Oscillantions in phase transitions

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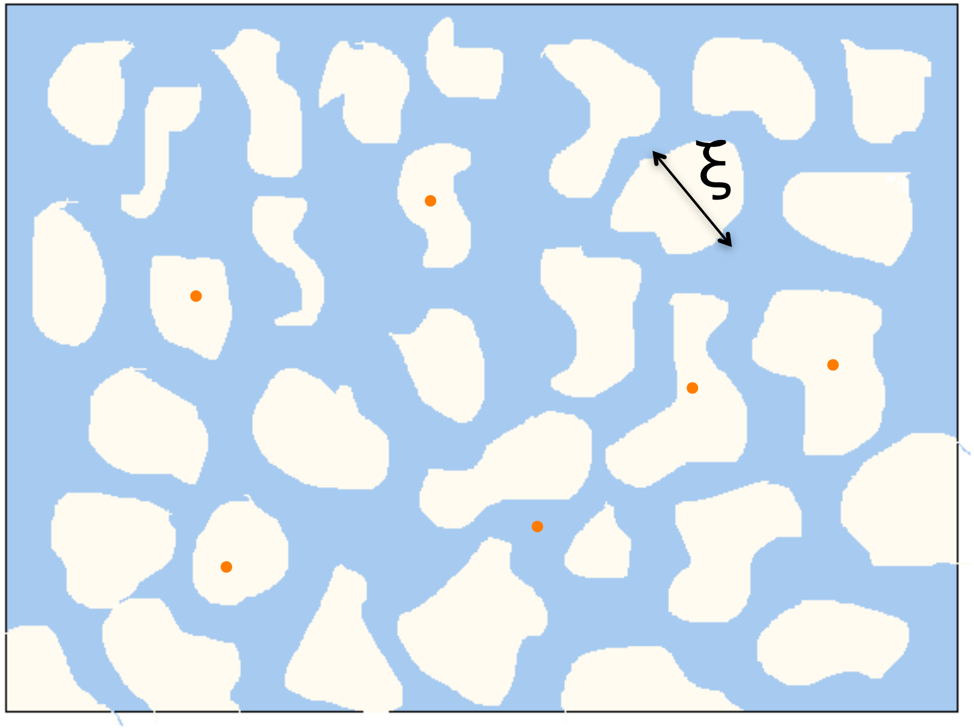
Outline

- Motivation for experiments in phase transitions
- The binary mixture
- The experimental set up
- The oscillating behaviour and its features
- A full model and a simplified one
- Conclusions
- Some features of actractive forces close to a critical points

Local measurements < correlation length

Binary mixture near critical point



Particles are "stuck" in fluctuations

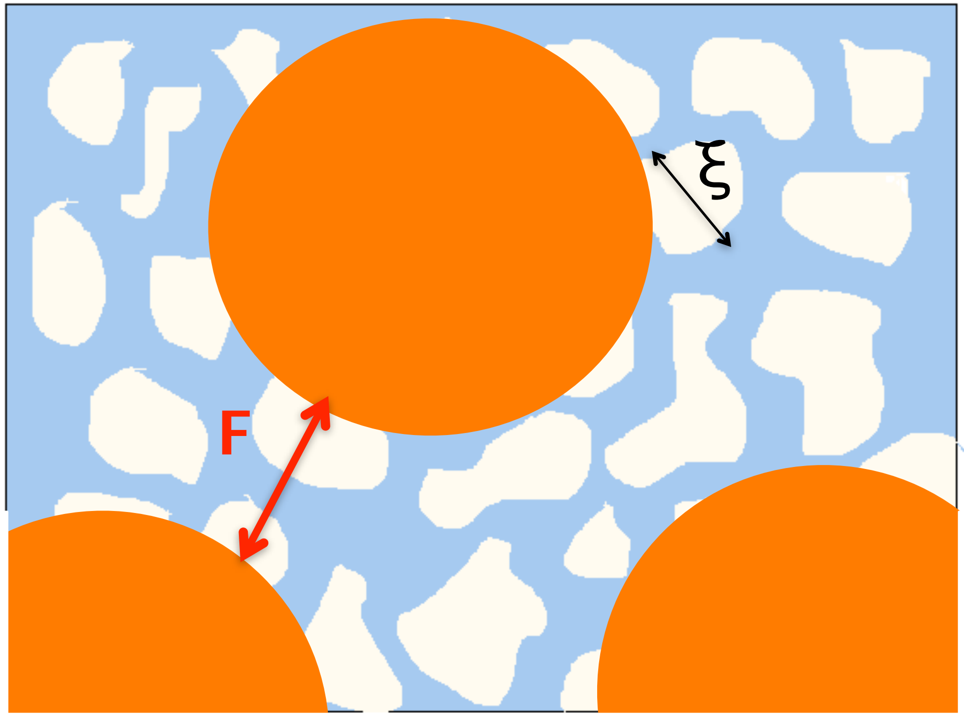
⇒**brownian motion is modified**
⇒ **Effect on diffusion coefficient and viscosity**

V. Démery D.Dean PRE, 2011

Sekimoto PRL 2014.

Local measurements ≥ correlation length

Binary mixture near critical point



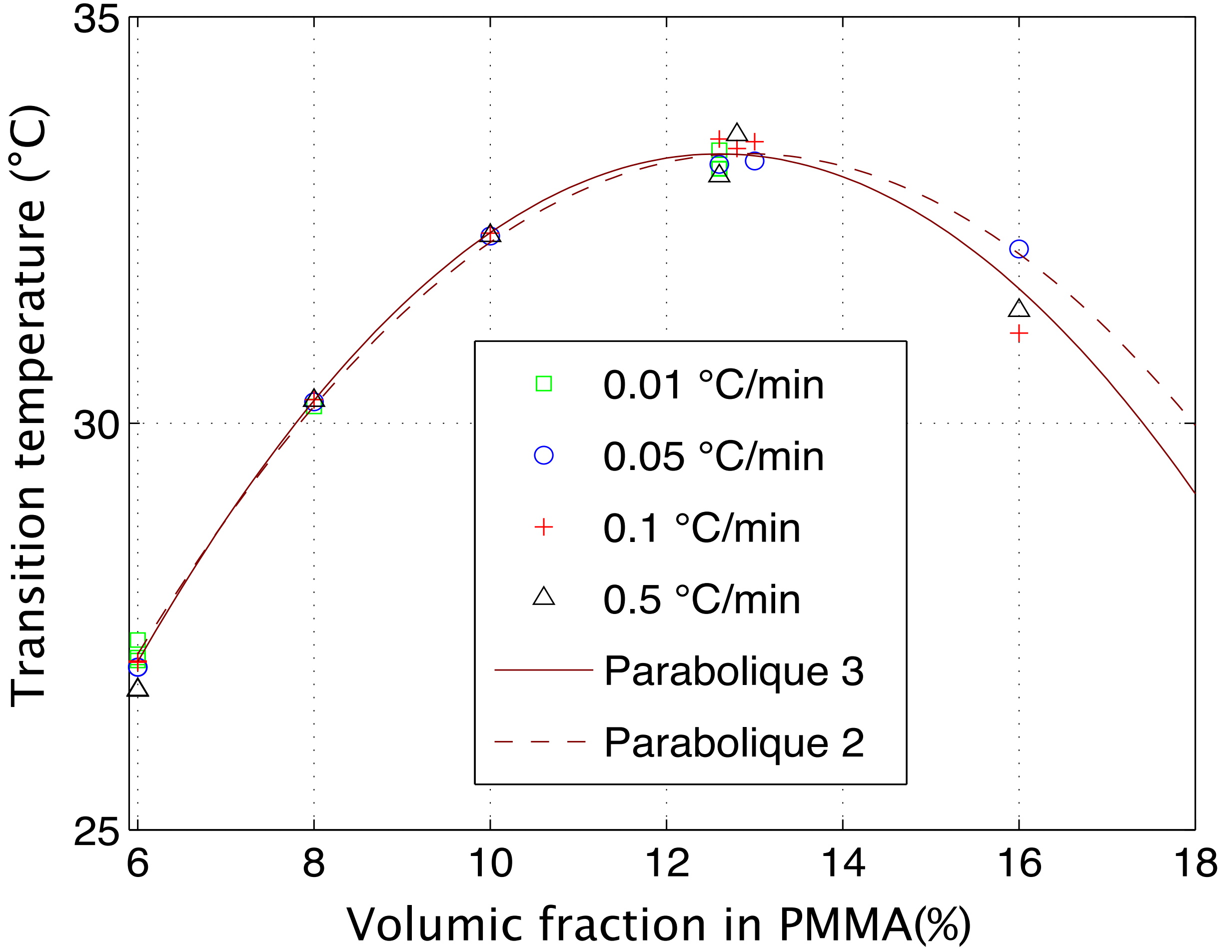
Attractive force between particles
if same particles : **Critical Casimir force**
Fisher and de Gennes

$S=1\mu m^2$, $L=100nm$, $F<4pN$

particle aggregation
Van Duc Nguyen et al. Nature Communication 2013
attractive force measurments
C. Hertlein et al. Nature 2008

Open questions : transient behaviour ?
out of equilibrium ?
fluctuations ?

Phase transition : binary mixture



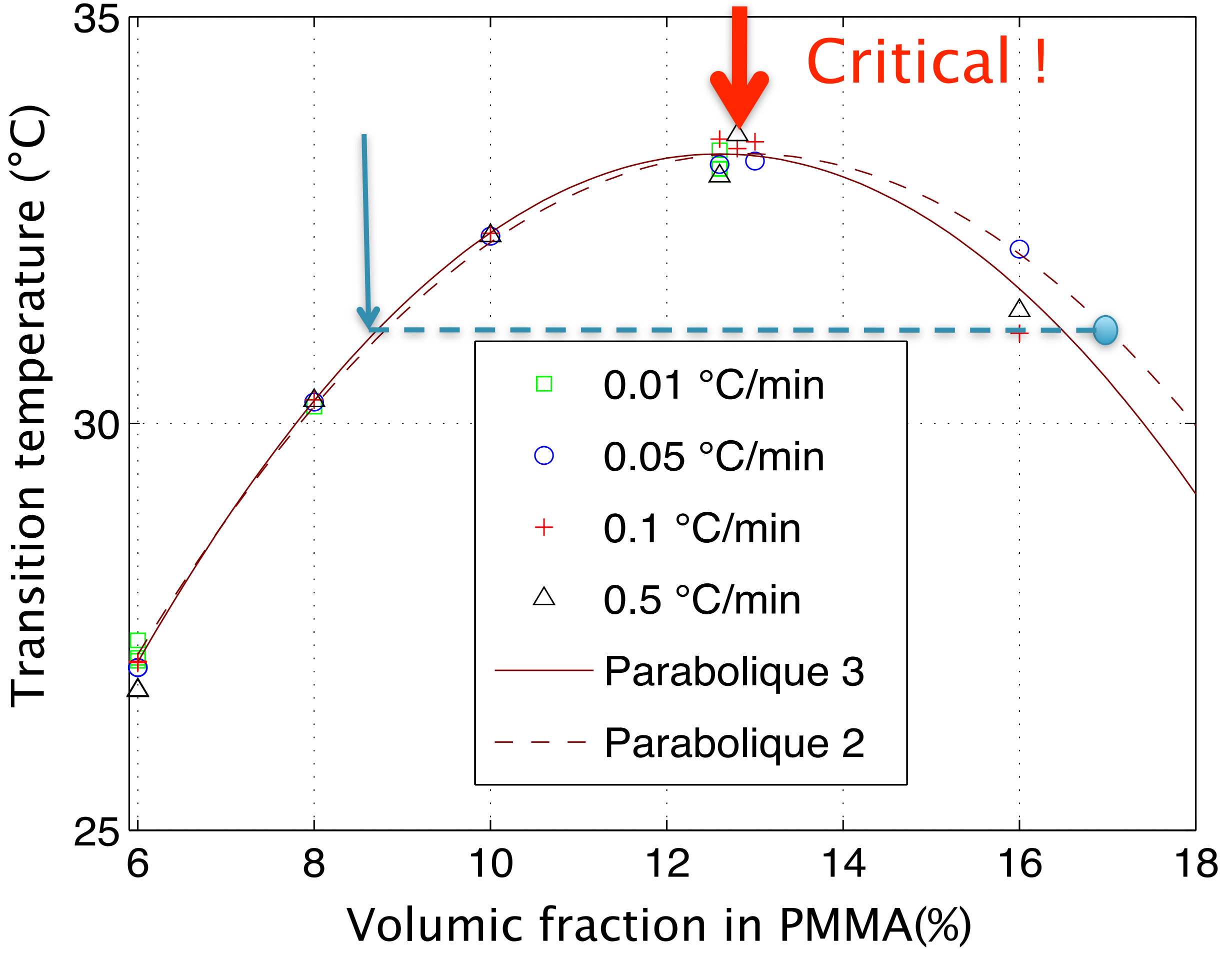
PMMA/octanone

polymer - solvant

Tc = 33.5 °C

Cc = 12.8 % ± 0.1%

Mixture characterisation : phase diagram



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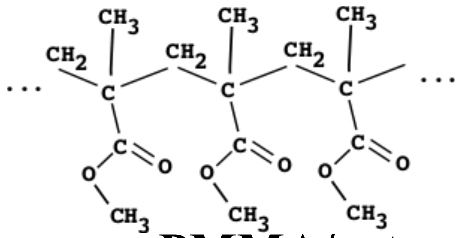
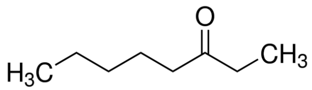
Binary mixtures

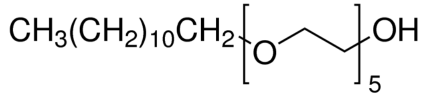
Two kind of mixture



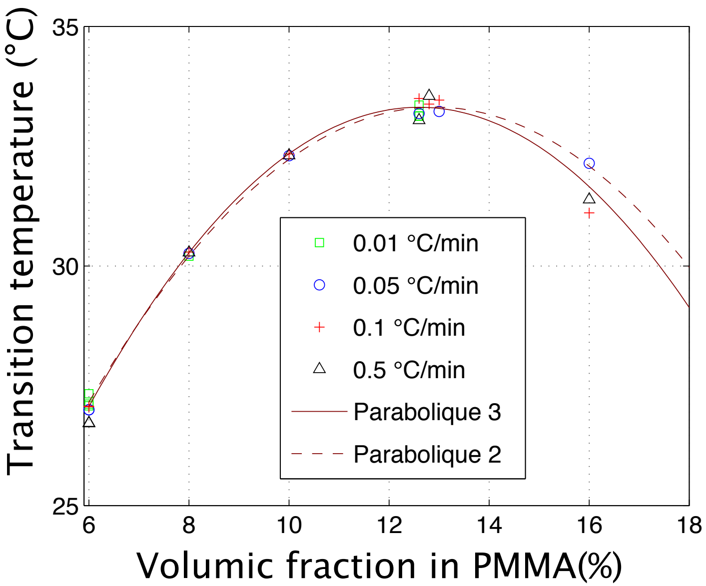
PMMA/octanone



Water/C12E5

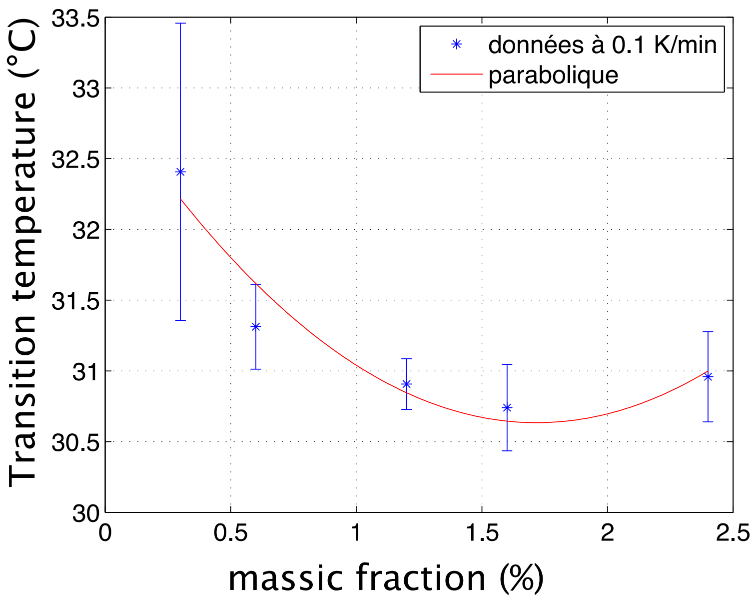


polymer - solvant



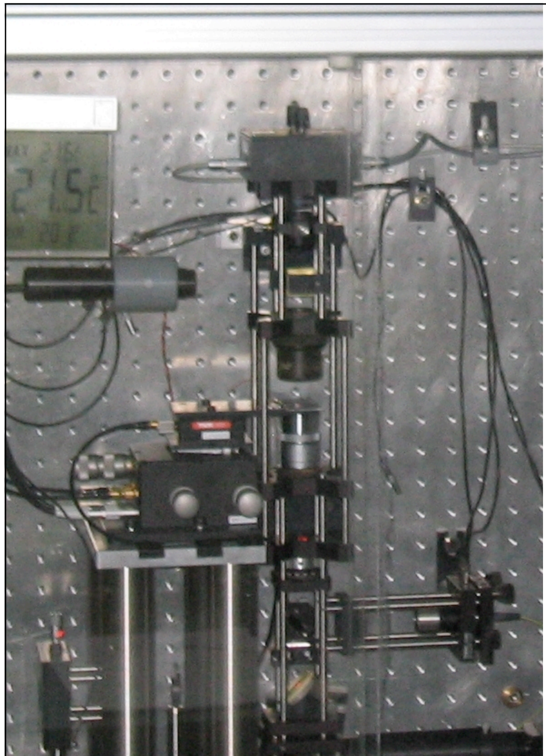
Tc = 33.5 °C φc = 12.8 % ± 0.1%

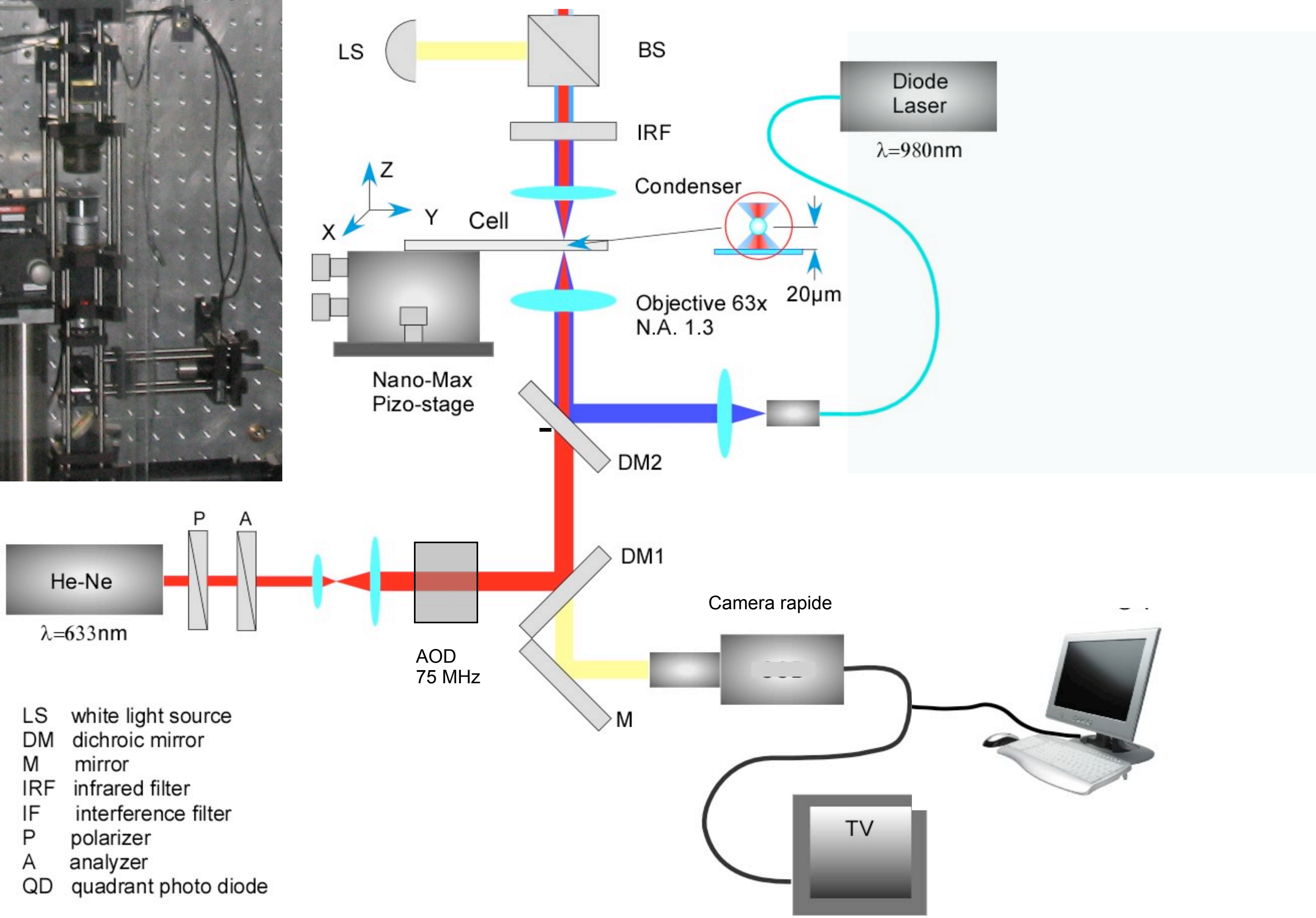
water - micelles



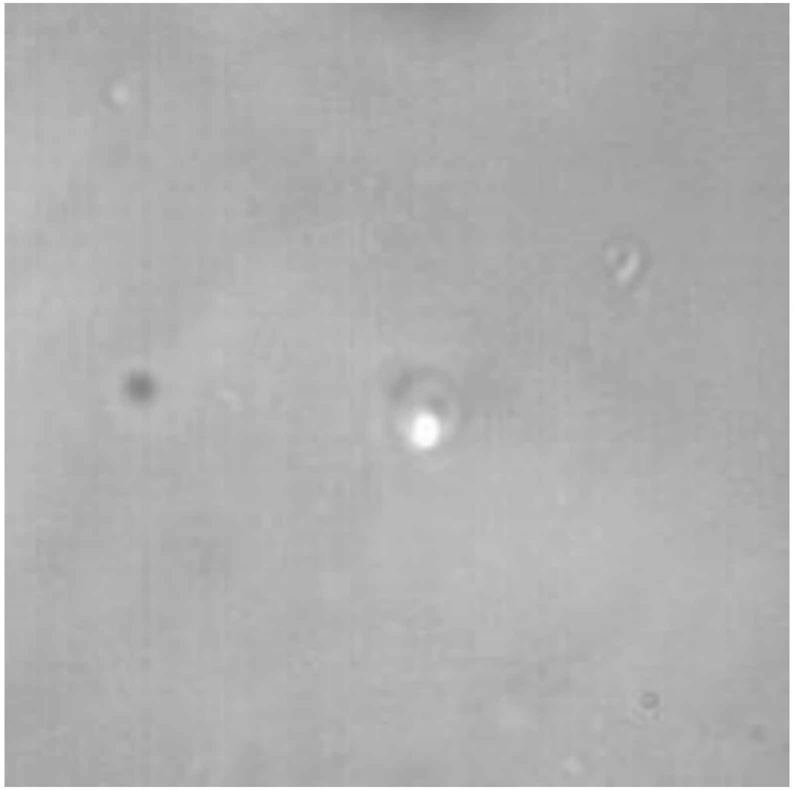
Tc = 30.5 °C φmc = 1.6 % ± 0.4 %

Experimental set-up Optical trap



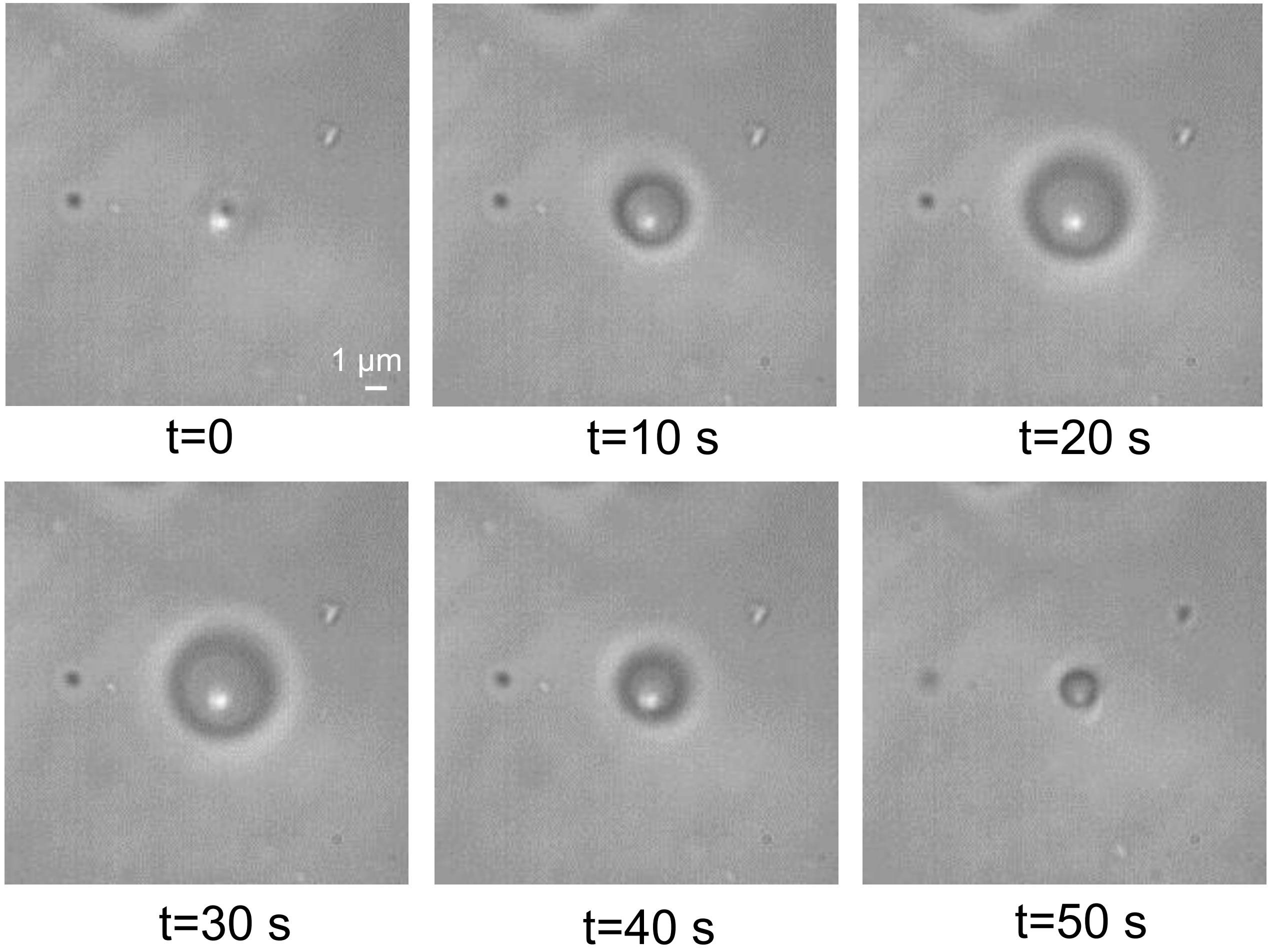


Tests in binary mixture



PMMA/octanone mixture 12.8 % at RT enlightened with a focus laser beam at 130 mW
speed up 10x

Tests in binary mixture



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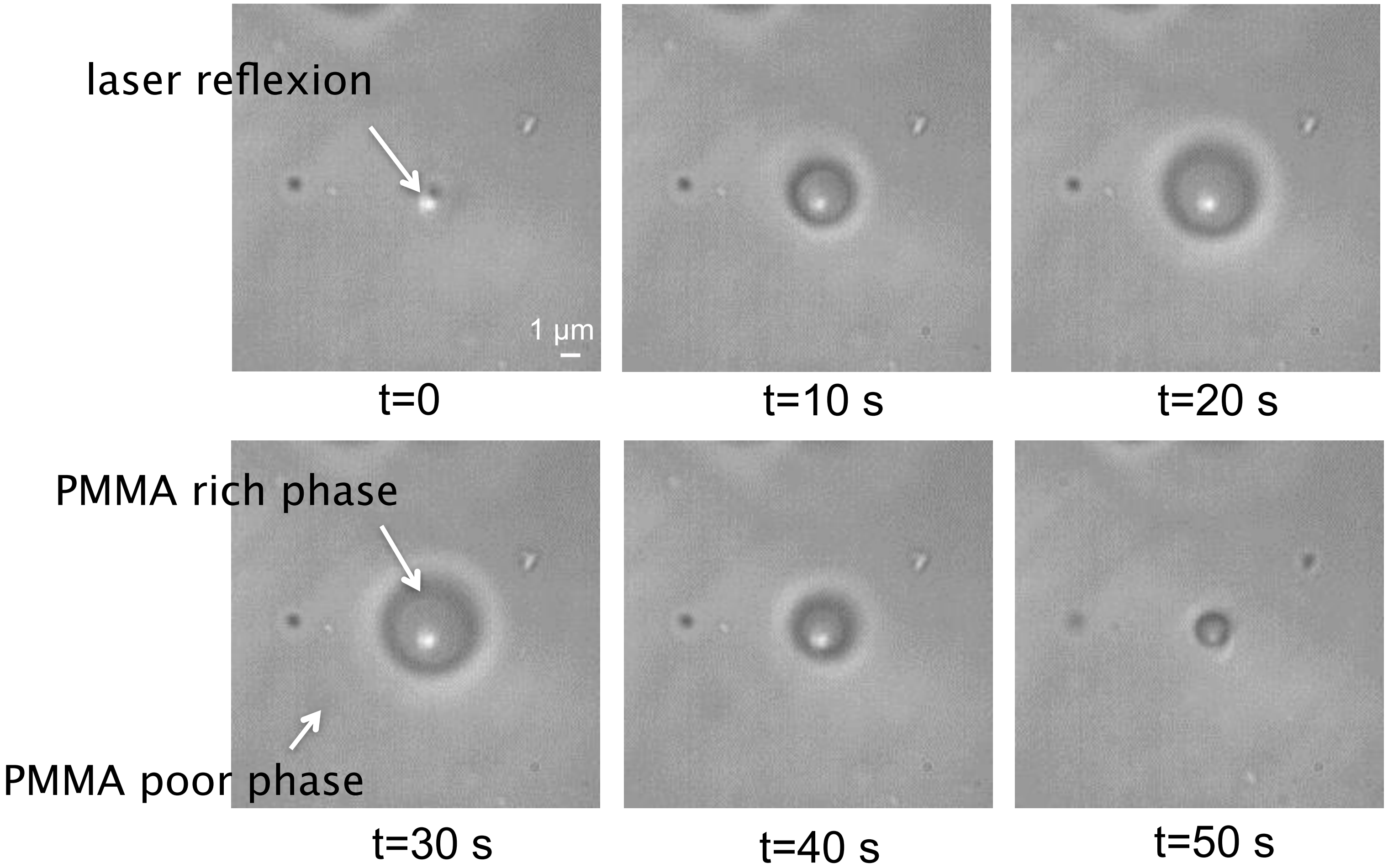
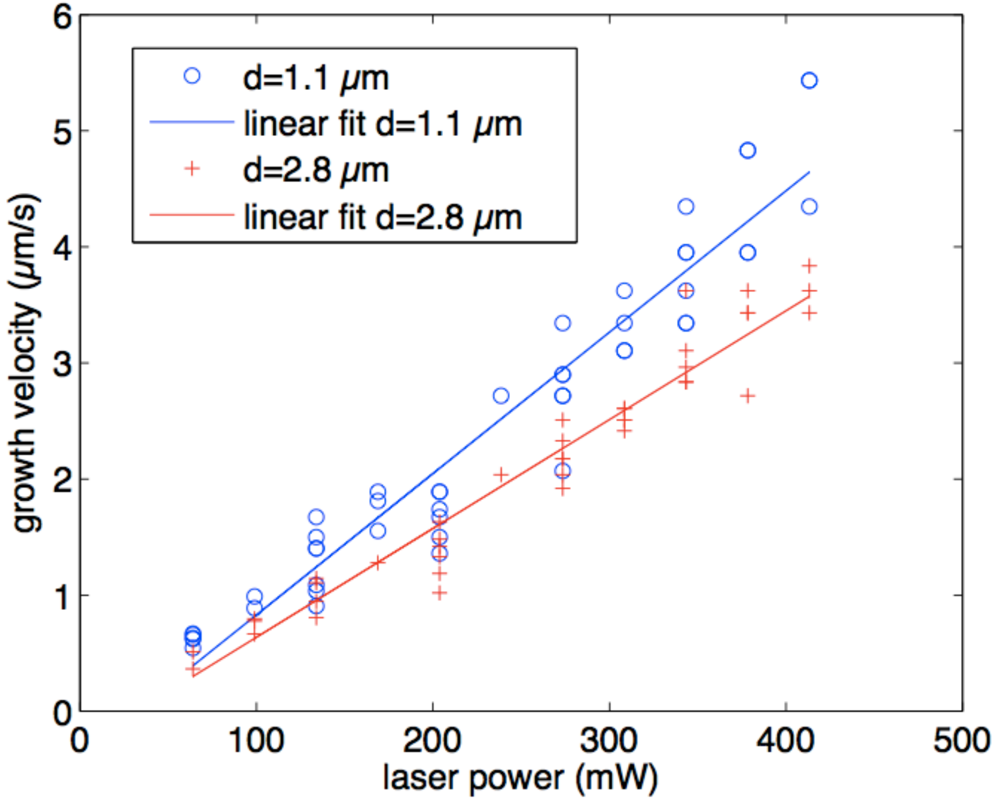


PMMA/octanone mixture 12.8 % at RT enlightened with a focus laser beam at 130 mW

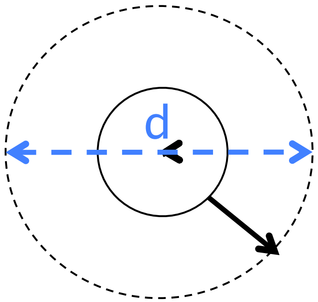
Short time



growth velocity

$$v_g = \frac{d}{\Delta t_d}$$

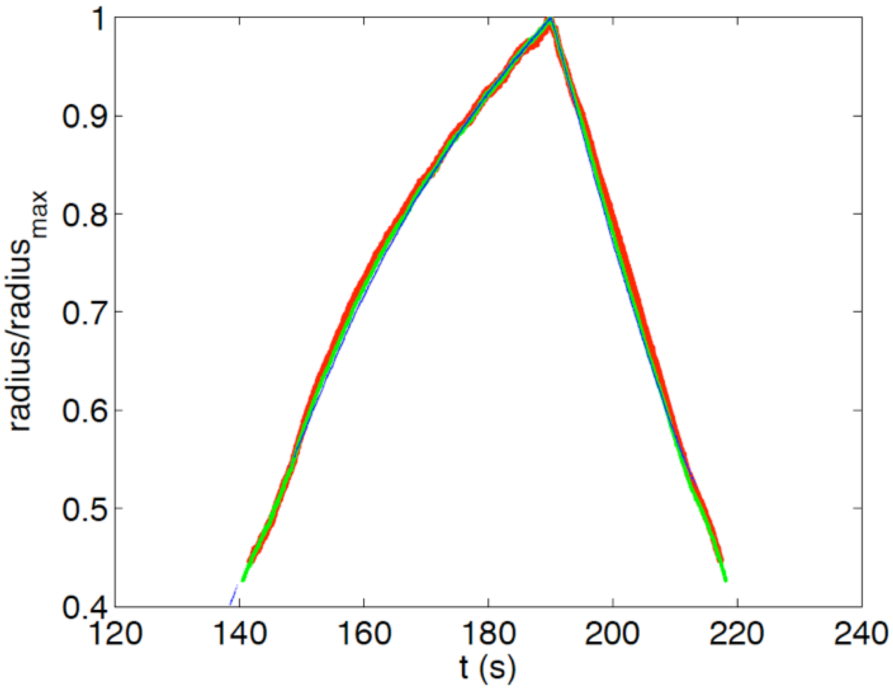
- Laser intensity threshold : no growth below 80 mW
- linear vs laser power
- velocity decrease when size increase



Δt_d ?

The drop size as a function of time

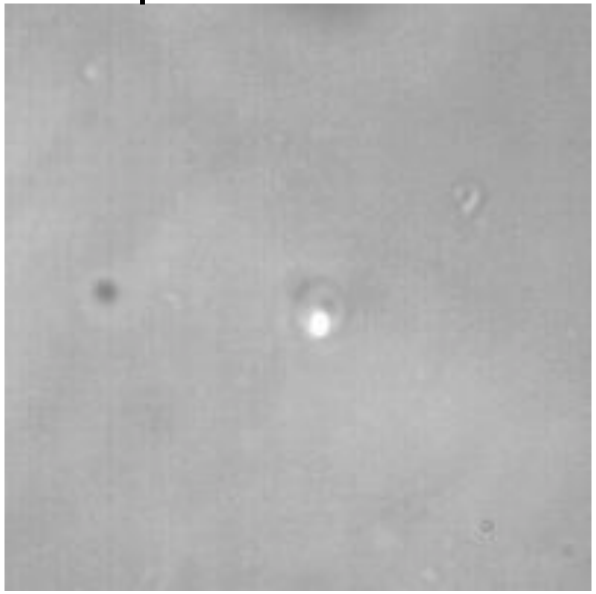
Times evolution of the
the drop radius normalized
to its maximum



The different curves correspond to different values of the threshold used to detect the drop edge.

IMAGE ANALYSIS

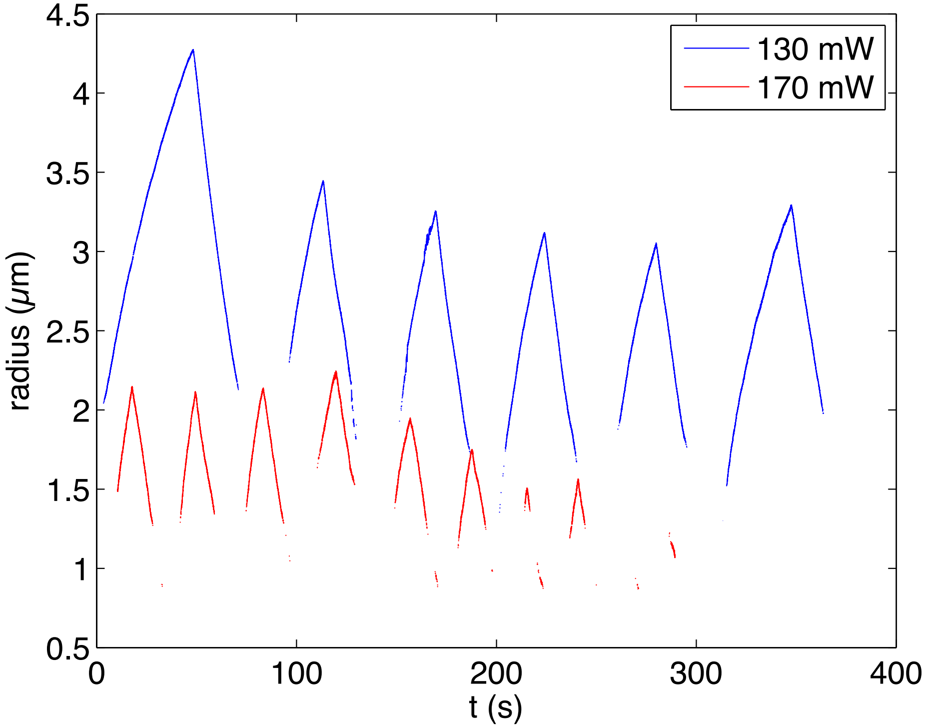
An algorithm based on an intensity threshold method is used to determine the edge of the drop and its radius.

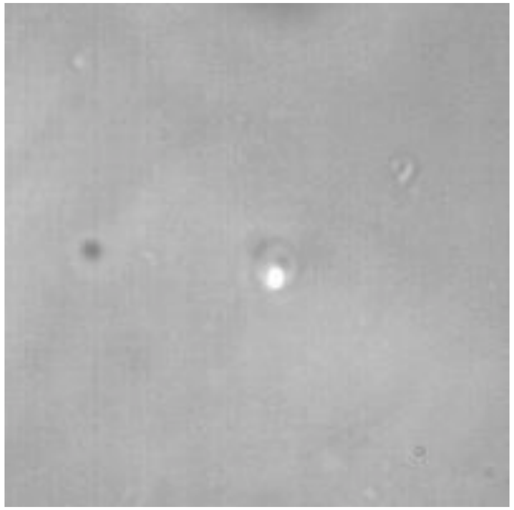


The time evolution does not depend on the threshold value

Long time behavior

Time evolution of the droplet size at the same point for two different laser powers





When the laser power increases :

a) The oscillation frequency incrases
b) The maximum radius decreases

Physical phenomena

What is the origin of this laser induced transition ?

A droplet of PMMA rich phase is initiated in the PMMA poor phase and then oscillates.

Where does this PMMA accumulation come from?

It can not be a simple effect of heating because this binary mixture has a UCST, so an increase in temperature should provoke an homogenization of the solution.

Temperature and light intensity gradients are important

Physical phenomena

- Particle trapping by the focused laser beam

- Thermal gradients induced by the local heating

- The Soret effect :

- Electrostriction

Physical phenomena

Particle trapping by the focused laser beam

Is this trapping possible ?

The radius of gyration of the polymer is about 1nm

Using the Rayleigh approximation the ratio between the scattering force and the gradient force on the particles is $10^{-7} < 1$. The trap is thus stable.

The trapping force must be bigger than the thermal forces acting on the PMMA bead. The Boltzmann factor $\exp(-U_{grad}/(k_B T)) << 1$

U_{grad} **is the potential of the gradient force which in our experiment is:** $U_{grad} \simeq 5\ 10^{-26}$**J**

So even if the trap is stable, the gradient force is not sufficient to trap the polymer.

Physical phenomena

- Particle trapping by the focused laser beam : The trap is stable but it can be neglected because trapping energy is smaller than thermal energy

- Thermal gradients induced by the local heating

- The Soret effect :

- Electrostriction

Physical phenomena

Local heating because of absorption :

The measured extinction coefficient of the mixture is $\simeq 9m^{-1}$

The temperature increase, is about $5K$ at the focal point.

This increase should be enough to observe a thermophoretic effect.

Physical phenomena

- Particle trapping by the focused laser beam : The trap is stable but it can be neglected because trapping energy is smaller than thermal energy

- Thermal gradients induced by the local heating
  Temperature increases at the focal point of about 5K.

- The Soret effect :

- Electrostriction (contrary of piezoelectricity) :

Physical phenomena

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- The Soret effect :
  depending on the sign of the Soret coefficient particles are attracted to hot or cold regions.
  We measured the Soret coefficient and for Octanone/PMMA ($\approx 0.1 K^{-1}$) is positive.
  Thus PMMA is attracted towards cold regions

- Electrostriction

Physical phenomena

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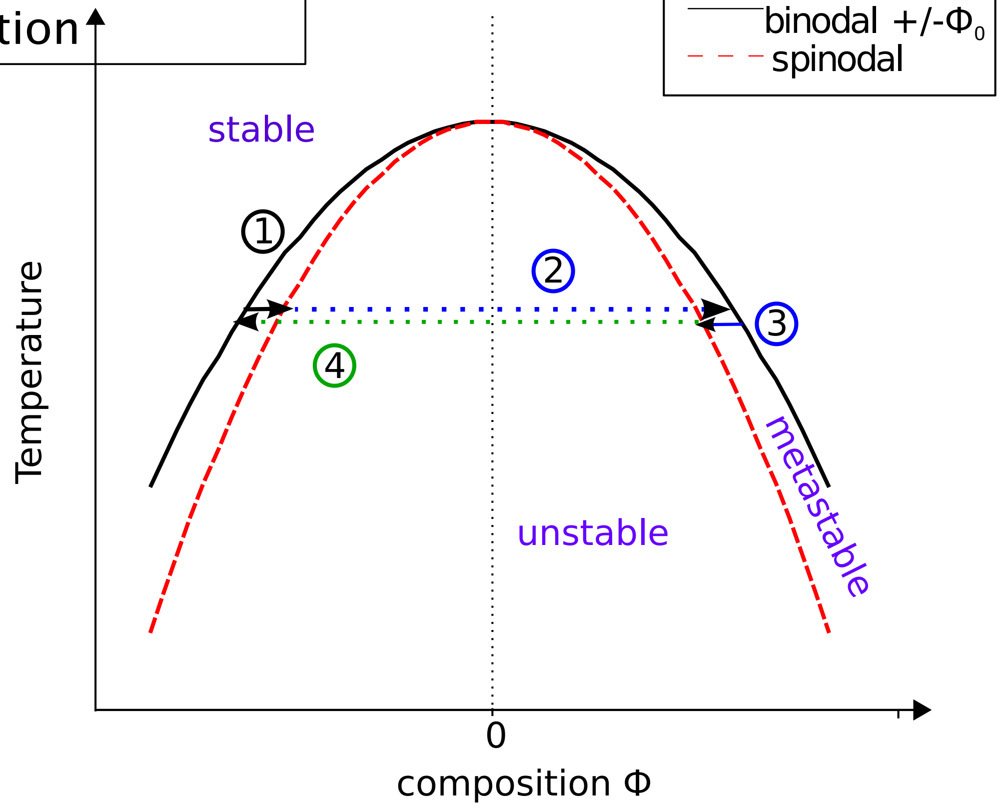
- Electrostriction (contrary of piezoelectricity) :
  Change of volume due to an electric field.
  Concentration flux by osmotic pressure

A simple mechanism

1. PMMA accumulate thanks
   to electrostriction

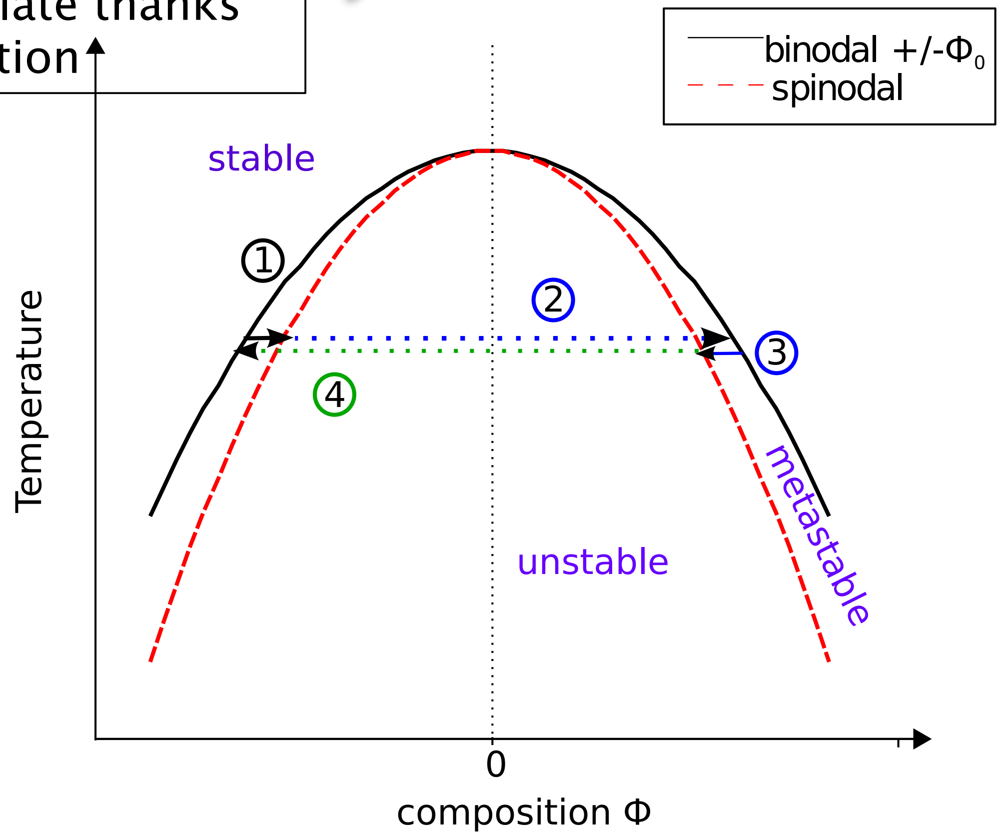


*Soret : Temperature gradient leads to a particle flux to cold region

A simple mechanism

1. PMMA accumulate thanks to electrostriction

2. Excess of PMMA unstable => phase transition



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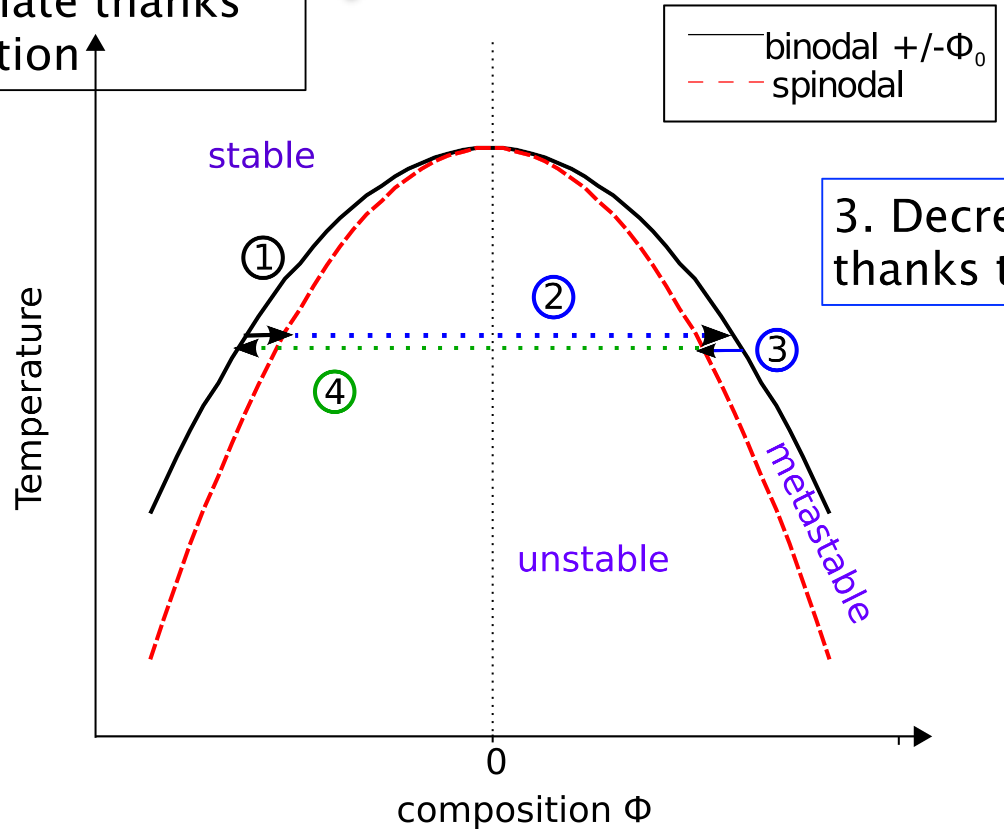
3. Decreasing of PMMA thanks to Soret* effect



A simple mechanism

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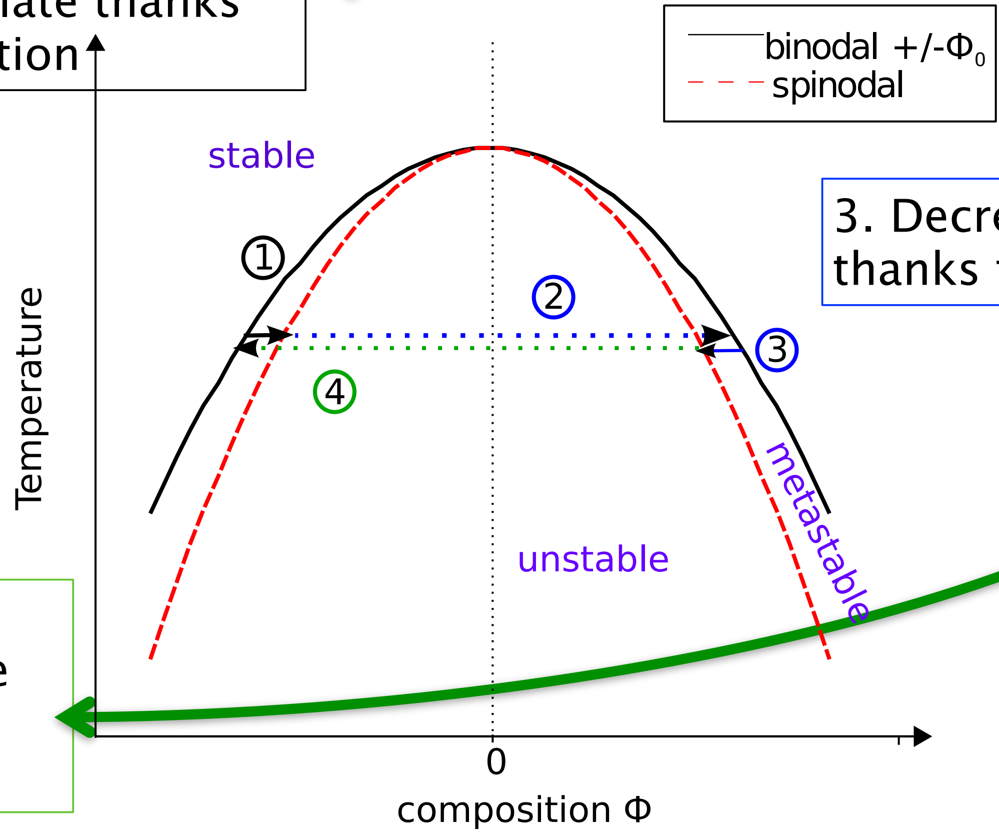
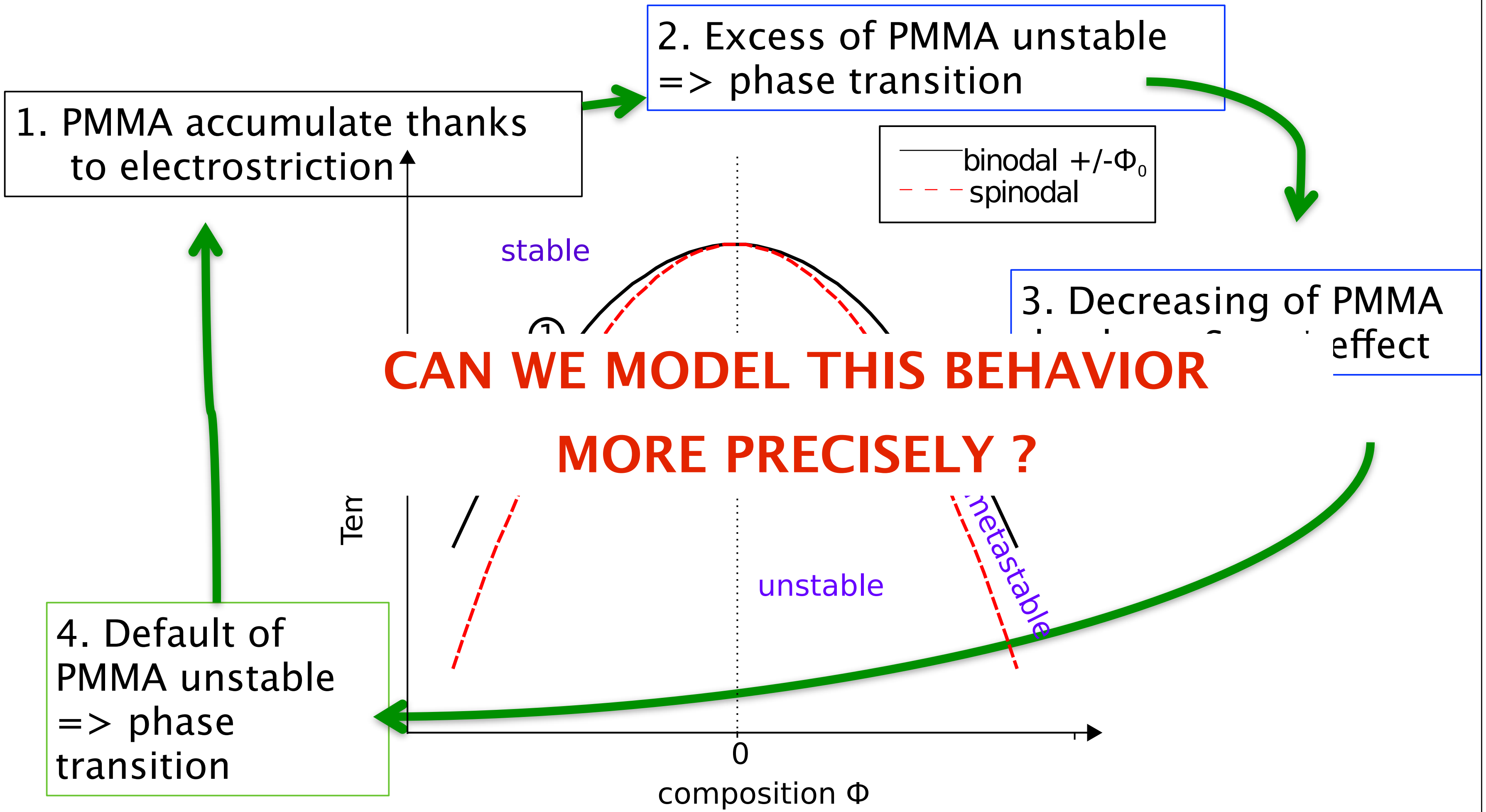


3. Decreasing of PMMA thanks to Soret* effect

4. Default of PMMA unstable => phase transition

*Soret : Temperature gradient leads to a particle flux to cold region

A simple mechanism

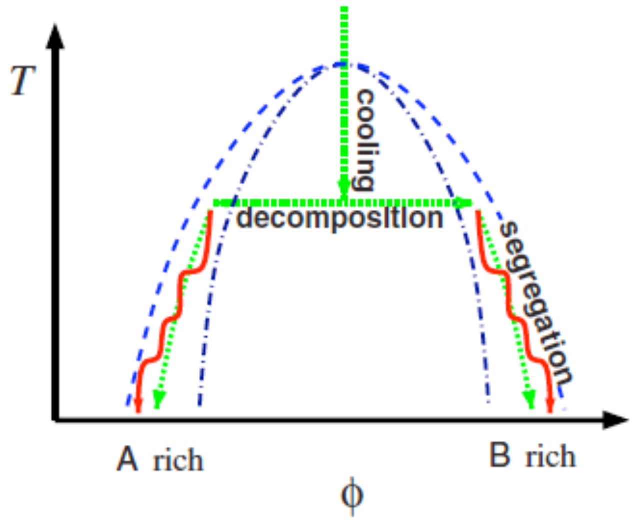


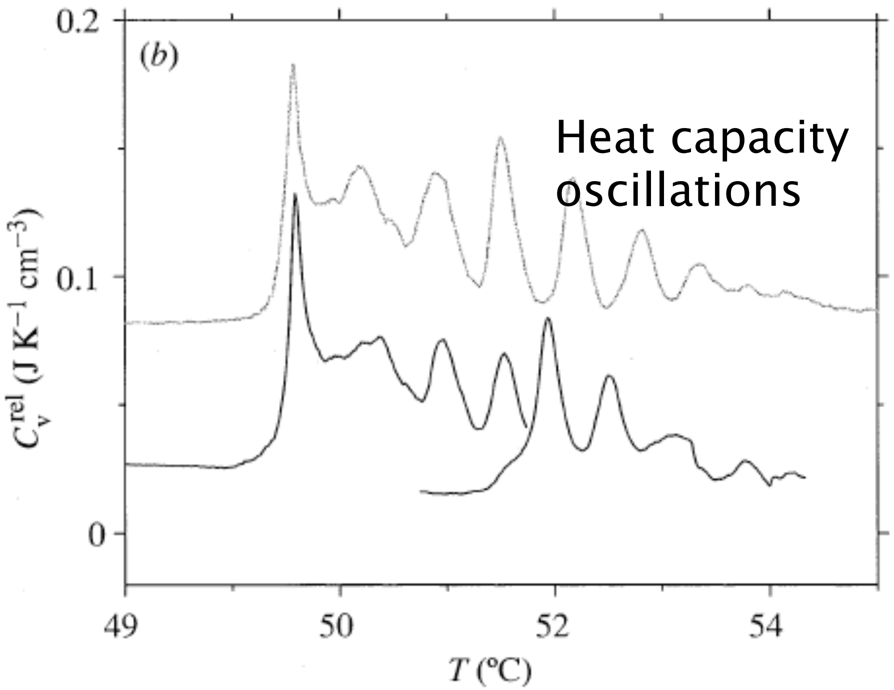
CAN WE MODEL THIS BEHAVIOR MORE PRECISELY ?

Does an oscillating phase transition have been observed elsewhere ?

Phase separation in binary fluid mixtures with continuously ramped temperature M. E. Cates, J. Vollmer, A. Wagner, D. Vollmer, *Philosophical Transaction*, **361** 1805 (2003).

A slow temperature ramp is applied to the mixture





An interesting model has been proposed in this article

The full model

The Gindzburg-Landau approach for Binary mxture is used

The free energy in the ϕ^4 model is given by :

$$\mathcal{F}([\phi], t) = \int \mathrm{d}\vec{x} \left[\frac{b}{4}\phi^4 - \frac{a}{2}\phi^2 + \frac{\sigma}{2}(\nabla\phi(\vec{x}, t))^2 \right]$$

where $\phi(x, t)$ is the PMMA concentration centered at the critical one. a, b depend on T.

Equilibrium solutions are given by :

$$\partial_\phi \left[\frac{b}{4}\phi^4 - \frac{a}{2}\phi^2 + \frac{\sigma}{2}(\nabla\phi(\vec{x}, t))^2 \right] = 0$$

$$\text{Two soulitions : } \pm\phi_0 \text{ where } \phi_0 = \sqrt{\frac{\mathrm{a}}{\mathrm{b}}}$$

The full model

A minimal model is : $b(T) = b_0$ and $a(T) = a_0(T_c - T)$

$$\phi_0 = \sqrt{\frac{a_0(T_c - T)}{b_0}}$$

with coexistence curve : $T_{eq}(\phi) = T_c - \frac{b_0}{a_0}\phi^2$

Diffusion equation : $\partial_t \phi(\vec{x}, t) = \alpha \nabla^2 \mu(\phi(\vec{x}, t))$

diffusion coefficient : α

Chemical potential : $\mu(\phi(\vec{x}, t)) \equiv \delta \mathcal{F}([\phi], t)/\delta\phi$

$$\partial_t \phi = \alpha \nabla^2 \left(b_0 \phi^3 - a_0(T_c - T)\phi)\right) - \alpha\sigma\nabla^4 \phi.$$

The full model

$$\varphi = \phi/\phi_0 \qquad \phi_0 = \sqrt{a_0(T_c - T)/b_0}$$

$$\phi_0 \partial_t \varphi = \alpha b_0 \nabla^2 \left(\phi_0^3 (\varphi^3 - \varphi) \right) - \alpha\sigma \nabla^4 (\phi_0 \varphi).$$

Non linear diffusion

Interface smoothing

The full model

$$\varphi = \phi/\phi_0 \qquad \phi_0 = \sqrt{a_0(T_c - T)/b_0}$$

$$\phi_0 \partial_t \varphi = \alpha b_0 \nabla^2 \left(\phi_0^3 (\varphi^3 - \varphi) \right) - \alpha \sigma \nabla^4 (\phi_0 \varphi).$$

Non linear diffusion

Interface smoothing

1D model for slow cooling

Phase separation in binary fluid mixtures with continuously ramped temperature M. E. Cates, J. Vollmer, A. Wagner, D. Vollmer, *Philosophical Transaction*, **361** 1805 (2003).

Phase separation under ultraslow cooling Vollmer, JCP 129, (2008)

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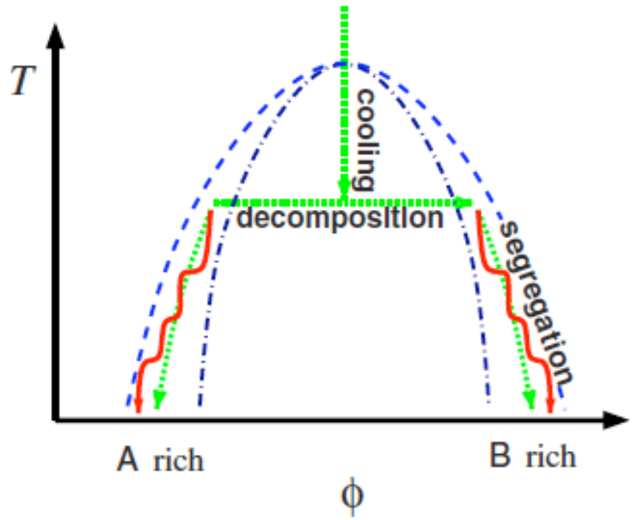

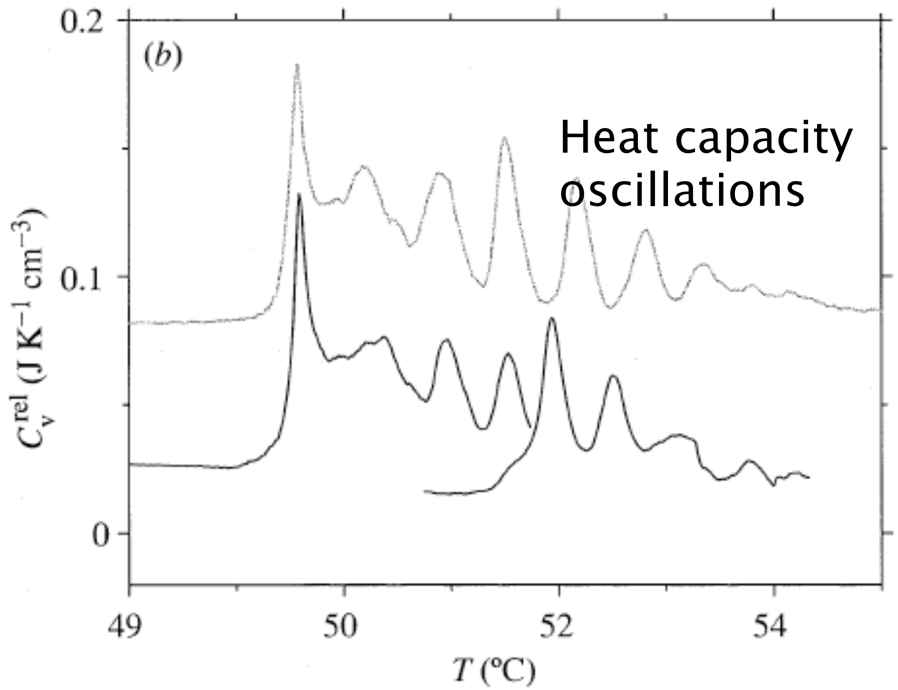

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The full model

$$\varphi = \phi/\phi_0 \qquad \phi_0 = \sqrt{a_0(T_c - T)/b_0}$$

$$\phi_0 \partial_t \varphi = \alpha b_0 \nabla^2 \left(\phi_0^3(\varphi^3 - \varphi)\right) - \alpha\sigma\nabla^4(\phi_0\varphi).$$

1D the model for slow cooling

Phase separation under ultraslow cooling Vollmer, JCP 129, (2008)

Because of slow cooling $\phi_0 = \sqrt{a_0(T_c - T(t))/b_0}$ is a function of time

$$\partial_t \varphi(x,t) = \partial_x \left[(3\varphi^2 - 1)\partial_x \varphi\right] - M^2 \partial_x^4 \varphi + \xi\varphi.$$

driving force

In the original model by Cates et al. $\xi = \frac{\partial_t \Phi_o}{\Phi_o}$

M is the chacteristic length defining the interface thickness

The full model

Can a similar model be applied to our experimental results ?

$$\varphi = \phi/\phi_0 \qquad \phi_0 = \sqrt{a_0(T_c - T(\vec{x}))/b_0}$$

$$\phi_0 \partial_t \varphi = \alpha b_0 \nabla^2 \left(\phi_0^3(\varphi^3 - \varphi)\right) - \alpha\sigma\nabla^4(\phi_0\varphi).$$

In our system

$\nabla T \neq 0$ implies that also $\nabla \phi_0 \neq 0.$

Temperature diffusion with a pumping term imposed by the laser intensity

$$\partial_t T = D_\theta \triangle T + \kappa I(\vec{x})$$

Laser intensity

Stationary solution of T obtained from the laser intensity distribution

$$D_\theta \triangle T = -\kappa I(\vec{x})$$

The full model

The Soret effet

The presence of the gradient produces thermophoresis ;

$$\begin{aligned}\vec{j_S} &= -D_T c(\vec{x},t)(1-c(\vec{x},t))\nabla T = \\ &= -D_T(\phi(\vec{x},t)+c_c)(1-\phi(\vec{x},t)-c_c)\nabla T\end{aligned}$$

$\vec{j}_s$ mass current
c_c critical concentration
∇T the temperature gradient due to the laser
D_T Soret diffusion coefficient
D_T is positive when particles are attracted in cold region.

The full model

$$\varphi = \phi/\phi_0$$

$$\phi_0 \partial_t \varphi = \alpha b_0 \nabla^2 \left(\phi_0^3 (\varphi^3 - \varphi) \right) - \alpha\sigma \nabla^4 (\phi_0 \varphi) - \nabla \vec{j_s}$$

which taking into account the temperature gradients and the Soret effet gives the following result

$$\begin{aligned}\partial_t \varphi = {} & \alpha b_0 \phi_0^2 \nabla \left((3\varphi^2 - 1) \nabla \varphi) \right) + 6\alpha b_0 (3\varphi^2 - 1) \phi_0 \nabla \phi_0 \nabla \varphi \\ & + \alpha b_0 (\varphi^3 - \varphi)[6(\nabla \phi_0)^2 + 3\phi_0 \nabla^2 \phi_0] - \alpha\sigma \nabla^4 \varphi \\ & + D_T (\varphi(x,t) + c_c/\phi_0) \nabla^2 T \\ & + D_T (\nabla \varphi + \varphi \nabla \phi_0 / \phi_0) \nabla T.\end{aligned}$$

Too complex ; Too many parameters

Minimal Numerical model 1D

We simplify the full model

$$\partial_t \varphi = \partial_x^2 \left((\varphi^3 - \varphi) \right) - M^2 \partial_x^4 (\varphi) - \xi \varphi - \xi_1 \partial_x \varphi$$

where now ξ and ξ_1 depend on x.

Can a localized forcing produce oscillations ?

$$\partial_t \varphi(x,t) = \partial_x \left[(3\varphi^2 - 1) \partial_x \varphi \right] - M^2 \partial_x^4 \varphi - \xi \varphi$$

driving force

Minimal Numerical model 1D

$$\partial_t \varphi(x,t) = \partial_x \left[(3\varphi^2 - 1)\partial_x \varphi\right] - M^2 \partial_x^4 \varphi - \xi\varphi$$

driving force

we use a space dependent driving force

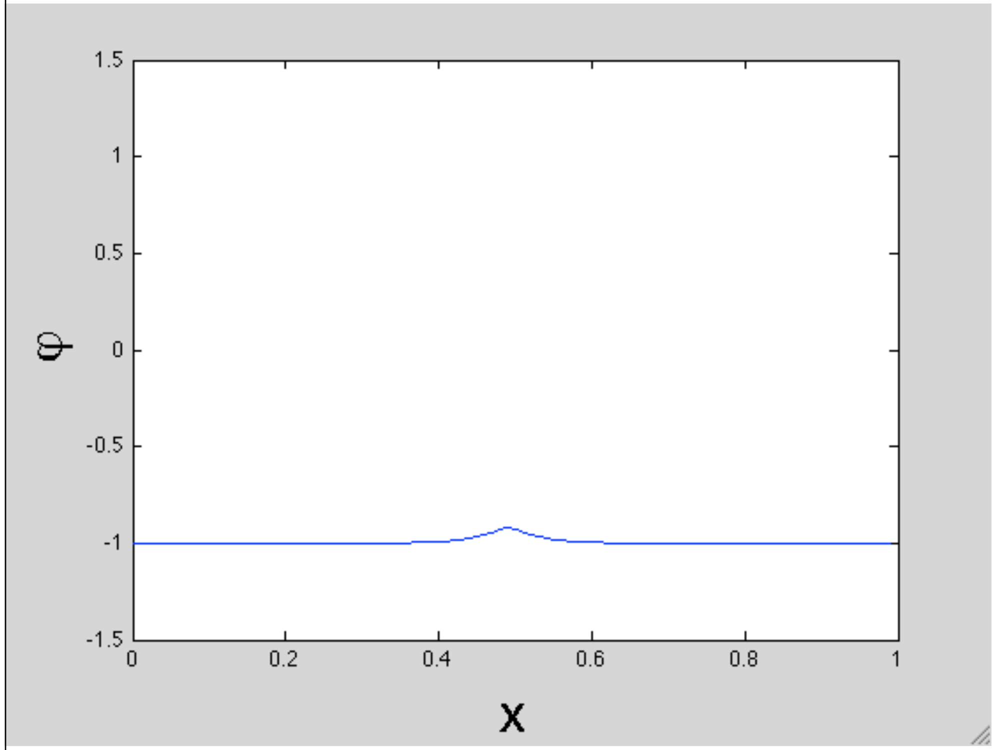
$$\xi = \begin{cases} \xi_o = \xi'_o / S_\xi \text{ for } (x_o - S_\xi/2) \le x \le (x_o + S_\xi/2) \\ 0 \text{ elsewhere} \end{cases}$$

Oscillations appear if
$M < S_\xi$ **and** $\xi_o >$ **threshold value**

with $M = 0.002$ and $S_\xi = 0.01$
then $\xi_o > 150$ to get oscillations

Numerical model 1D

$M = 0.002,\ \xi_o = 300,\ S_\xi = 0.01$



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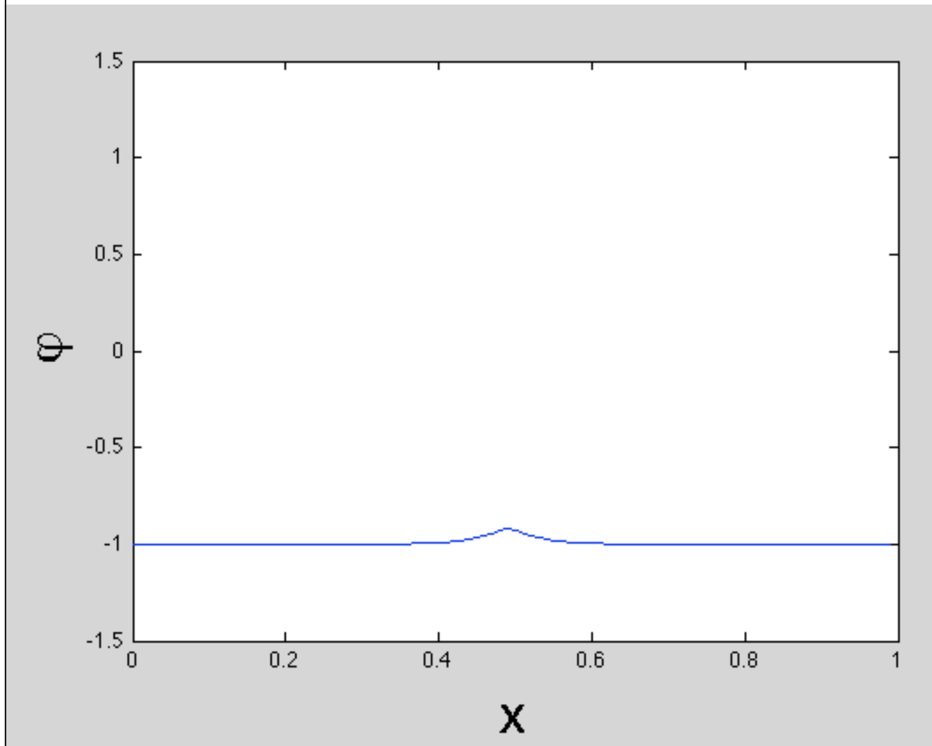
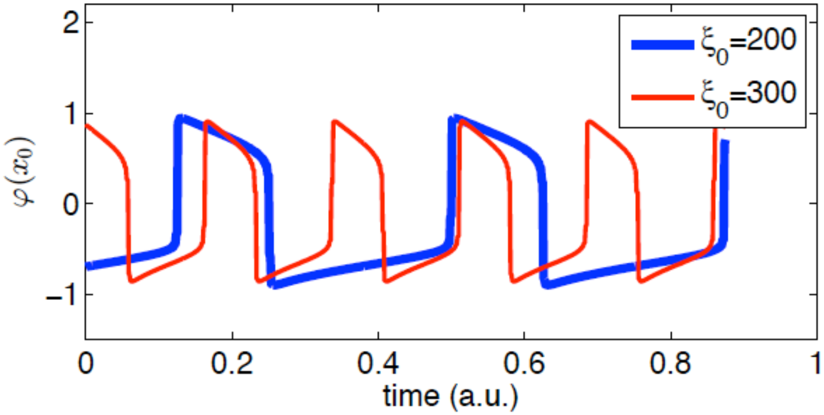
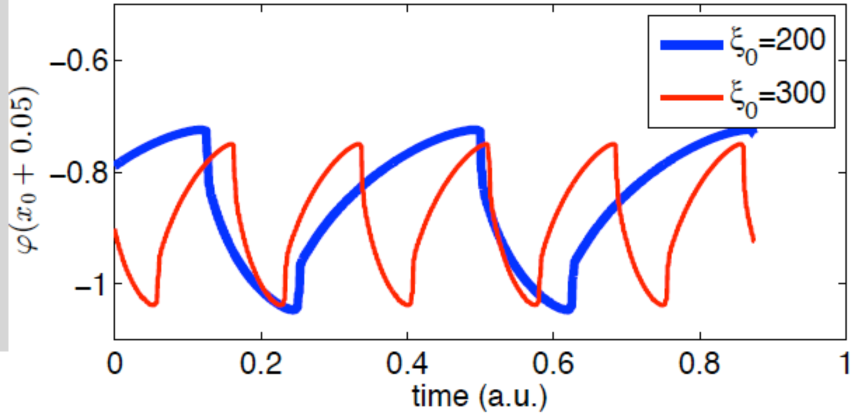


local concentration at the driving point



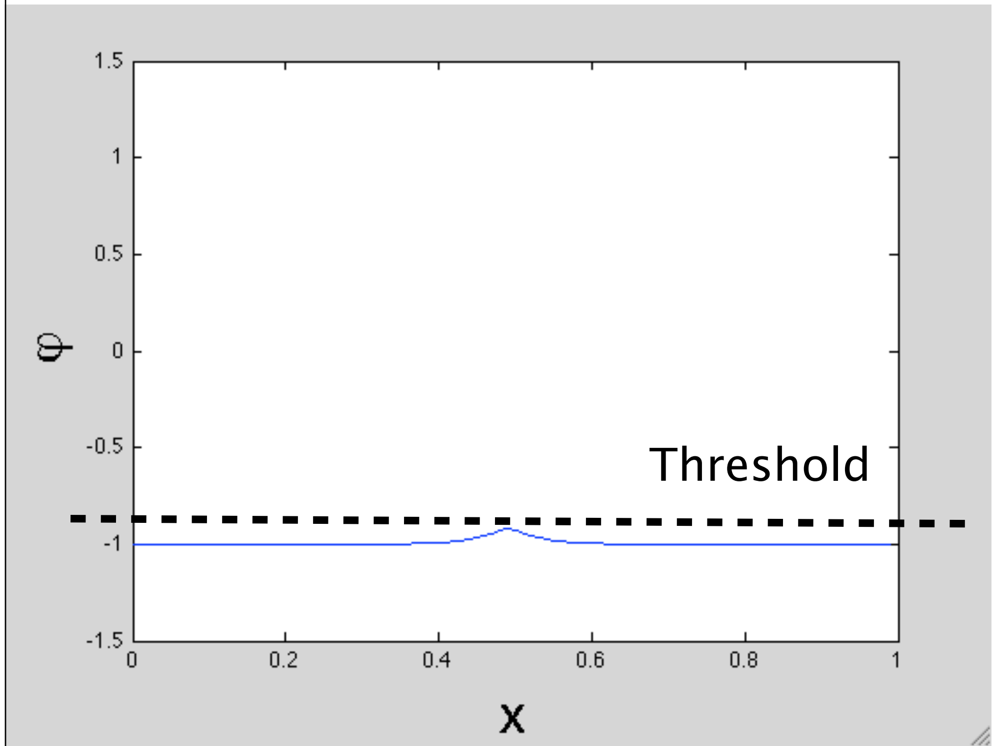
local concentration at 0.05 from the

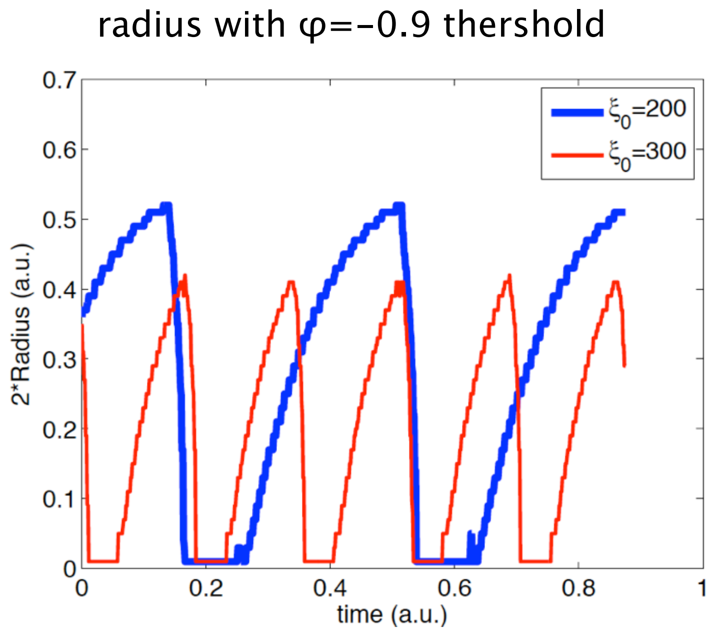


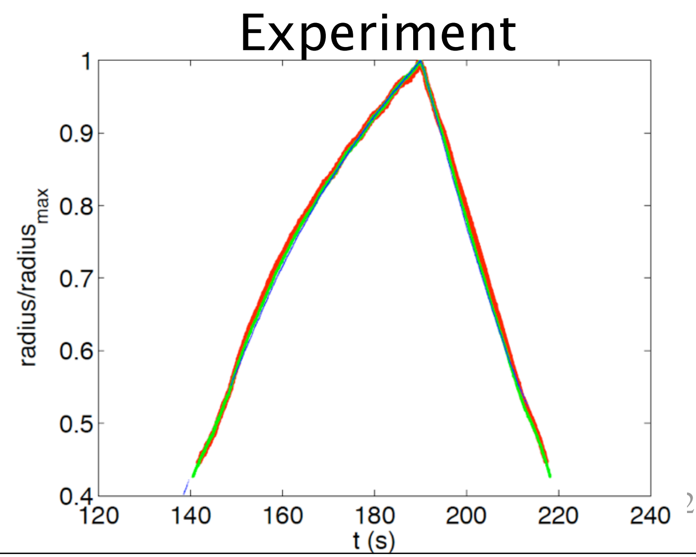
As in the experiment the frequency of the oscillations depends on the driving intensity

Numerical model 1D

$M = 0.002,\ \xi_o = 300,\ S_\xi = 0.01$







a) The radius dynamics is similar to the experimental one
b) The maximum radius decreases when the driving increases

Conclusions

- We have observed a new and puzzling oscillatory phenomenon in the phase separation of a binary mixture, which is induced by a local pumping

- test on water/$C_{12}E_5$: no similar effects are observed. Droplets can be trapped in the heterogeneous phase

- We have proposed several physical mechanisms that can induce these oscillations: Temperature gradients, Thermophoresis ,Electrostriction

- A simplified model based on the Gindzburg-Landau apporach for binary mixture on which we add a local forcing, reproduces the general features of the oscillations.

Things to be done :
- confirm the model by a proper estimation of the relative strength of Soret and electrostriction effects
- develop a more complete numerical model

-Check wether this can be a general features of phase transitions.

What about our original questions on Brownian motion near critical points ?

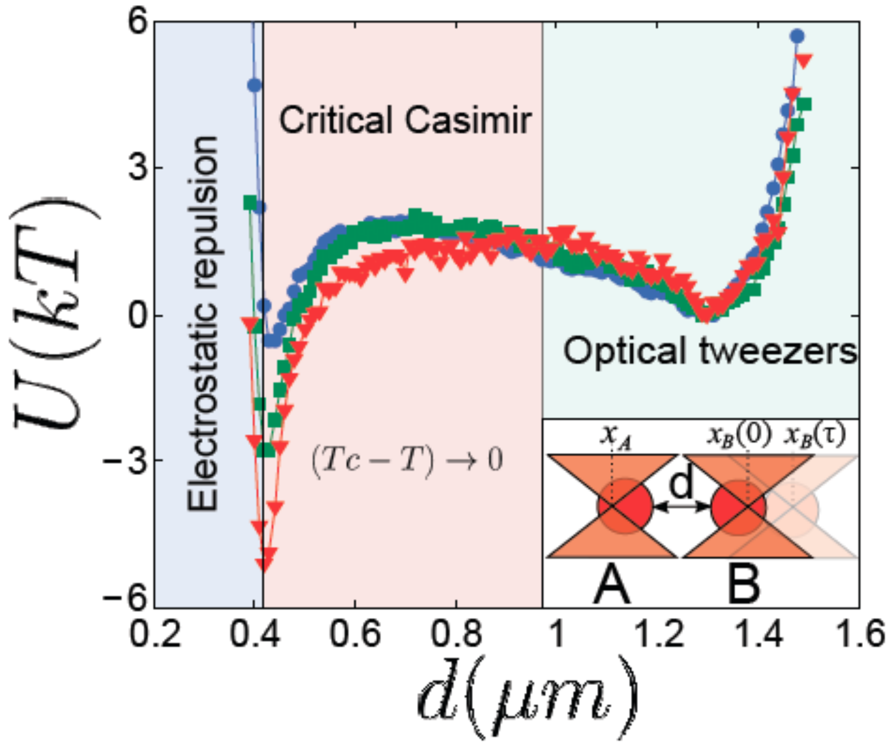
- laser effects on PMMA/octanone : it is not the good sample to study local effects in phase transition

- water/$C_{12}E_5$ is a very good mixture because it has no spurious effects and its correlation length is very large.

Two silica beads trapped by two laser beads
in a critical mixture of water/$C_{12}E_5$

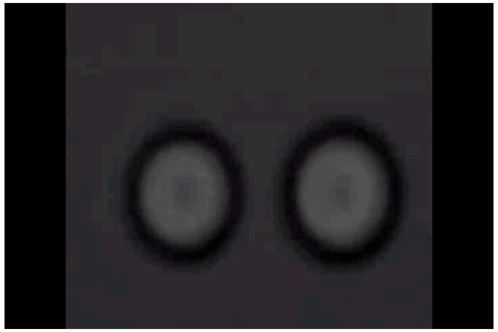
Two silica beads trapped by two laser beams in a critical mixture of water/$C_{12}E_5$

Measure of Casimir forces and potentials



Temperature dependent synchronisation

Non synchronised T<Tc



Synchronised T≅Tc