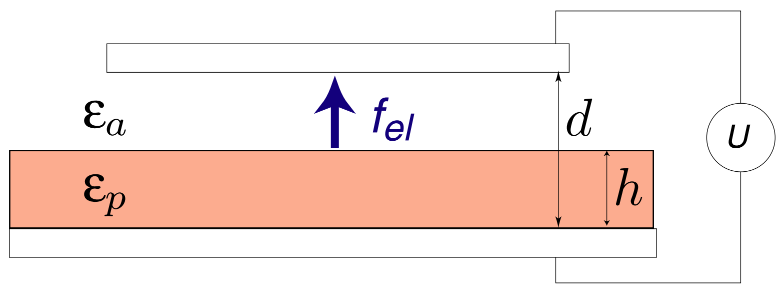
In Cooperation with Tom Russell, Univeristy of Massachusetts at Amherst

Evolution of the Instability



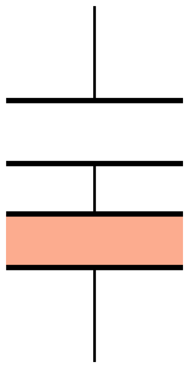
Nature, **403**, 874 (2000)

2 Dielectrics in a Capacitor



Free Energy $\quad F_{el} = \mathrm{Q}\ \mathrm{U} = \frac{1}{2}\, C U^2$

Force $\quad f_{el} = -\frac{\mathrm{d}F_{el}}{\mathrm{d}h} = -\frac{1}{2}\, U^2 \frac{\mathrm{d}C}{\mathrm{d}h}$



Electric Field in the Film: $\quad E_p = \frac{U}{h + \varepsilon_p(d - h)}$

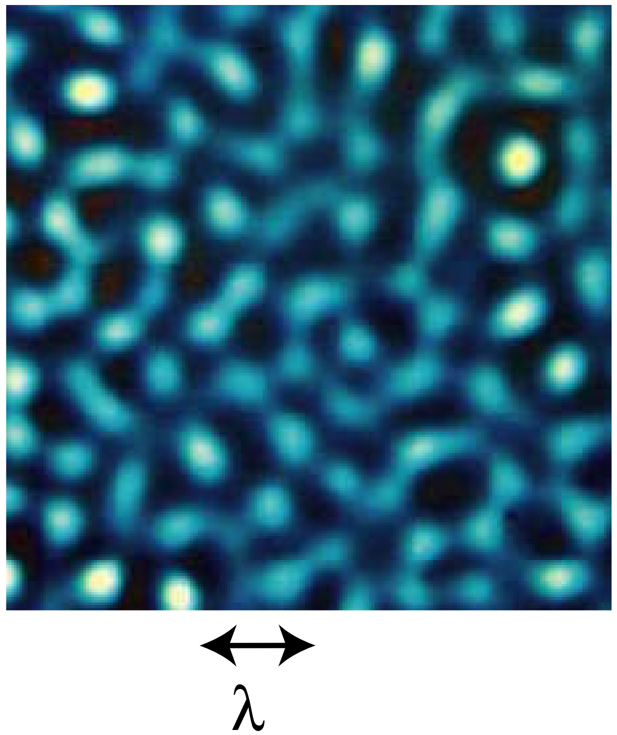
Interfacial Pressure: $\quad p_{el} = \frac{f_{el}}{A} = -\frac{1}{2}\, \varepsilon_0\, \varepsilon_p(\varepsilon_p - 1) E_p^{\,2}$

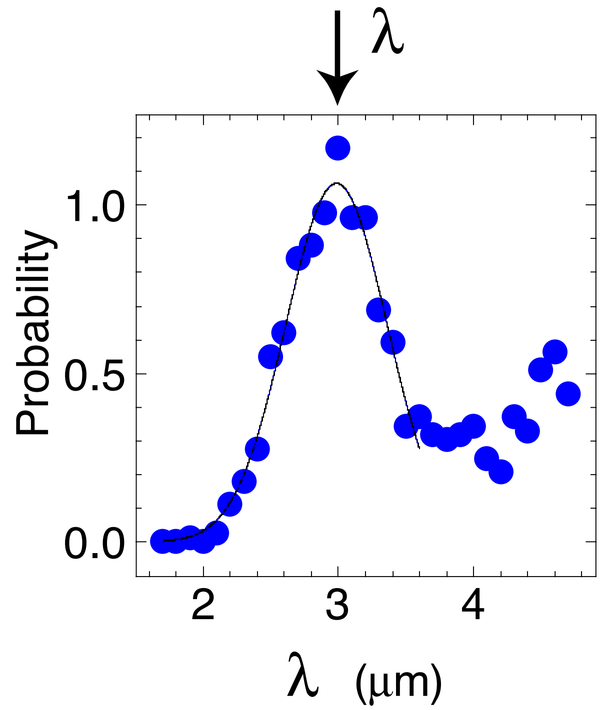
Plug into the generic instability equation:

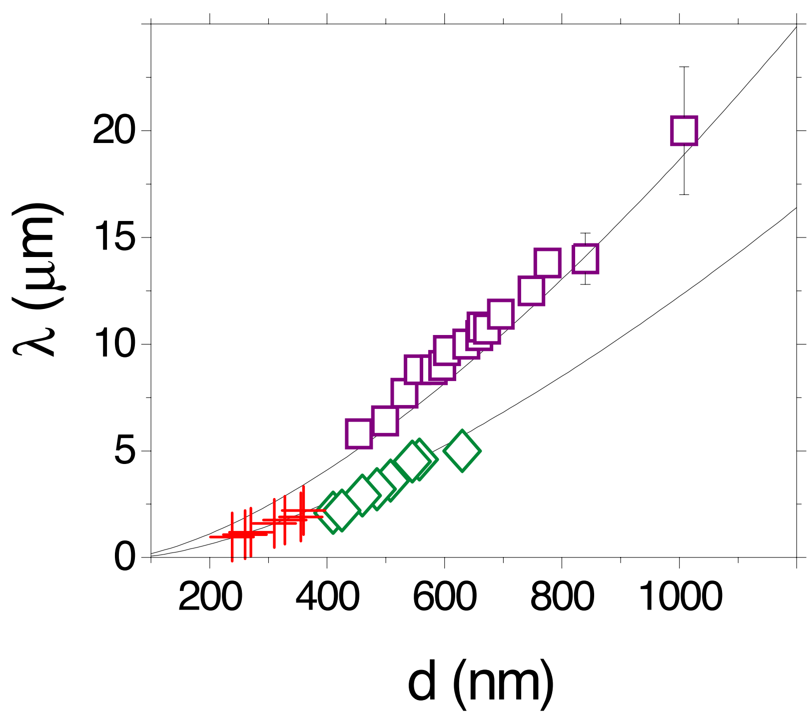
$$\lambda = 2\pi\sqrt{2\gamma\left(\frac{\partial p}{\partial h}\right)^{-1}} = 2\pi\sqrt{\frac{\gamma\, U}{\varepsilon_0\, \varepsilon_p\, (\varepsilon_p - 1)^2}}\quad E_p^{-\frac{3}{2}}$$

Electrohydrodynamic Instability

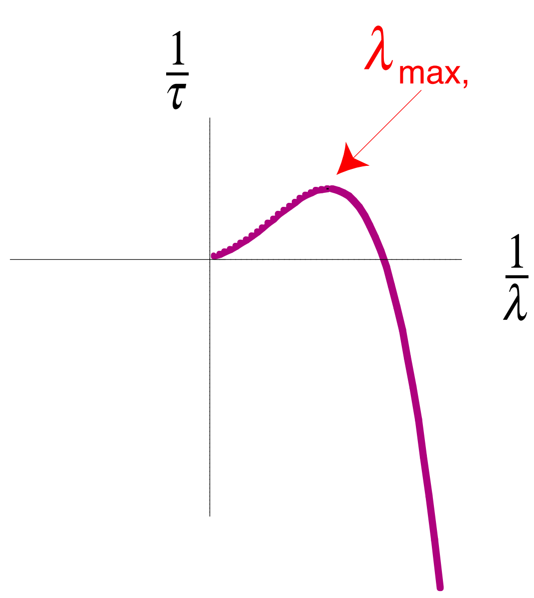
Experiment







Theory



Electrohydrodynamic Instability

Dimensionless Equation:

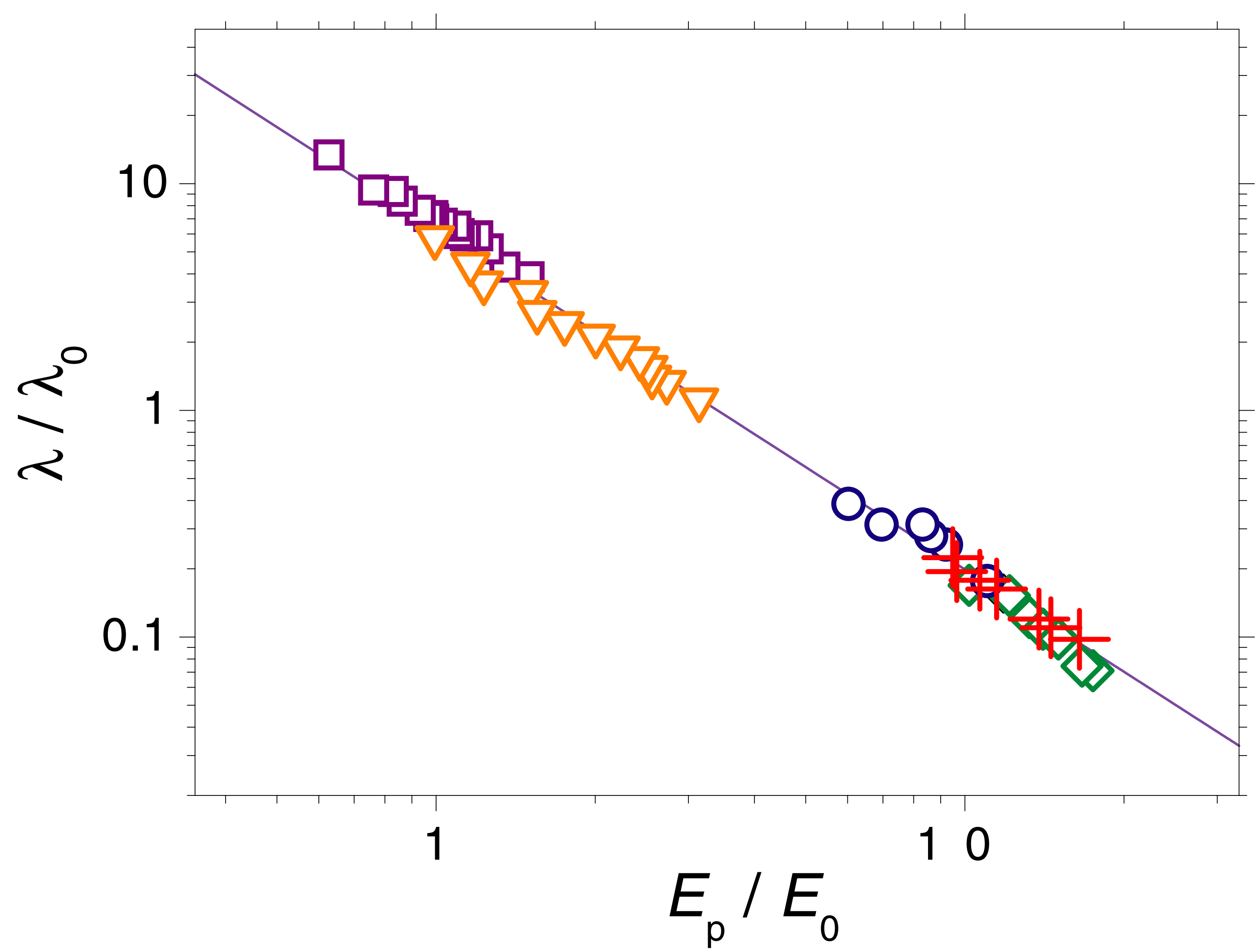
$$\frac{\lambda}{\lambda_0} = 2\,\pi \left(\frac{E_p}{E_0}\right)^{-\frac{3}{2}}$$

All experimental paramters are absorbed into λ_0 and E_0:

$$\lambda_0 = \varepsilon_0 \varepsilon_p \,(\varepsilon_p - 1)^2 \,\frac{U^2}{\gamma}$$

$$E_0 \lambda_0 = U$$

Master Curve:



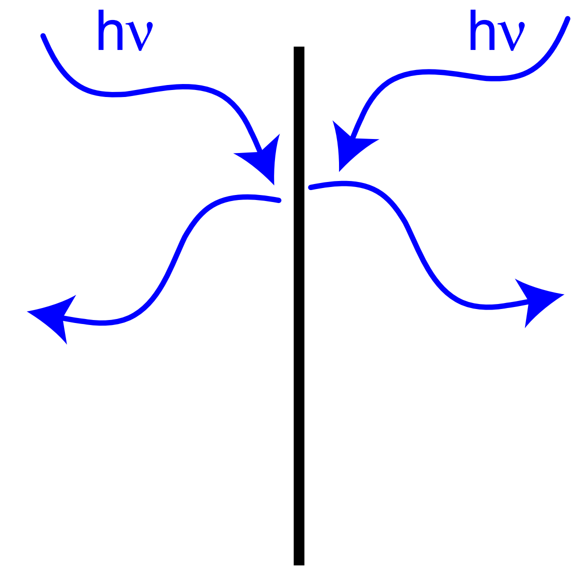
Europhysics Letters **53**, 518 (2001)

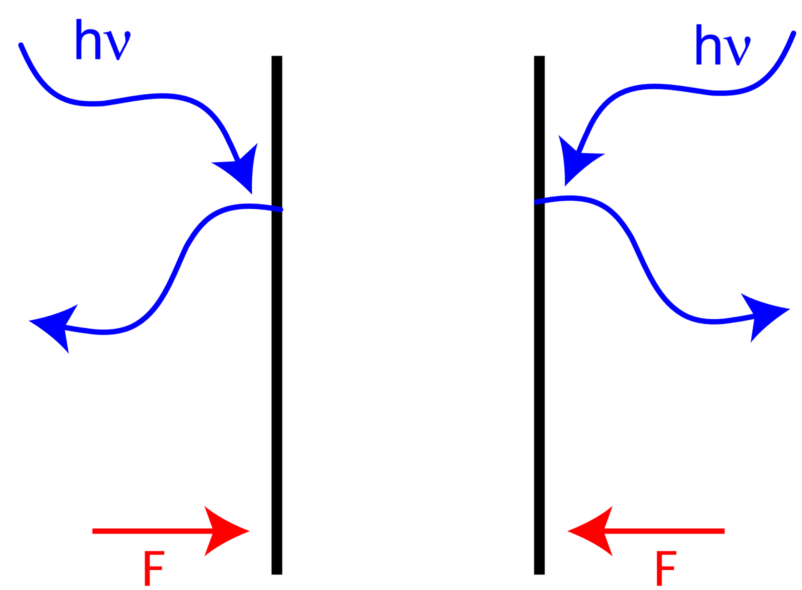
Casimir Effect

Attractive Force Between Two Metal Plates

1. Explanation: Photon Picture

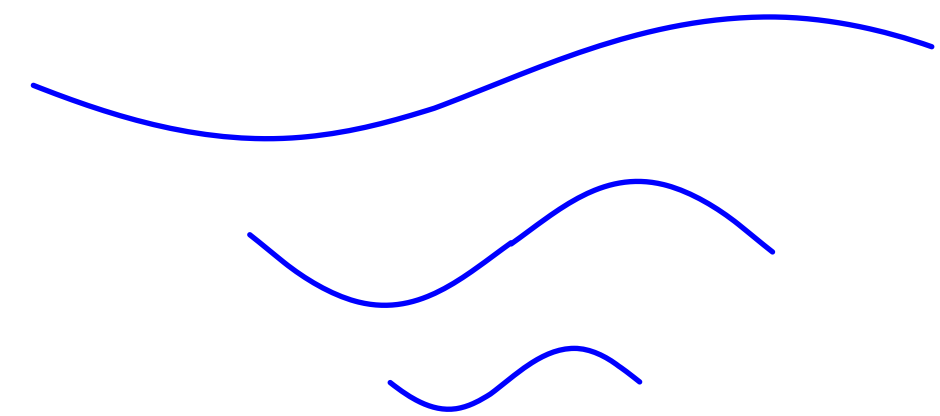
   - zero-point fluctuations exert radiation pressure
   - no long wavelength photons inside the gap
   - uncompensated radiation pressure

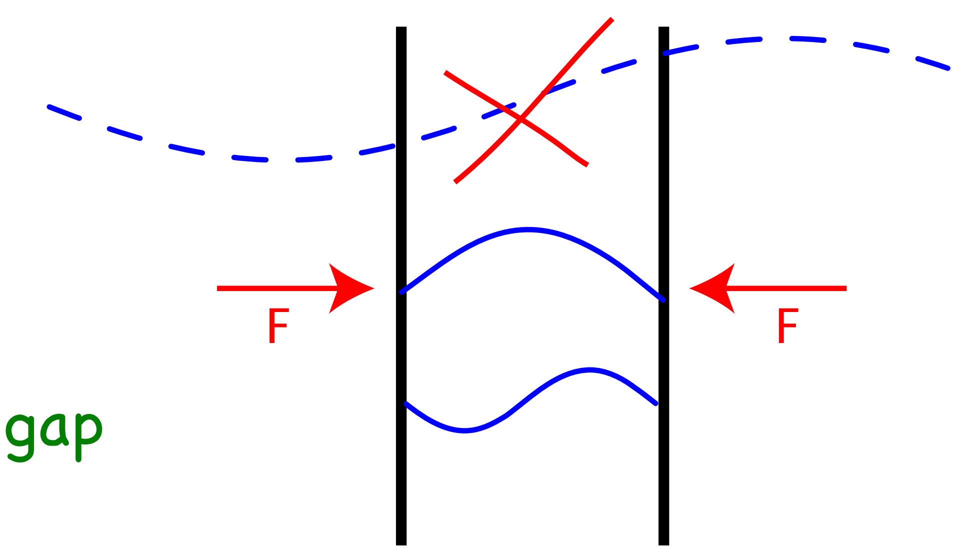




Casimir Effect

Attractive Force Between Two Metal Plates





2. Explanation: Wave Picture

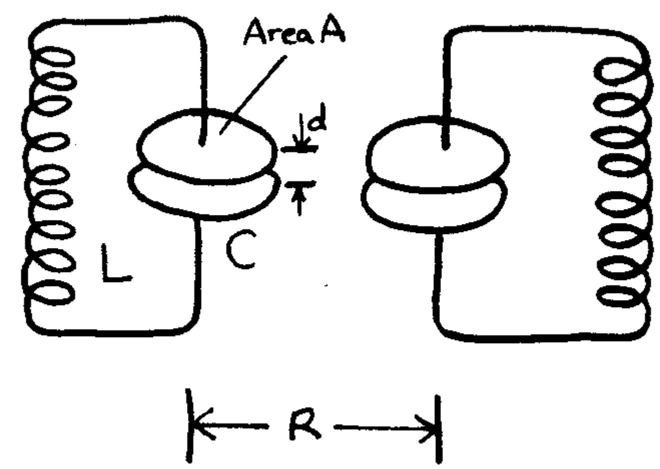
- long wavelength modes are excluded from the gap
- reducing the gap increases the unconfined space
- more configurations for e-m noise

Casimir force is an entropic force

Van der Waals Forces

Forces Between any Media at small distances

Consider two harmonic oscillators (identical LC circuits) at a distance R



- Ground State Energy for $R \to \infty$:
- At finite R, the two oscillators interact via their dipole fields: Mode splitting:
- Interaction Energy: $\Delta E = E' - E_0$

$$\Delta E = \frac{\hbar\omega_0}{8}\frac{\alpha^2}{R^6}$$

Van der Waals Forces: 2 Explanations:

1. Correlation between the instantaneous dipoles of two atoms molecules
2. Change in the vacuum energy due to the confinement of the e-m modes

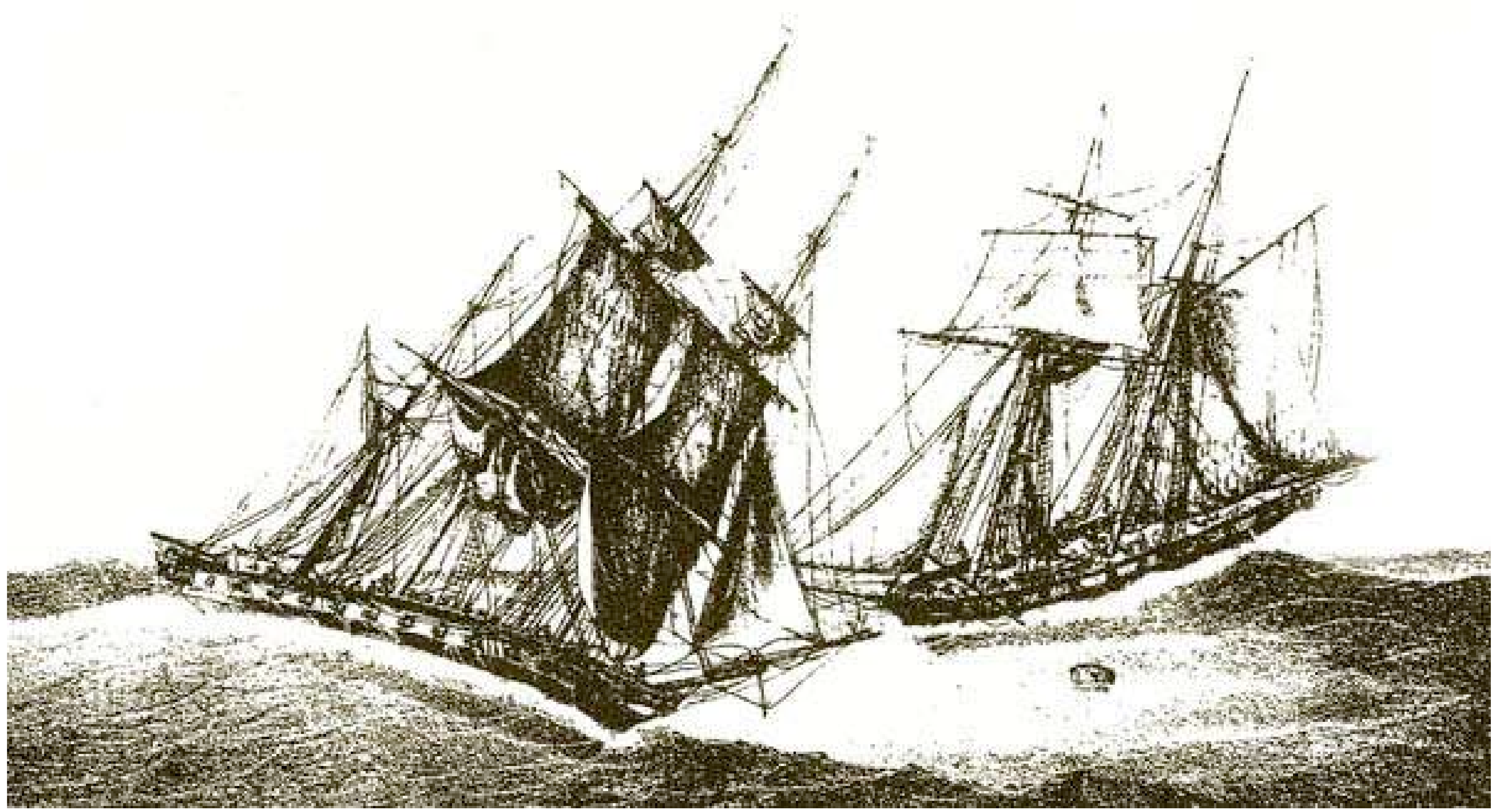
Van der Waals forces: generalization of the Casimir Effect for any media

D. Kleppner, Physics Today, October 1990

A Generalized Casimir Effect

Forces arising from the confinement of any fluctuating field

What about the confinement of other types of fluctuations (noise)?



A Casimir-Effect at sea: In the days of the square riggers, sailors notices that, under certain condition. Ships lying close to one another would be myteriously drawn together, with various unhappy outcomes. Only in the 1990s was the phnomenon explained as a maritime analogy of the Casimir force." (Buks & Roukes, 2002)

More Examples:
(Kadar & Golestanian, 1999)

- binary mixtures near T_c
- superfluid films
- liquid crystals
- membrane inclusions

Acoustic Disjoining Pressure

Thin Films: confined mode spectrum:

electromagnetic modes: van der Waals disjoining pressure: confined photons
acoustic modes: thermal excitations: confined phonons:

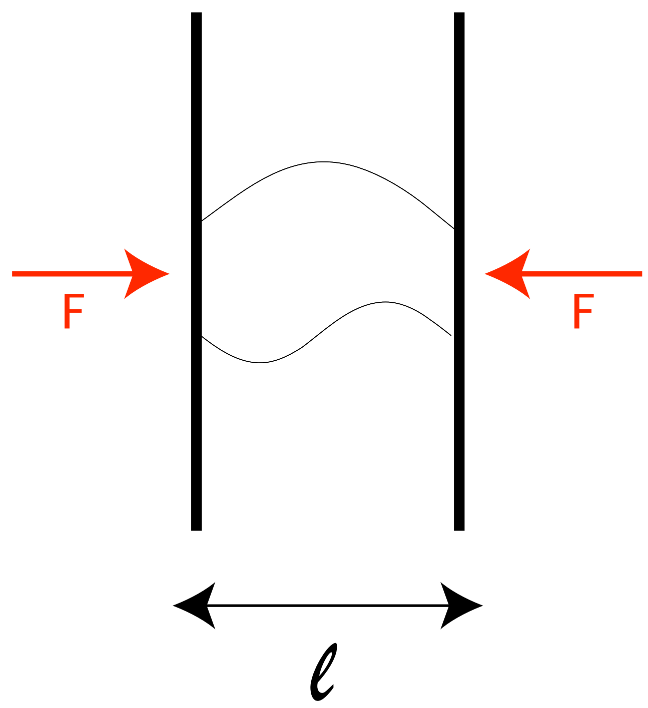
Dimensional Analysis:

$T >> 0$:	Electromagnesism:	quantum mechanics:	hc
	Acoustics:	classical effect:	kT

Electromagnetic Pressure:

- non-retarded vdW: $p_{em} \sim hc/a\,\ell^3 \sim A/\ell^3$

Acoustic Analogue: $p_{em} \sim kT/\,\ell^3$



- same scaling with confinement length ℓ
- similar interaction energy

Acoustic Disjoining Pressure

Quantitatively: Difference of integrated (Debye) density of states:

inside vs. outside

$$p_{ac} = \frac{1}{3}\int_0^{\nu_D^{(out)}} kT\ dn_1 - \frac{1}{3}\int_{\nu_c}^{\nu_D^{(in)}} kT\ dn_2$$

$$= \frac{kT}{18\,\ell^3} + p_0'$$

Cut-off frequency: ν_c

Overall pressure balance:

$$p(\ell) = p_0 - \gamma\partial_{xx}d + \frac{A}{6\pi\,\ell^3} + \frac{kT}{18\,\ell^3}$$

Polymers on solid substates at ambient temperatures

$$A \approx kT$$

Predictions:

- both terms (vdW and acoustic) should be equally important
- both terms have the same scaling with the confinement ℓ
- both terms are of the same order of magnitude (kT)

Eur. Phys. J. E 8, 347 (2002)

Acoustic Disjoining Pressure: Experiments

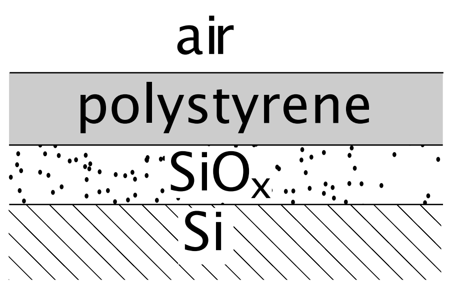
Tricky Business: how to distinguish between vdW and thermo-acoustic confinement forces

3 Experiments:

1. Temperature dependence: Hamaker constant A varies only weakly with temperature
2. Force Balance: vdW forces stabilize the film, acoustic confinement destabilizies the film
3. Acoustic Boundary Conditions: switch off the acoustic confinement

Experiment 1: Temperature Dependence

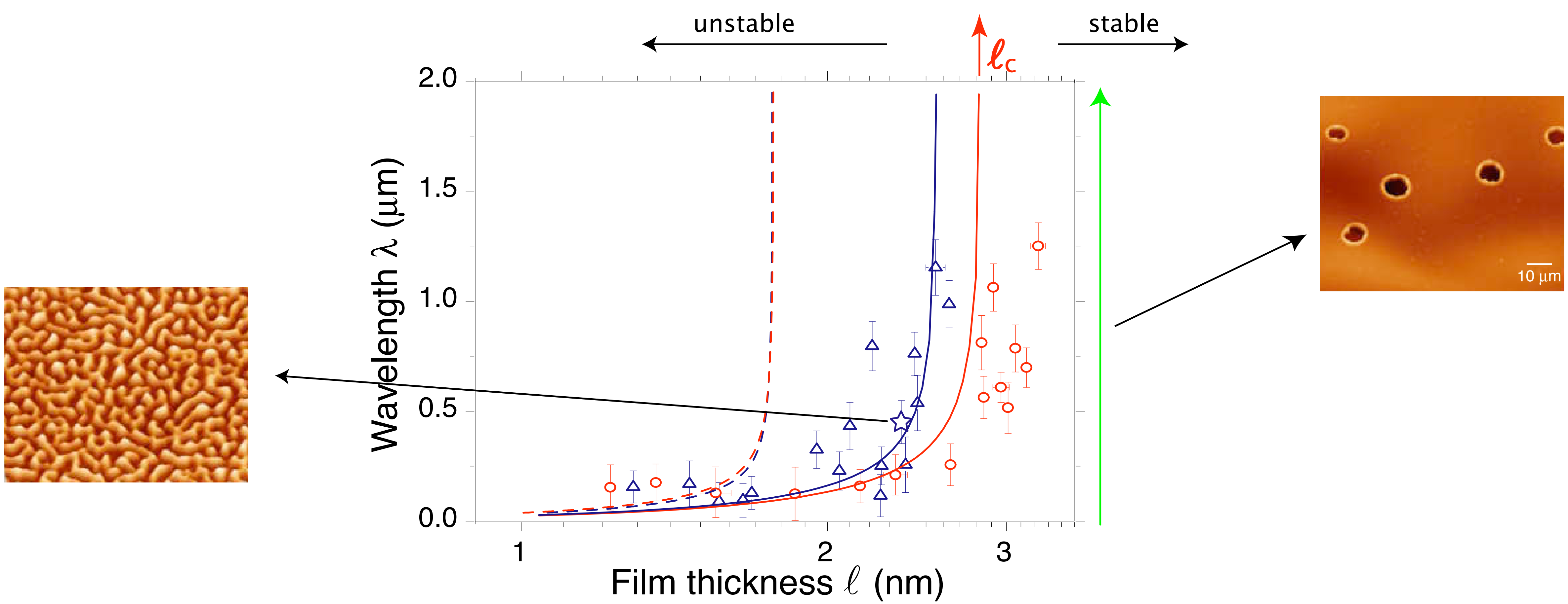
Temperature Dependence: Seemann-Jacobs-Herminghaus experiment



- PS on Si is stable
- PS on SiO_x is unstable

→ film stability cross-over for approximately equal layer thicknesses of PS and SiO_x ($\ell \approx \ell_c$)

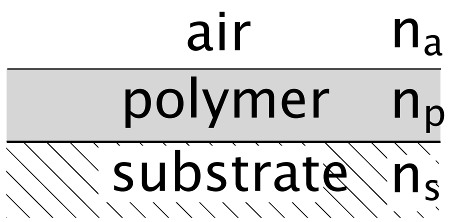
At $\ell = \ell_c$ vdW forces are (≈) switched off: other forces dominate



Experiment 2: Force Balance

Force Balance: $p_{ac} > 0$ destabilizing

$p_{vdW} < 0 \quad (A < 0)$ stabilizing



$n_s > n_p > n_a \qquad A < 0$

$n_p > n_s \;\&\; n_p > n_a \qquad A > 0$

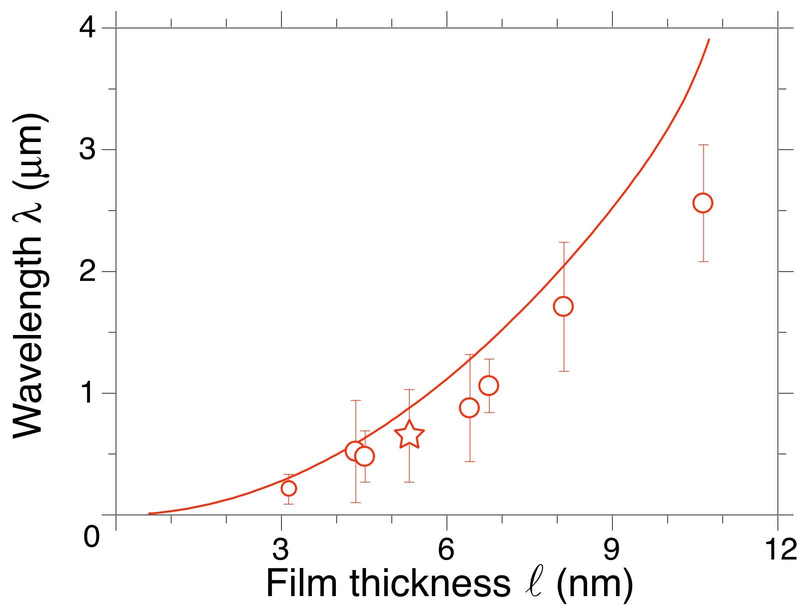
Experimental Set-up: $p_{vdW} < 0$ and $|p_{vdW}| < p_{ac}$

$n_p \lesssim n_s$

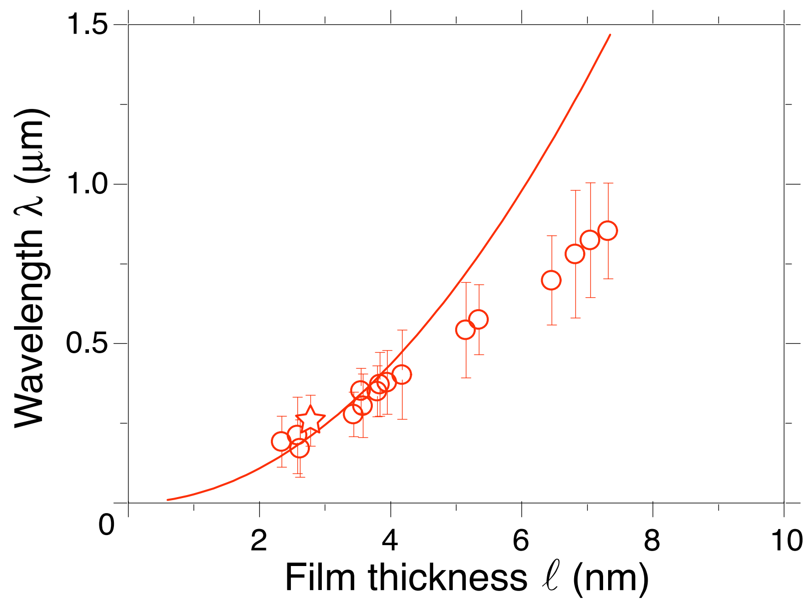
System 1: PMMA (n=1.49) on glass (n=1.52)

unstable on glass with n = 1.50, n = 1.60

stable on glass with n=1.70



System 2: polyacrylamide (n=1.45)
on silicon oxide (n=1.49)



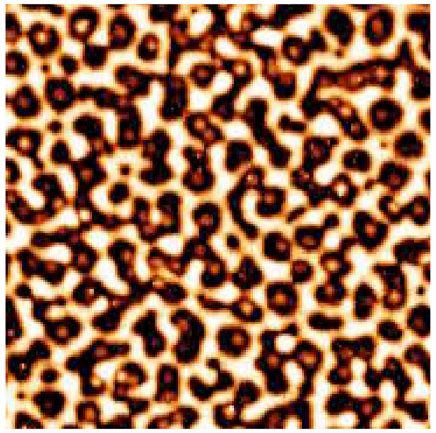
Experiment 3: Boundary Conditions

Acoustic Boundary Condition: switch off the acoustic disjoining pressure

-> substrate mechanically similar to the film

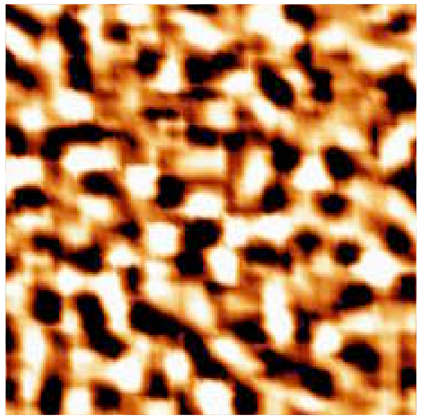
System 1:

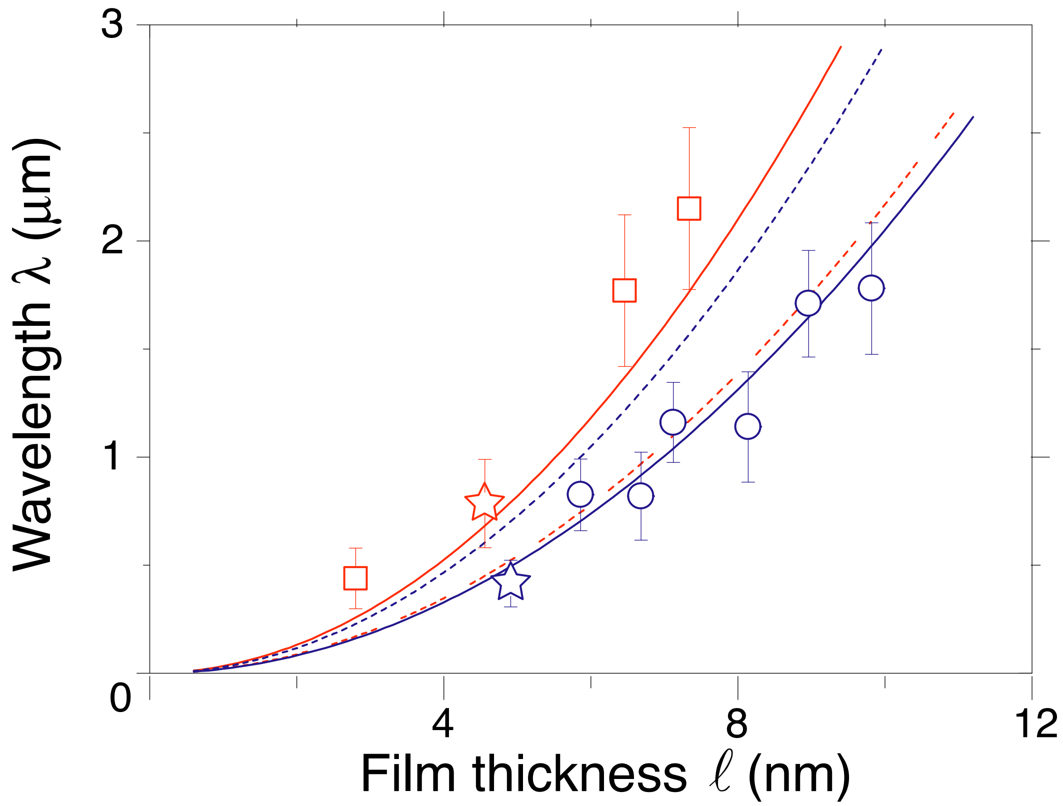
PS (n=1.59) on silcon oxide (n=1.49)



vs

PS (n=1.59) on PMMA (n=1.49)

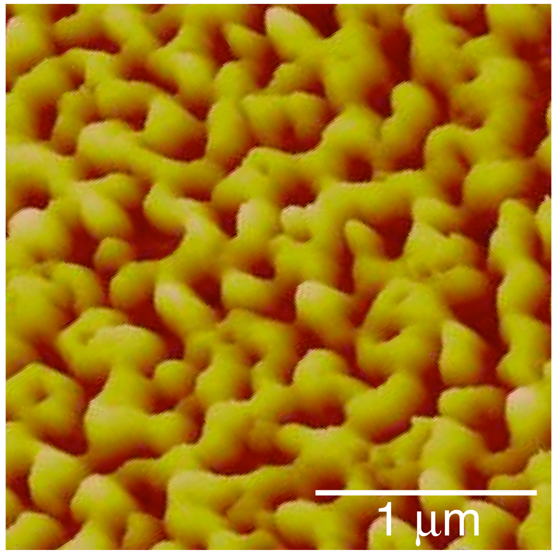




Experiment 3: Boundary Conditions

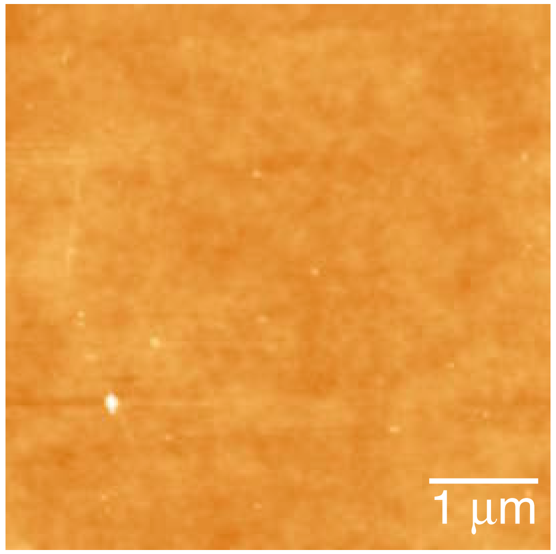
System 2:	PMMA on a substrate with n = 1.6: stabilizing van der Waals forces

PMMA (n=1.49) on glass (n=1.60)

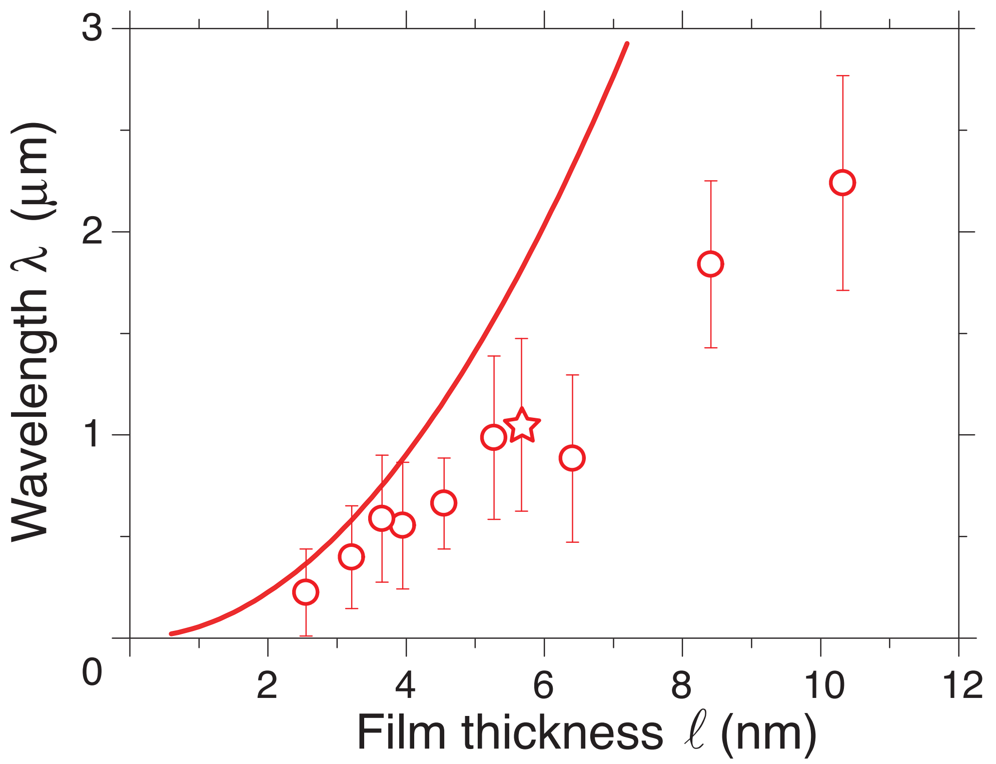


$p_{ac} > 0$

PMMA (n=1.49) on PS (n=1.59)



$p_{ac} = 0$



Polymer Melts: Ambivalent Liquids

Low frequencies (–> 0 Hz): • highly viscous liquid

Low frequencies (GHZ-THZ): • glass

Consequences:

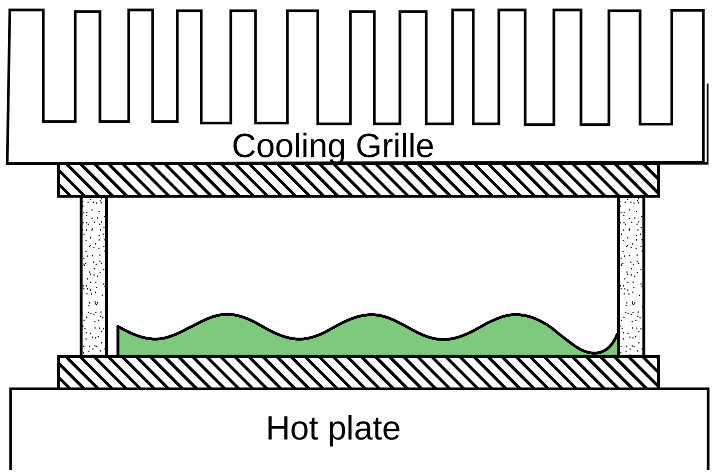
viscous deformation of the films (~0 HZ) –> film instability

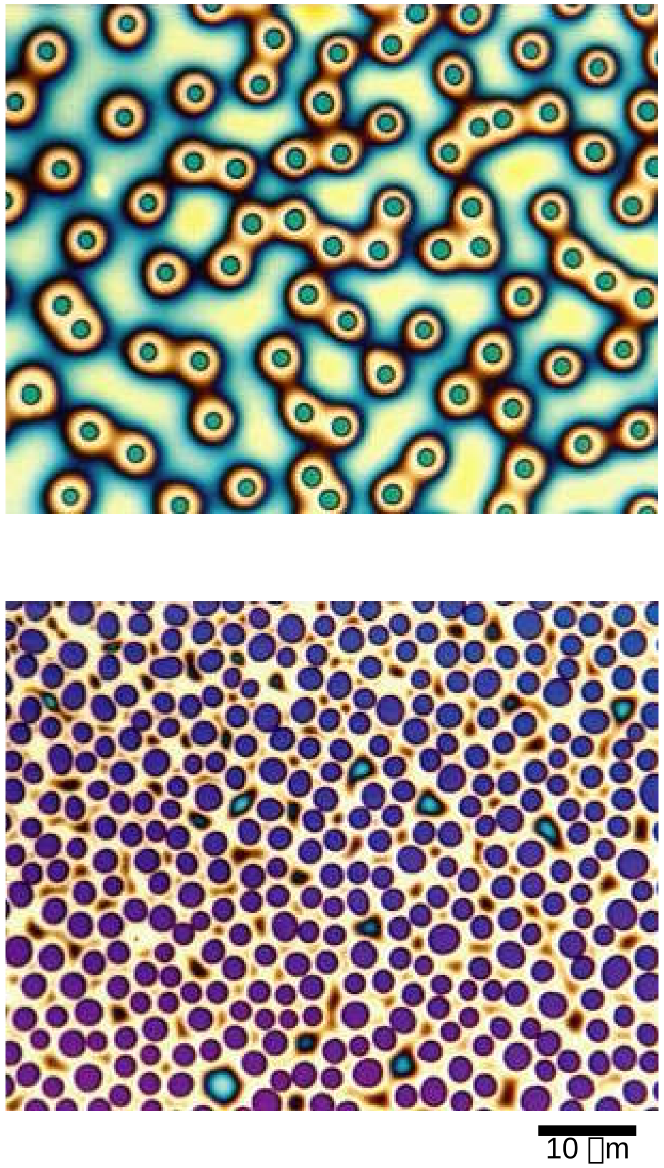
acoustic propagation of 100 GHz phonons: –> large enough correlation length

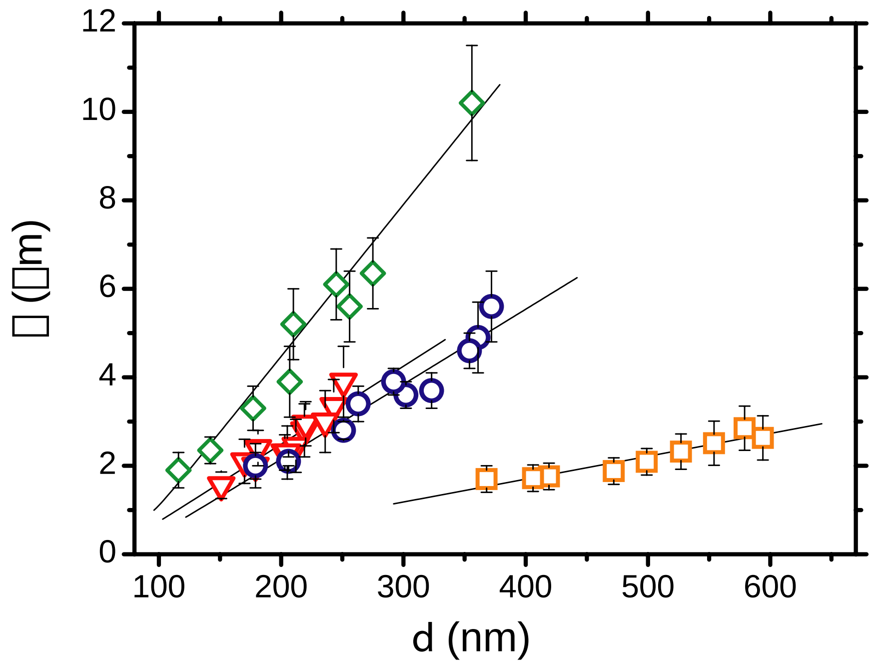
Prediction for simple liquids: no glassy regime in the 100 GHz range

–> no instability expected

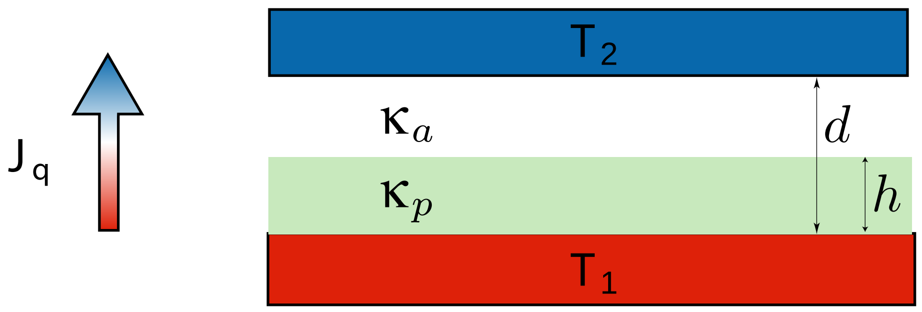
Experiments on a Hot Plate







Interface in a Temperature Gradient



Flow of thermal energy from T_1 to T_2

How is heat conducted?

1.	Convection:	Rayleigh-Bénard	$R/R_c \sim 10^{-16}$
2.	Convection:	Marangoni-Bénard	$M/M_c \sim 10^{-8}$
3.	Diffusion of Heat:	Thermal Excitations	
4.	Radiation:	only at very high temperatures	

Instability: (1) no convetion rolls (2) not driven by surface tension variations

Differences to previous instabilities:

van der Waals forces, electric fields:

- Systems develops from an unstable to a stable state
- Quasistatic: free energy of the system is always defined

Temperature Gradient:

- non-equilibrium steady state
- transition from on non-equilibrium steady state to another
- no Gibb's free energy framework

Mechanism of the Instability

Diffusion of Heat: Thermal Exitations

Debye: Propagation of acoustic phonons:

Heat Flux: $$J_q = -\Box \frac{T}{z}$$

associated Momentum Flux $$J_p = \frac{J_q}{u}$$

Rayleigh: particles that are reflected off a surface exert a radiation pressure:

Radiation Pressure: $$p_{ph} = 2\,R\,J_p = 2\,R\,\frac{J_q}{u}$$

Contradiction: heat is conducted (Fourier's law), but phonons are reflected (R ~1)?

Frequency Dependence

Way out: frequency depence of phonon diffusion

Low frequency phonons (~100 GHz):

- in polymers: long mean-free path length (~ 1μm)
- phonons propagate acoustically
- phonons reflect off interfaces

High frequency phonons (~1 THz):

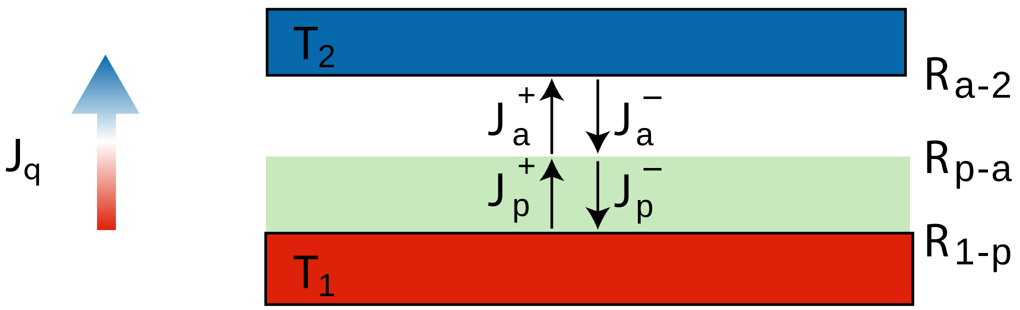
- very short mean-free path length (few Å)
- phonons scatter constantly
  –> propagation by diffusion
- interfaces are rough on these length scales
  –> diffuse interfacial scattering

Team Work:

Low frequency phonons cause destabilizing interfacial pressure

High frequency phonons conduct most of the heat

Scaling Approach



Heat Flux: $$J_q = J_p^+ - J_p^- = J_a^+ - J_a^-$$

Interfacial Pressure: $$p_{ph} = \frac{1}{u_a}(J_a^+ + J_a^-) - \frac{1}{u_p}(J_p^+ + J_p^-)$$

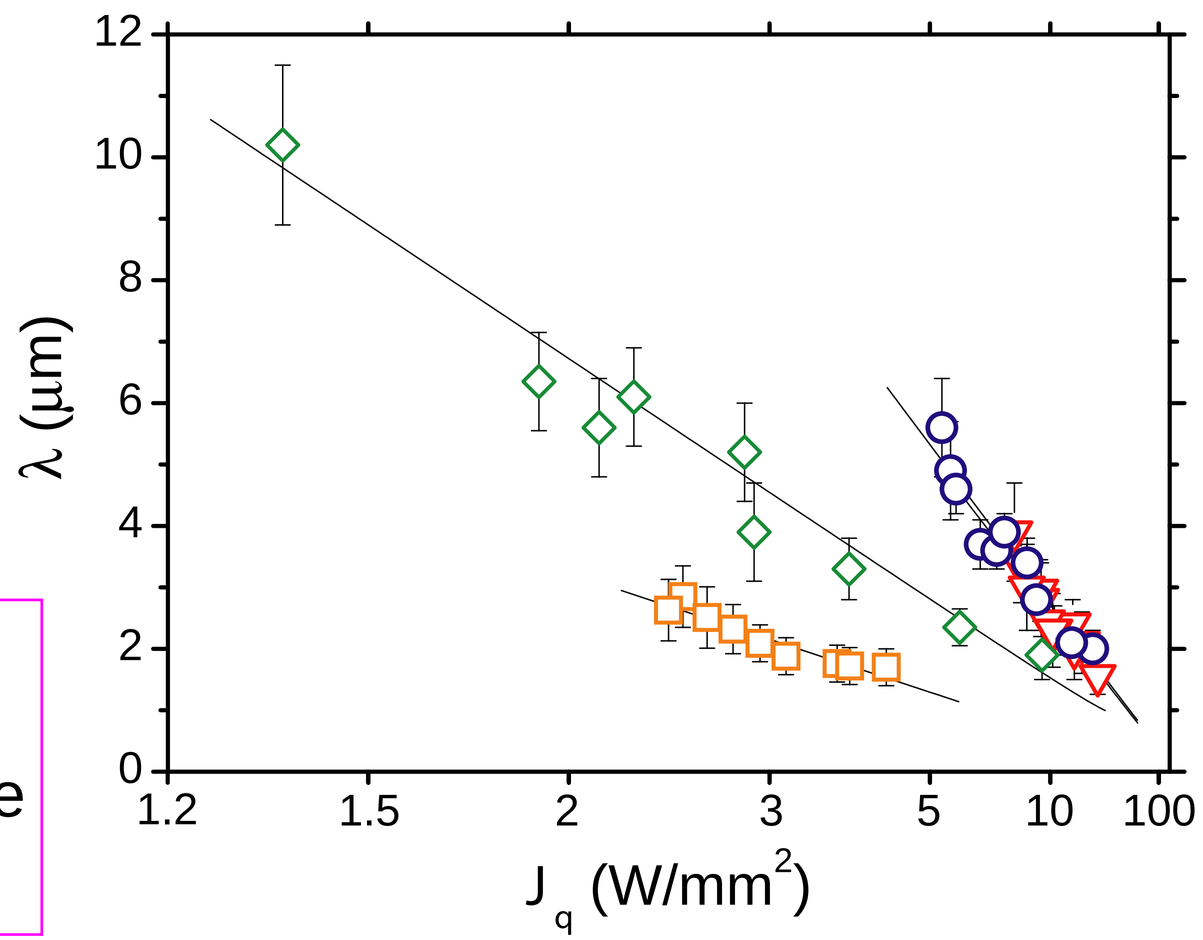
Individual components of the heat flux:

- scale linearly with the heat flux
- depend on all the complexity of the system

Scaling Relation: $$p_{ph} = \bar{Q}\,\frac{J_q}{u_p}$$

Linear Stability Analysis for Film Instability:

$$\lambda \sim \frac{1}{\sqrt{\bar{Q}\,J_q}}$$

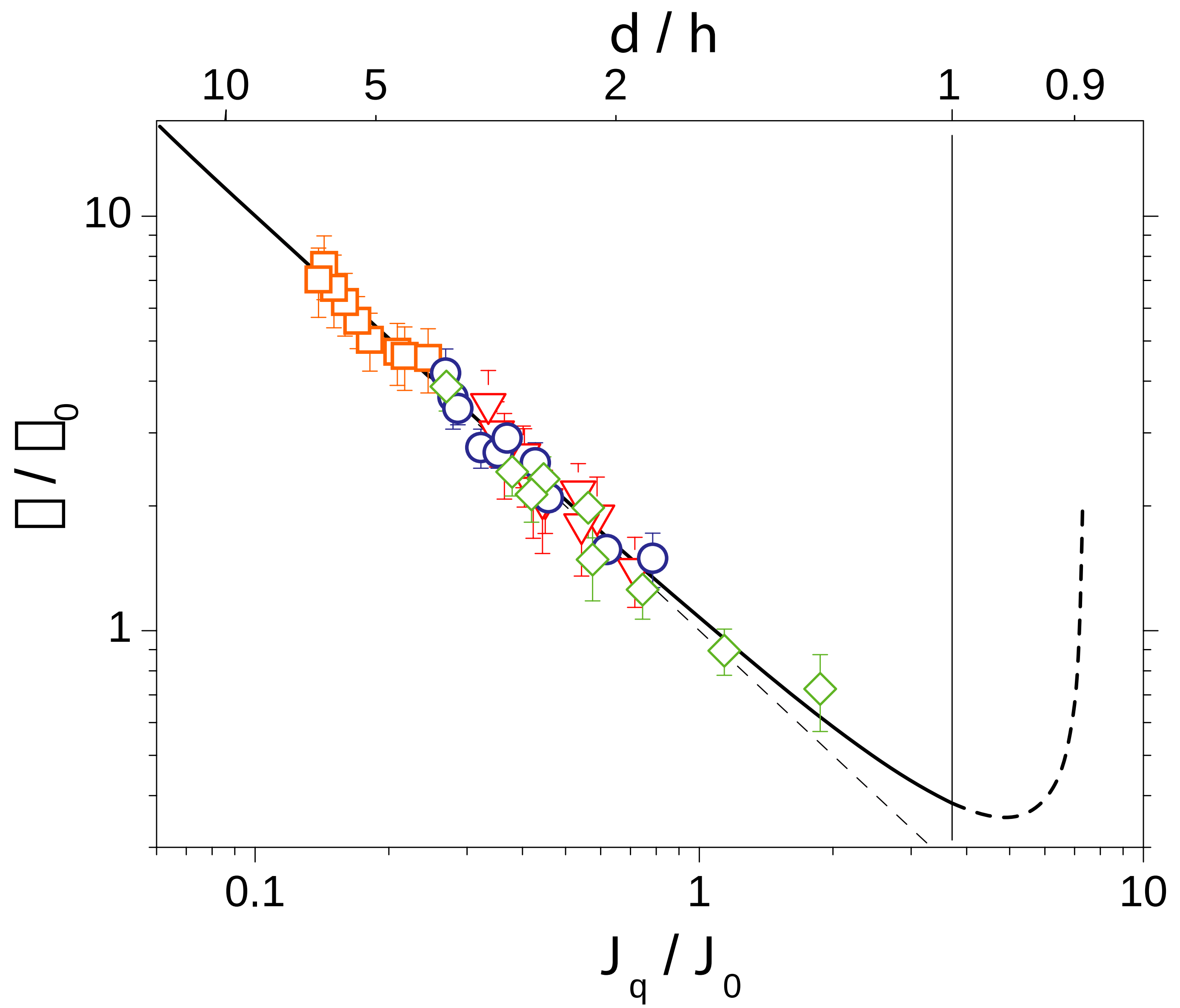


$\bar{Q}$ factor:
- contains details of heat conduction
- integration of J_q and p_{ph} over the Debye density of states

Temperature Gradient: Experimental Results

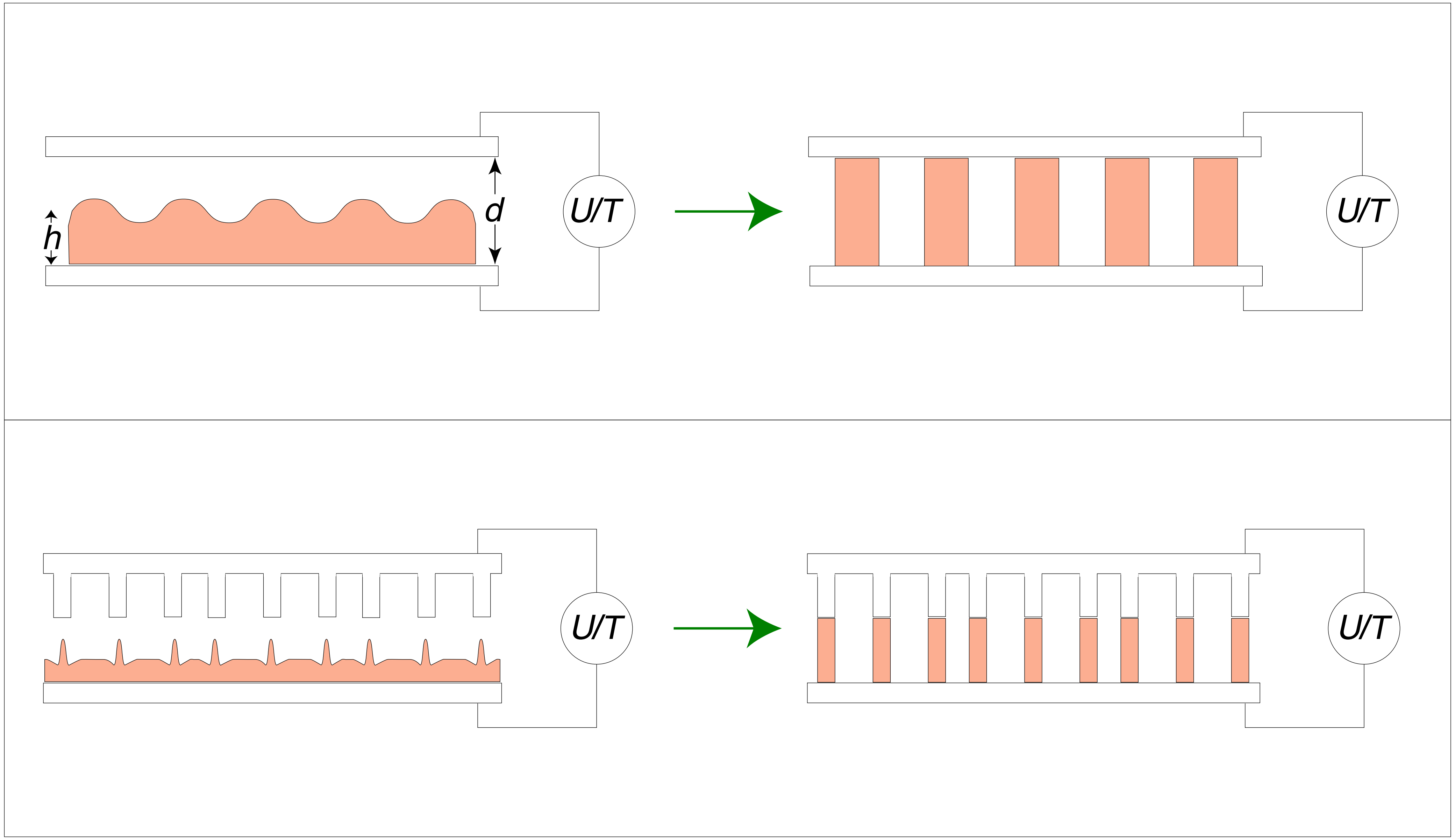
scaling-equation:

$$\square = 2\square\sqrt{\frac{\square\square_a\square_p(T_1 \square T_2)}{\bar{Q}\,(\square_p \square\square_a)}}\;\frac{1}{J_q}$$

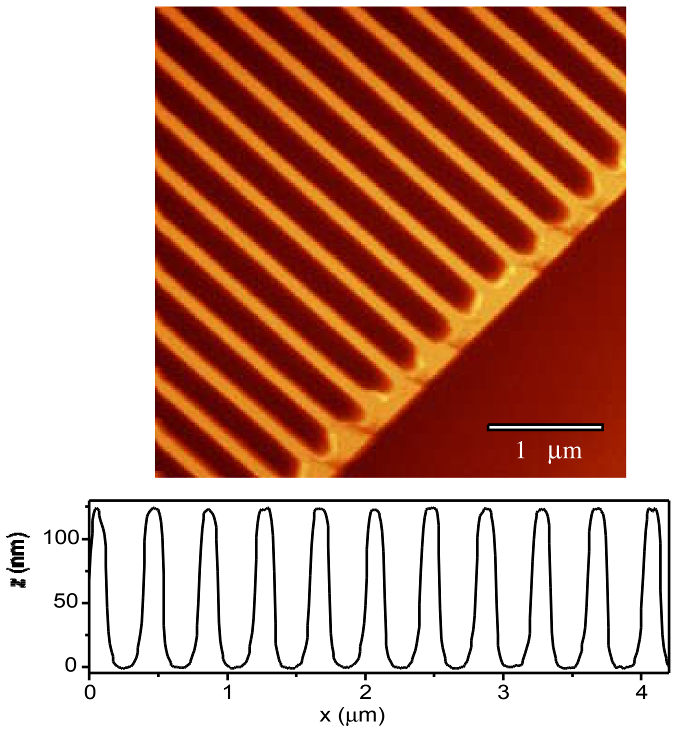


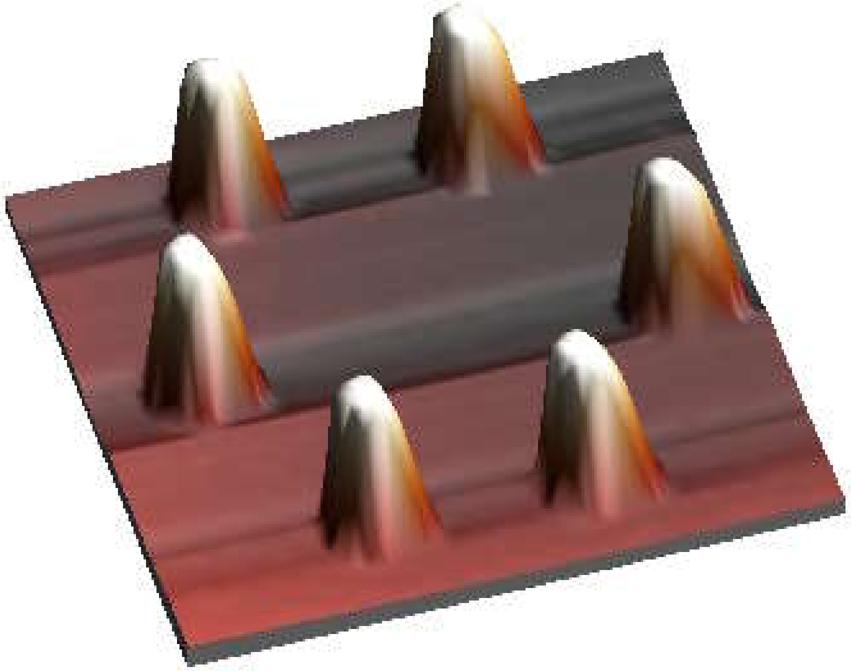
Europhysics Letters, **60**, 255 (2002)

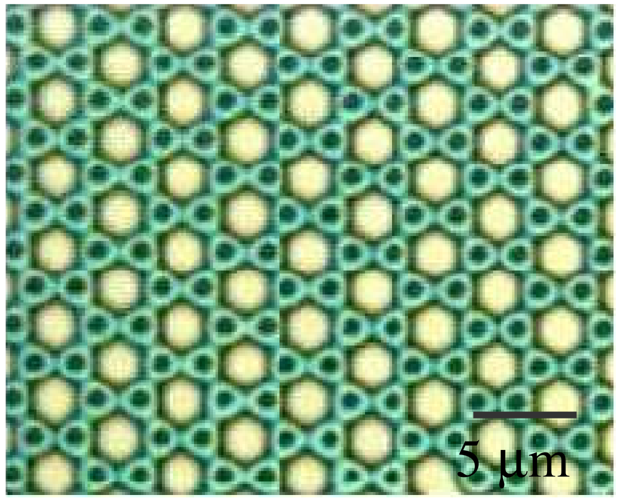
Lithography using Capillary Instabilities



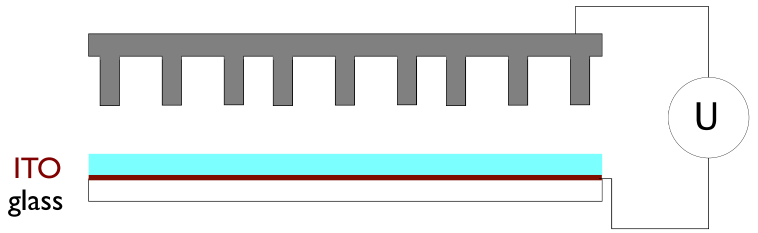
Electrohydrodynamic Lithography







Pattern Replication



Conclusions:

Film instabilities are not only artifacts!

We can use them:

1. to measure forces
2. as a lithographic strategy

Acknowledgments

Collaborators

- Tom Russell (Amherst)
- Ralf Blossey (Lille)
- Uli Wiesner (Cornell)
- Marc Hillmyer (Minneapolis)

Thanks

- University of Groningen, Materials Science Center
- Irene von Lampe, TU Berlin – Polymer based ceramics
- Tom Palstra, Tijpke Hibma, Groningen

Students + post docs

- Erik Schaffer
- Mihai Morariu
- Stefan Harkema
- Nicoleta Voicu
- Ole Göbel
- Jakob Heier
- Mihaela Nedelcu
- Peter van der Wal
- Comert Sagiroglu

- Materials Science Center Groningen
- FOM (Fundamental Research on Matter (NL)
- DPI (Dutch Polymer Institute)
- BioMaDe