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Introduction to Optofluidics

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Optical manipulation of binary liquid mixtures

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Introduction to Optofluidics
Optical manipulation of binary liquid mixtures

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Outline

I. General overview

II. Field variations of thermodynamic variables

III. Applications of electrostrictive and thermodiffusive variations of concentration

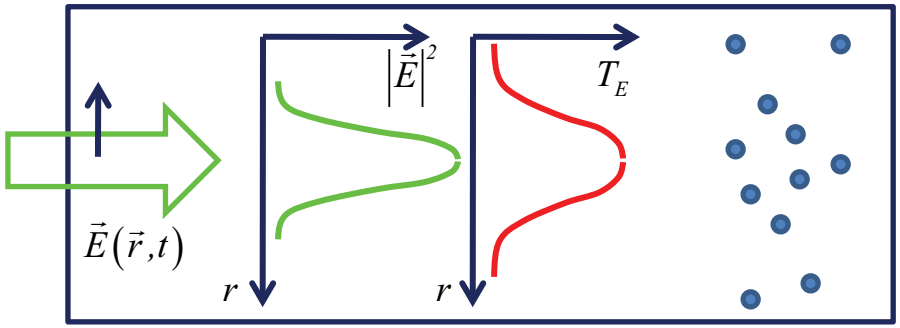
IV. Laser-induced first-order phase transitions

V. Droplet growth in a laser beam

VI. Related and Recent developments

VII. Concluding remarks

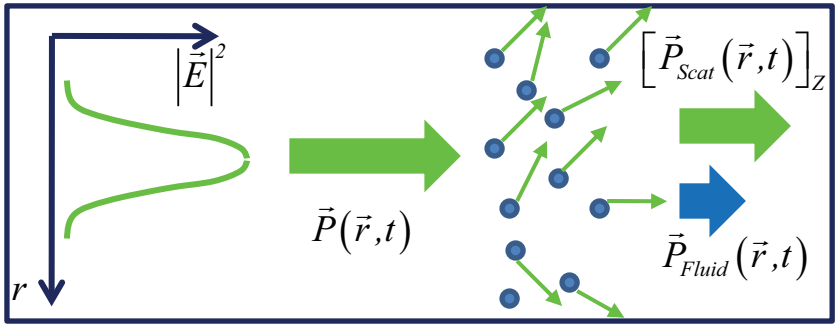
Light-fluid interaction in a liquid mixture



Electrostriction
Heating
Thermodifusion

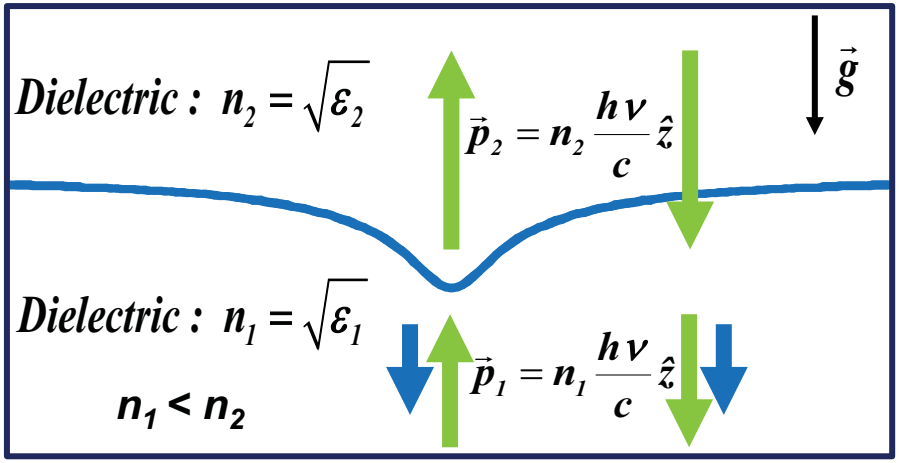
Diffusion

$r << \lambda$



Scattering

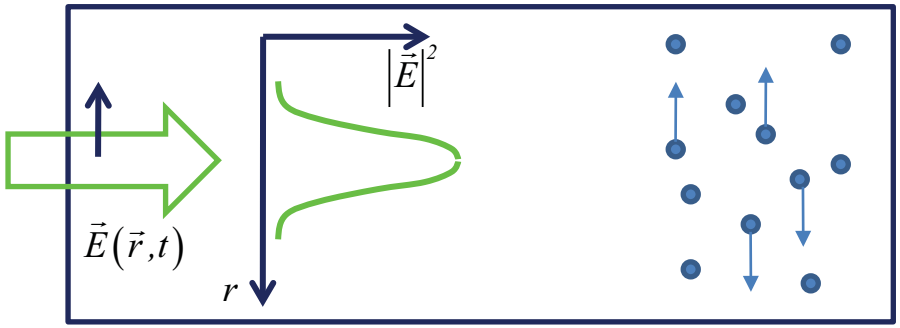
Flow



Surface Force:
Radiation pressure

Deformation

Electrostriction in a binary liquid mixture



Field $\vec{E}(\vec{r},t) \longrightarrow$ **Induced dipole:** $\vec{d}(\vec{r},t)=\alpha\vec{E}(\vec{r},t) \longrightarrow$ **Electrostrictive Force:** $\vec{F}_{el}(\vec{r},t)=\left[\vec{p}(\vec{r},t)\cdot\vec{\nabla}\right]\vec{E}(\vec{r},t)$

$$\left(\vec{\nabla}\vec{E}^2=2\left(\vec{E}\cdot\vec{\nabla}\right)\vec{E}+2\vec{E}\times\left(\vec{\nabla}\times\vec{E}\right),\vec{\nabla}\times\vec{E}=0\right)$$

$$\vec{F}_{el}(\vec{r},t)=\left\langle\vec{F}_{el}(\vec{r},t)\right\rangle_T=\frac{1}{2}\alpha\vec{\nabla}\left\langle\vec{E}(\vec{r},t)^2\right\rangle_T=\frac{1}{4}\alpha\vec{\nabla}\left|\vec{E}(\vec{r},t)\right|^2$$

$$\longrightarrow \quad \vec{F}_{el}(\vec{r},t)=\frac{\alpha}{2n_p\varepsilon_0 c}\vec{\nabla}I(\vec{r},t)$$ where the beam intensity is: $I(\vec{r},t)=\frac{n_p\varepsilon_0 c}{2}\left|\vec{E}(\vec{r},t)\right|^2$

Osmotic Pressure: $\vec{\nabla}\delta\Pi_{el}(\vec{r},t)=N\vec{F}_{el}(\vec{r},t)$ where *N*: particle number/unit volume

$$\longrightarrow \quad \delta\Pi(\vec{r},t)=\frac{\alpha N}{2n_p\varepsilon_0 c}I(\vec{r},t)$$

Concentration variation: $\delta N=\left(\frac{\partial N}{\partial\Pi}\right)\delta\Pi(\vec{r},t) \longrightarrow \delta N=\left(\frac{\partial N}{\partial\Pi}\right)\frac{\alpha N}{2n_p\varepsilon_0 c}I(\vec{r},t)$

$$\longrightarrow \quad \frac{\delta N}{N}=\frac{\alpha N K_T}{2n_p\varepsilon_0 c}I(\vec{r},t)$$ where $K_T=\frac{1}{N}\left(\frac{\partial N}{\partial\Pi}\right)$ Osmotic compressibility $\left(K_T\big|_{\substack{perfect\\gas}}=\frac{1}{Nk_BT}\right)$

Nonlinear optics in aerosols

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Received August 6, 1979; revised manuscript received October 1, 1979

We identify an aerosol of dielectric particles as a broadband, low-power nonlinear-optics medium. We demonstrate theoretically that a room-temperature volume of 5-μm-radius glass spheres will exhibit a third-order susceptibility in the visible equal to $\sim 10f$ esu, where f is the volumetric packing fraction of the spheres. The response of the system is broadband throughout the visible, and the nonlinear-optic gain coefficient is shown to exceed the extinction coefficient because of scattering at pump-power levels on the order of 0.3 W/cm^2. Two techniques for levitation of the aerosol are quantitatively evaluated.

→ **Four-wave mixing in an artificial Kerr medium**

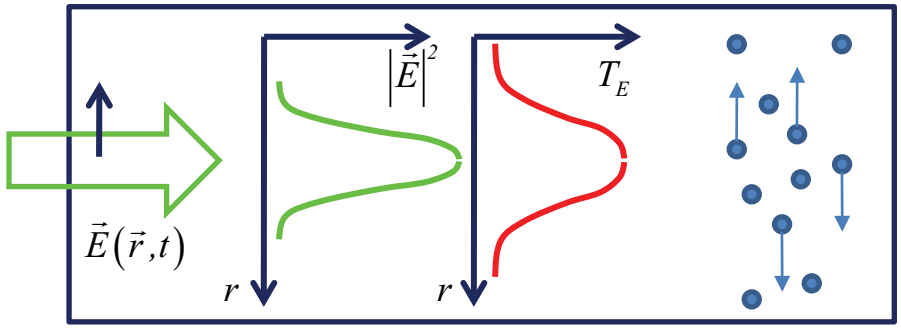
Use of a liquid suspension of dielectric spheres as an artificial Kerr medium

Studies of self-focusing bistable devices using liquid suspensions of dielectric particles

Continuous-wave self-focusing and self-trapping of light in artificial Kerr media

A. Ashkin et al, Optics Letters 1981-84

Thermal effects in a binary liquid mixture



Temperature rise induced by a laser beam

Pure Heating:

M. Lax

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and
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 February 1977; accepted for publication 11 May 1977)

$$T_E(r) \approx \frac{\alpha_a P}{4\pi\Lambda_T}\left[\ln\left(\gamma\frac{\omega_{bc}^{\ 2}}{\omega_0^{\ 2}}\right)-\frac{2r^2}{\omega_0^{\ 2}}\right]$$

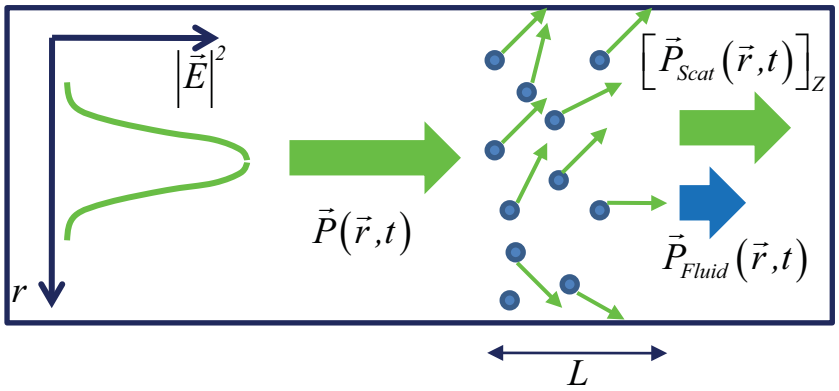
Optical absorption: α_a Thermal conductivity: Λ_T

Soret Effect (Thermodiffusion): $\vec{\nabla}T_E(r) \longrightarrow \vec{\nabla}\Phi_E(r)$

$$\Phi_E(r) = -\frac{\rho_0}{\rho_d}\frac{k_T}{T_0}T_E(r)$$

Soret Coefficient: k_T

Scattering effects in a binary liquid mixture



Scattering Force density: $\vec{f}_{Scat}(\vec{r},t)=\frac{\tau n}{c}\langle\vec{S}\rangle$

Time average Poynting vector: $\langle\vec{S}\rangle=I(r)\vec{z}$

Turbidity: $\tau=-\frac{1}{I}\left(\frac{\partial I}{\partial z}\right)\sim N\sigma_{scat}$ $\quad(\tau L<<1)$

Scattering cross section: σ_{scat}

Work per unit time: $\dot{W}\sim f_{Scat}u\left(\omega_0{}^2L\right)$ $\longrightarrow$ **Average suspension velocity:** $u\sim\frac{\omega_0{}^2 f_{Scat}}{\eta}$

Viscous dissipation rate: $\dot{D}=\int\sigma\cdot\nabla u dV\sim\eta\left(\frac{u}{L}\right)^2L^3$

η: shear viscosity, σ: viscous stress

Individual particle: $\vec{F}_{Scat}(\vec{r},t)=\frac{\sigma_{scat}n}{c}\langle\vec{S}\rangle$ $\quad\vec{F}_{drag}(\vec{r},t)=-6\pi r\eta\vec{u}_p$ $\longrightarrow$ **Average particle velocity:** $u_p\sim\frac{\sigma_{scat}nI}{cr\eta}$

Collective flow: $u_p<<u$ $\longrightarrow$ $\Phi=\frac{4}{3}\pi r^3N>>\left(\frac{r}{\omega_0}\right)^2$

Rayleigh scattering: $\sigma_{scat}=\frac{8}{3}\pi(kr)^4r^2\left(\frac{n_p{}^2-n^2}{n_p{}^2+2n^2}\right)^2$

$\tau L<<1$ $\longrightarrow$ $(\Delta n)^2(kr)^4\left(\frac{r}{\omega_0}\right)^2\frac{L}{r}<<1$

Bulk versus individual scattering effects in a binary liquid mixture

Collective flow: $u_p << u$ $\longrightarrow (\Delta n)^2 (kr)^4 \left(\frac{r}{\omega_0}\right)^2 \frac{L}{r} << 1$

« radiation pressure » on individual particle: $u_p >> u$ $\longrightarrow (\Delta n)^2 (kr)^4 \left(\frac{r}{\omega_0}\right)^2 \frac{L}{r} >> 1$

$\longrightarrow$ **Optical Chromatography**

APPLIED PHYSICS LETTERS VOLUME 83, NUMBER 25 22 DECEMBER 2003

Refractive-index-driven separation of colloidal polymer particles using optical chromatography

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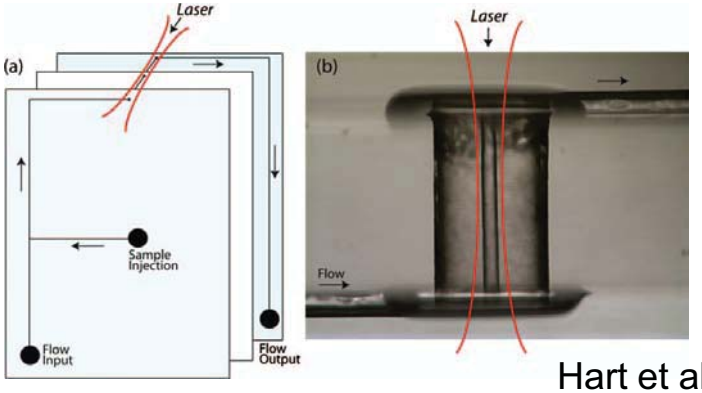
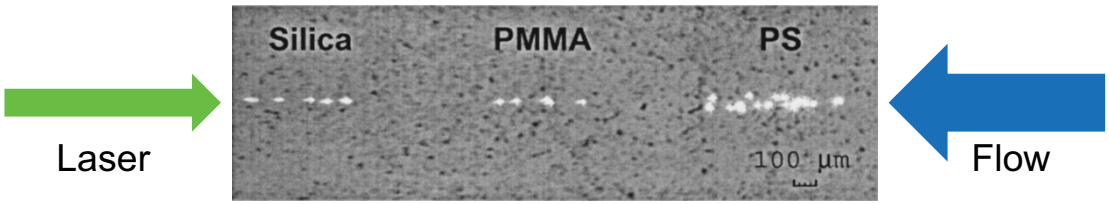
Alex V. Terray
Geo-Centers Incorporated, P.O. Box 441340, Fort Washington, Maryland 20749





Hart et al 2007-08

Field variations of thermodynamic variables

Incompressible Fluid mixture: $dP = 0 \longrightarrow df = -sdT - \cancel{Pd\left(\frac{1}{\rho_0}\right)} + \mu dC + \frac{\vec{E}\cdot d\vec{D}}{\rho_0}$ (free energy per mass unit)

Note: *s* and *μ are field modified quantities!*

$$\vec{E}\cdot d\vec{D} = \varepsilon_0\left(\frac{3}{2}E_0{}^2 d\sqrt{\varepsilon} + \sqrt{\varepsilon}E_0 dE_0\right) \qquad \vec{D} = \varepsilon_0\varepsilon\vec{E} \qquad \left|\vec{E}\right|^2 = \left|\vec{E}_0\right|^2 \Big/ \sqrt{\varepsilon} \qquad \vec{E}_0 : \text{field in vacuum}$$

$$d\sqrt{\varepsilon} = \left(\frac{\partial\sqrt{\varepsilon}}{\partial T}\right)_{P,C,E_0} dT + \left(\frac{\partial\sqrt{\varepsilon}}{\partial C}\right)_{P,T,E_0} dC$$

$$\longrightarrow \quad df = \left(-s + \frac{3}{2}\frac{\varepsilon_0}{\rho_0}E_0{}^2\left(\frac{\partial\sqrt{\varepsilon}}{\partial T}\right)\right)dT + \left(\mu + \frac{3}{2}\frac{\varepsilon_0}{\rho_0}E_0{}^2\left(\frac{\partial\sqrt{\varepsilon}}{\partial C}\right)\right)dC + \frac{\varepsilon_0}{2\rho_0}\sqrt{\varepsilon}\,dE_0{}^2$$

Cross derivatives: $\mu = \mu_0 + \mu_E \longrightarrow \mu_E = -\frac{\varepsilon_0 E_0{}^2}{\rho_0}\left(\frac{\partial\sqrt{\varepsilon}}{\partial C}\right)$

$$s = s_0 + s_E \longrightarrow s_E = \frac{\varepsilon_0 E_0{}^2}{\rho_0}\left(\frac{\partial\sqrt{\varepsilon}}{\partial T}\right)$$

Mass diffusion in presence of light

Continuity equation: $\rho_0\left[\left(\frac{\partial C}{\partial t}\right)+\vec{u}\cdot\cancel{\vec{\nabla}C}\right]=-\vec{\nabla}\cdot\vec{i}$

$$Pe=\frac{(\vec{u}.\vec{\nabla})C}{D\Delta C}=\frac{u\langle x\rangle}{D}=0 \text{ or } <<1$$ Peclet number

Mass flux in the weak perturbation regime: $\vec{i}\approx-\alpha_\mu\vec{\nabla}\mu-\beta_T\vec{\nabla}T$

$$C=C_0+C_E \qquad T=T_0+T_E \qquad \vec{\nabla}\mu_0=\left(\frac{\partial\mu_0}{\partial C}\right)_T\vec{\nabla}C_E+\left(\frac{\partial\mu_0}{\partial T}\right)_C\vec{\nabla}T_E$$

$$\vec{i}\approx-\alpha_\mu\left(\frac{\partial\mu_0}{\partial C}\right)_T\vec{\nabla}C_E-\alpha_\mu\vec{\nabla}\mu_E-\left(\beta_T+\alpha_\mu\left(\frac{\partial\mu_0}{\partial T}\right)_C\right)\vec{\nabla}T_E$$

$$\longrightarrow \quad \frac{\partial C_E}{\partial t}=D\left[\Delta C_E+\frac{k_T}{T_0}\Delta T_E-\frac{\varepsilon_0}{\rho_0}\frac{\left(\frac{\partial\sqrt{\varepsilon}}{\partial C}\right)_{T_0}}{\left(\frac{\partial\mu_0}{\partial C}\right)_{T_0}}\Delta E_0{}^2\right]$$

Mass diffusion constant: $D=\frac{\alpha_\mu}{\rho_0}\left(\frac{\partial\mu_0}{\partial C}\right)_T=\left(\frac{k_BT}{6\pi r\eta}\right)$

Soret constant: $\frac{k_T}{T_0}=\frac{1}{\rho_0}\frac{\left(\beta_T+\alpha_\mu\left(\frac{\partial\mu_0}{\partial T}\right)_C\right)}{\alpha_\mu\left(\frac{\partial\mu_0}{\partial C}\right)_T}$

Thermal diffusion constant: $D_T=Dk_T$

B. Jean-Jean et al, PRA 39, 5268 (1989)

Thermal diffusion in presence of light

Heat transfer equation: $$\rho_0 T\left(\frac{\partial s}{\partial t}\right)+\vec{\nabla}\cdot\left[\vec{q}_T-\mu\vec{i}\right]=Q$$

$$\left(\frac{\partial s}{\partial t}\right)=\left(\frac{\partial s_0}{\partial T}\right)\left(\frac{\partial T_E}{\partial t}\right)+\left(\frac{\partial s_0}{\partial C}\right)\left(\frac{\partial C_E}{\partial t}\right)+\left(\frac{\partial s_E}{\partial t}\right) \qquad \left(\frac{\partial s_0}{\partial T}\right)=\frac{c_P}{T_0},\quad \left(\frac{\partial s_0}{\partial C}\right)=-\left(\frac{\partial^2 f}{\partial C\partial T}\right)=-\left(\frac{\partial \mu_0}{\partial T}\right),\quad \frac{\partial s_E}{\partial t}=\frac{\varepsilon_0}{\rho_0}\left(\frac{\partial\sqrt{\varepsilon}}{\partial T}\right)\frac{\partial {E_0}^2}{\partial t}$$

Thermal flow in the weak perturbation regime: $$\vec{q}_T=\left[k_T\left(\frac{\partial\mu_0}{\partial C}\right)_T-T_0\left(\frac{\partial\mu_0}{\partial T}\right)_C+\mu_0\right]\vec{i}-\Lambda_T\vec{\nabla}T$$

and: $$\vec{\nabla}\cdot\left[\vec{q}_T-\mu\vec{i}\right]\approx\vec{\nabla}\cdot\left[\vec{q}_T-\mu_0\vec{i}\right]$$

$$\vec{\nabla}\cdot\left[\vec{q}_T-\mu_0\vec{i}\right]=\rho_0\left[k_T\left(\frac{\partial\mu_0}{\partial C}\right)_T-T_0\left(\frac{\partial\mu_0}{\partial T}\right)_C\right]\frac{\partial C_E}{\partial t}-\Lambda_T\Delta T$$

Heat generated by optical absorption: $$Q=\alpha_a I$$

$$\longrightarrow\quad \frac{\partial T_E}{\partial t}-\frac{k_T}{c_p}\left(\frac{\partial\mu_0}{\partial C}\right)_T\frac{\partial C_E}{\partial t}+\frac{T_0}{\rho_0 c_p}\varepsilon_0\left(\frac{\partial\sqrt{\varepsilon}}{\partial T}\right)_C\frac{\partial {E_0}^2}{\partial t}=\chi_T\Delta T_E+\frac{\alpha_a}{\rho_0 c_p}I$$

Thermal diffusivity: $$\chi_T=\frac{\Lambda_T}{\rho_0 c_P}$$

B. Jean-Jean et al, PRA 39, 5268 (1989)

Summary

Per unit mass:

$$\begin{cases} \dfrac{\partial C_E}{\partial t} = D\left[\Delta C_E + \dfrac{k_T}{T_0}\Delta T_E - \dfrac{\varepsilon_0}{\rho_0}\dfrac{\left(\dfrac{\partial\sqrt{\varepsilon}}{\partial C}\right)_{T_0}}{\left(\dfrac{\partial\mu_0}{\partial C}\right)_{T_0}}\Delta {E_0}^2\right] \\ \dfrac{\partial T_E}{\partial t} - \dfrac{k_T}{c_p}\left(\dfrac{\partial\mu_0}{\partial C}\right)_T\dfrac{\partial C_E}{\partial t} + \dfrac{T_0}{\rho_0 c_p}\varepsilon_0\left(\dfrac{\partial\sqrt{\varepsilon}}{\partial T}\right)_C\dfrac{\partial {E_0}^2}{\partial t} = \chi_T\Delta T_E + \dfrac{\alpha_a}{\rho_0 c_p}I \end{cases}$$

Per unit volume: $\mu_{0m} = \dfrac{1}{\rho_p}\mu_{0v}, \quad \Phi = \dfrac{V_p}{V_0} = \dfrac{\rho_0}{\rho_p}C$

$$\begin{cases} \dfrac{\partial\Phi_E}{\partial t} = D\left[\Delta\Phi_E + \dfrac{\rho_0}{\rho_p}\dfrac{k_T}{T_0}\Delta T_E - \varepsilon_0\dfrac{\left(\dfrac{\partial\sqrt{\varepsilon}}{\partial\Phi}\right)_{T_0}}{\left(\dfrac{\partial\mu_0}{\partial\Phi}\right)_{T_0}}\Delta {E_0}^2\right] \\ \dfrac{\partial T_E}{\partial t} - \dfrac{k_T}{\rho_p c_p}\left(\dfrac{\partial\mu_0}{\partial\Phi}\right)_T\dfrac{\partial\Phi_E}{\partial t} + \dfrac{T_0}{\rho_0 c_p}\varepsilon_0\left(\dfrac{\partial\sqrt{\varepsilon}}{\partial T}\right)_\Phi\dfrac{\partial {E_0}^2}{\partial t} = \chi_T\Delta T_E + \dfrac{\alpha_a}{\rho_0 c_p}I \end{cases}$$

$$I(\vec{r},t) = \frac{\varepsilon_0 c\left|\vec{E}_0\right|^2}{2}$$

Note: $F(V,T,N) = Vf(T,\Phi)$

$$\Pi = -\frac{\partial F}{\partial V} = -f - V\frac{\partial f}{\partial\Phi}\frac{\partial\Phi}{\partial V} = -f + \Phi\mu \qquad \frac{\partial\Pi}{\partial\Phi} = \Phi\frac{\partial\mu}{\partial\Phi} \longrightarrow K_T = \frac{1}{\Phi}\left(\frac{\partial\Phi}{\partial\Pi}\right) = \frac{1}{\Phi^2}\left(\frac{\partial\Phi}{\partial\mu}\right)$$

Osmotic compressibility

Applications: artificial Kerr media

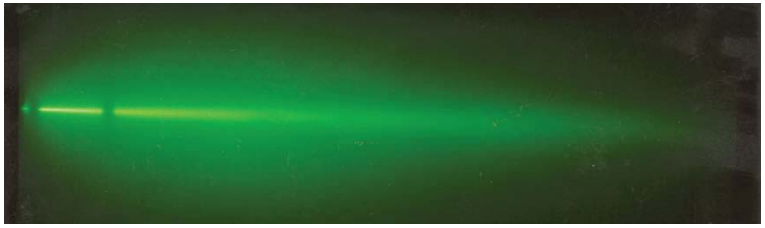
$$\varepsilon = \varepsilon_L + \varepsilon_E$$

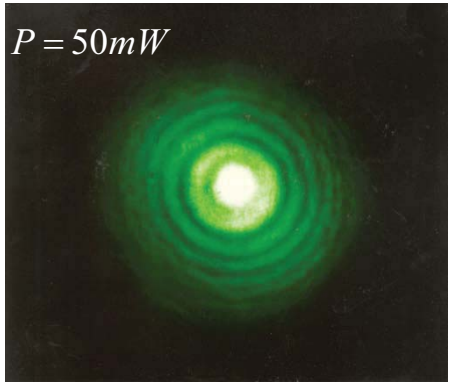
$$\varepsilon_E(\vec{r},t) = \left(\frac{\partial\varepsilon}{\partial\Phi}\right)_T \Phi_E(\vec{r},t) + \left(\frac{\partial\varepsilon}{\partial T}\right)_\Phi T_E(\vec{r},t)$$

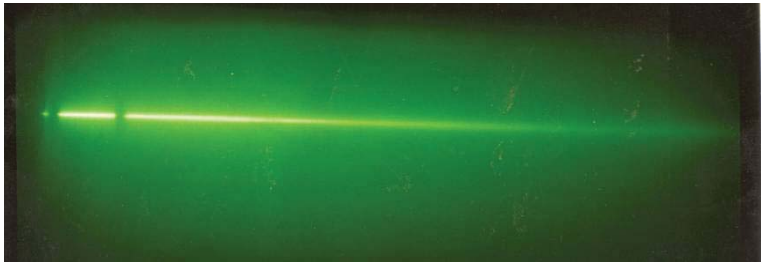
$$\Delta\Phi_E = -\frac{\rho_0}{\rho_p}\frac{k_T}{T_0}\Delta T_E + {\Phi_0}^2 K_T \varepsilon_0 \left(\frac{\partial\sqrt{\varepsilon}}{\partial\Phi}\right)_{T_0} {\Delta E_0}^2$$

Self-focusing in critical micellar phases of microemulsion (r=4nm):

$n_2 = 10^{-8}$ cm^2/W







Wave mixing, nonlinear refraction, …

B. Jean-Jean et al, Europhys Lett.7, 219 (1988)

Applications: characterization of transport coefficients

Thermodiffusion: more than 1000 publications since 2000 for a 150 years old problem!

sign, amplitude of k_T?

size, charge

INSTITUTE OF PHYSICS PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER

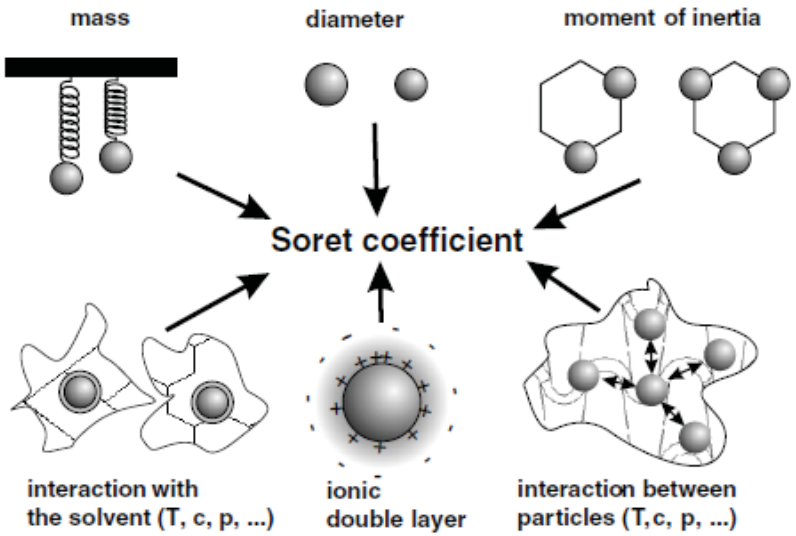
J. Phys.: Condens. Matter **16** (2004) R357–R379 — PII: S0953-8984(04)58752-0

TOPICAL REVIEW

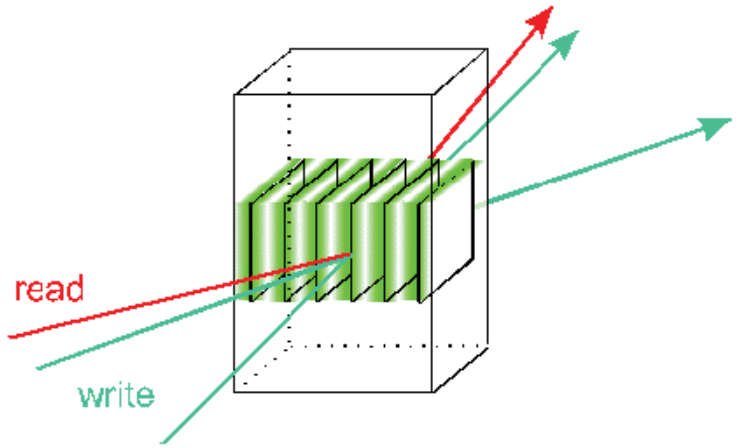
Thermal diffusion in liquid mixtures and polymer solutions

Simone Wiegand

Main features determining thermodiffusion behaviour



Detection method: forced Rayleigh scattering



Other methods: Thermal lens, Z-scan

Applications: segregation in microchannels

APPLIED PHYSICS LETTERS 86, 131921 (2005)

Two-dimensional colloidal crystals formed by thermophoresis and convection

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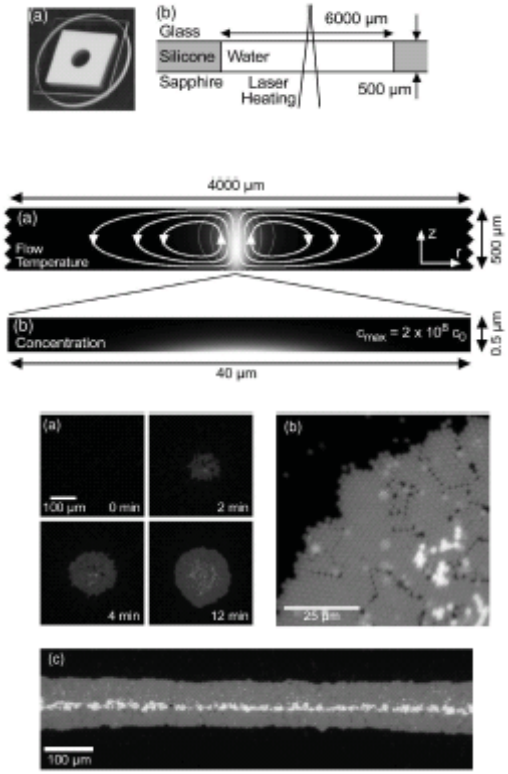

FIG. 2. Generation of two-dimensional colloidal crystal from thermophoresis and convection. (a,b) The chamber contains 2 μm polystyrene beads at low concentration. It is heated in the center by infrared absorption. Within 12 min, a two-dimensional colloidal crystal forms against the 5000-fold lower bead concentration in the liquid. (c) Heating along a line leads to the formation of an elongated crystal.

PRL 97, 038103 (2006) PHYSICAL REVIEW LETTERS week ending 21 JULY 2006

Optothermal Molecule Trapping by Opposing Fluid Flow with Thermophoretic Drift

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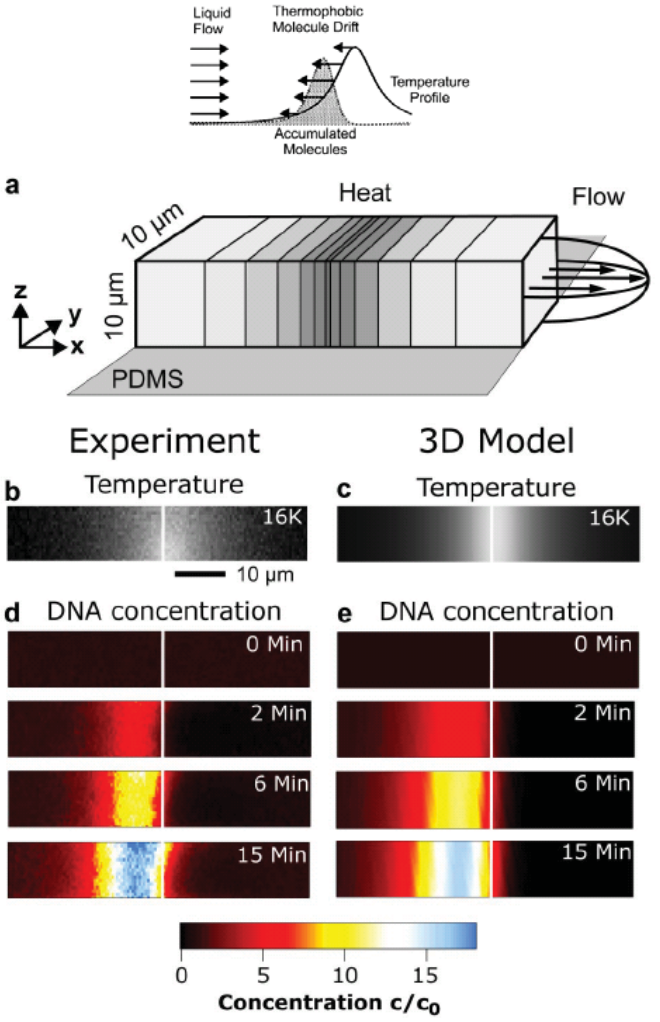

Applications: manipulation in microchannels

APPLIED PHYSICS LETTERS 91, 154104 (2007)

Stretching single molecular DNA by temperature gradient

Hong-Ren Jiang[a)] and Masaki Sano
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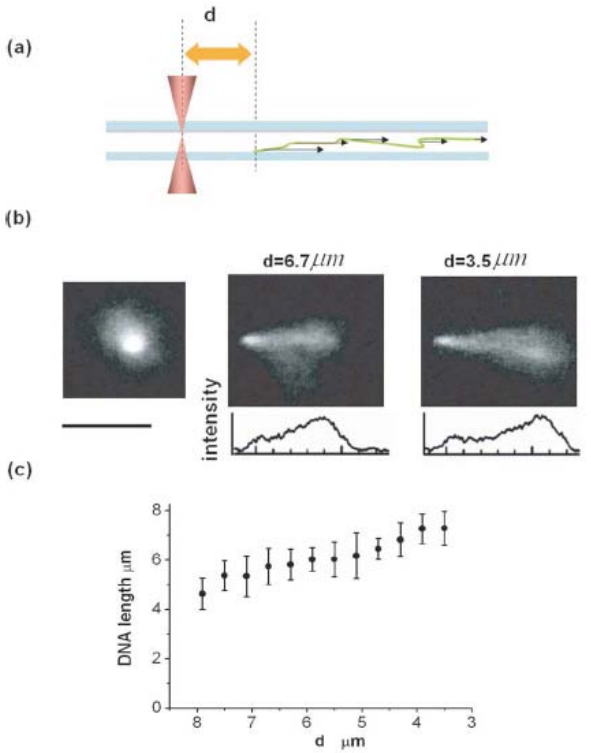
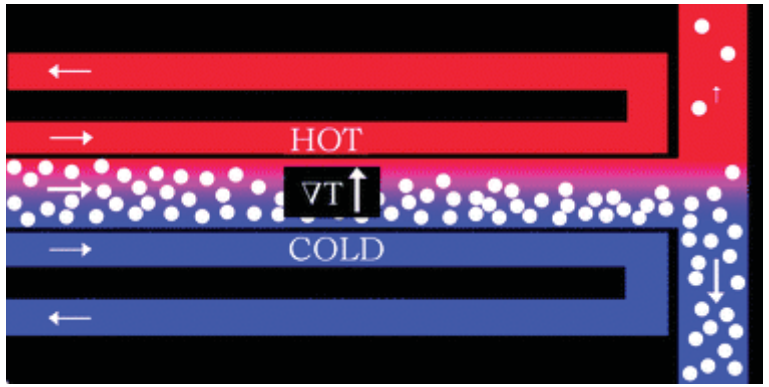


FIG. 2. (Color online) (a) DNA stretching by temperature gradient scheme. One end of DNA is tethered to the substrate. Temperature gradient is controlled by varying separation between laser center and tethered point. (b) One end tethered DNA fluorescence distribution. Left: without laser heating. Right: with laser heating; the distance between tethered end and laser is 6.7 and 3.5 μm. The scalar bar is 5 μm. The lower graphs are the intensity distribution in the temperature gradient direction. (c) The relation between the extension of one end tethered DNA (end to end distance) and the separations from laser heating spot.

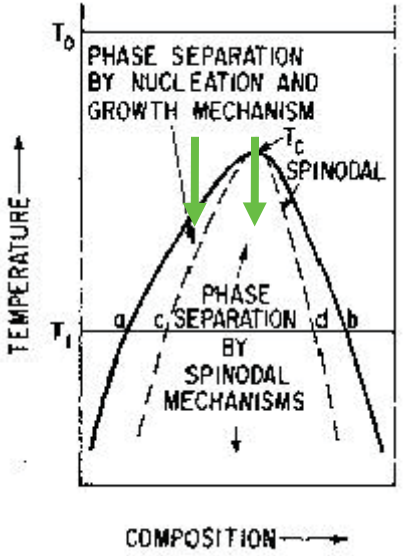
Thermophoresis: moving particles with thermal gradients

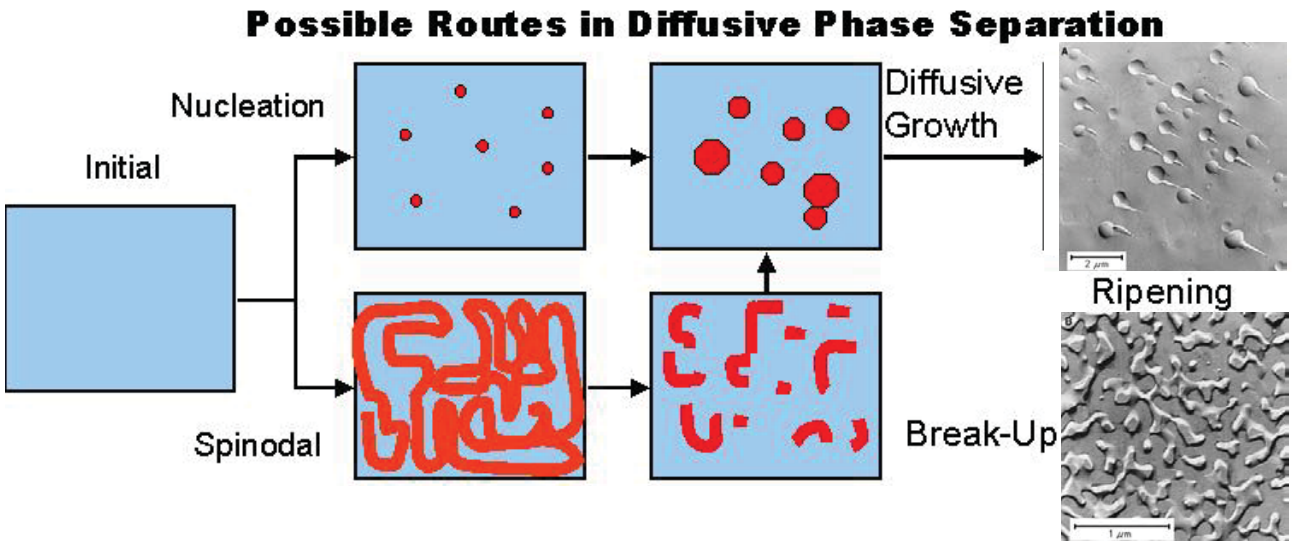
Roberto Piazza*

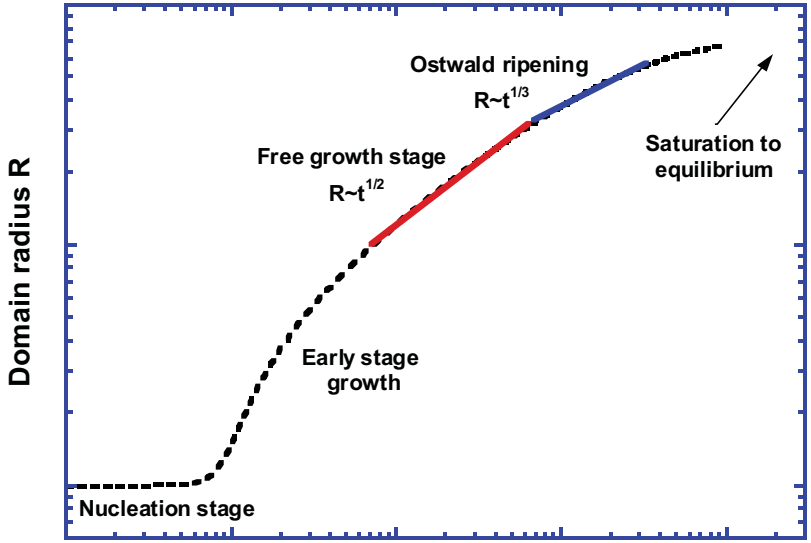
Thermophoresis is particle motion induced by thermal gradients. Akin to other nonequilibrium transport processes such as thermal diffusion in fluid mixtures, it is both experimentally and theoretically a challenging subject. New insights stemming from careful experimental surveys and strict theoretical models have however shed light on the underlying physical mechanisms, enabling depiction of thermophoresis as a subtle interfacial effect. These recent advancements open up alluring perspectives to exploit thermophoresis as a novel tool in macromolecular fractionation, microfluidic manipulation, and selective tuning of colloidal structures.



Kinetics of first-order phase transitions







Gravity wetting

Too many droplets polydispersity

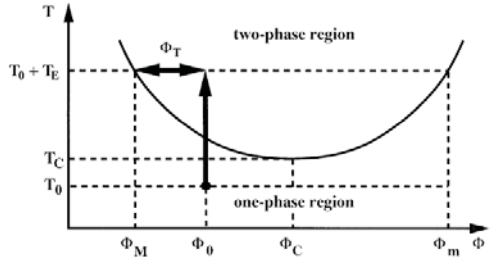
A. Onuki, Phase Transition Dynamics, Cambridge University Press (2008)

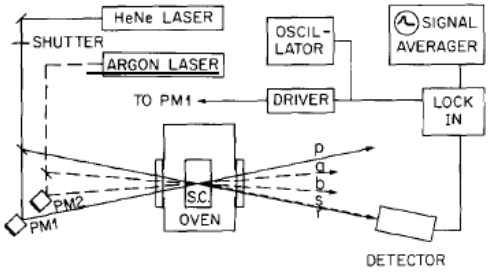
Laser-induced first-order phase transitions?

Volume 77A, number 1 PHYSICS LETTERS 28 April 1980

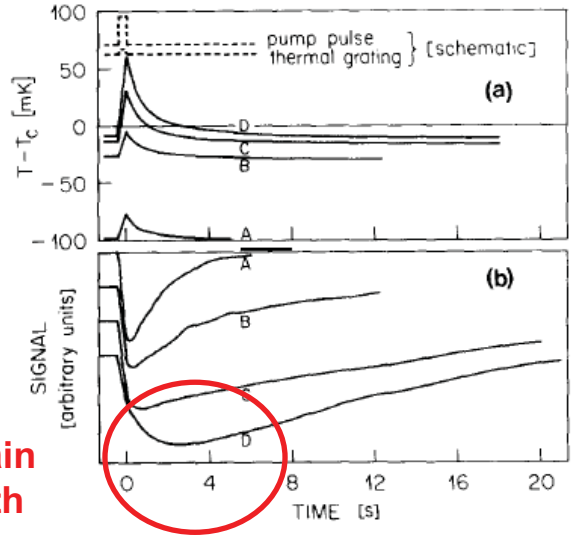
FIRST STAGE OF SPINODAL DECOMPOSITION OBSERVED BY FORCED RAYLEIGH SCATTERING

Dieter W. POHL [1]
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland





Lutidine/water
Tc=32°C

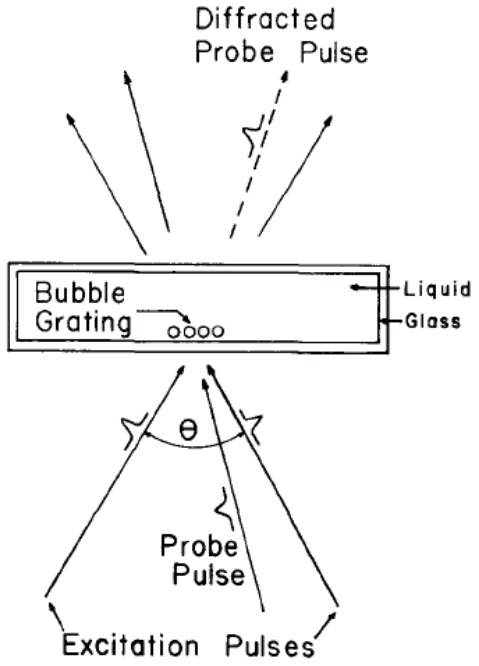


Domain growth

4072 J. Appl. Phys. **55** (11), 1 June 1984

Laser-induced phenomena at liquid-glass interfaces: Particle deposition and holographic bubble grating formation

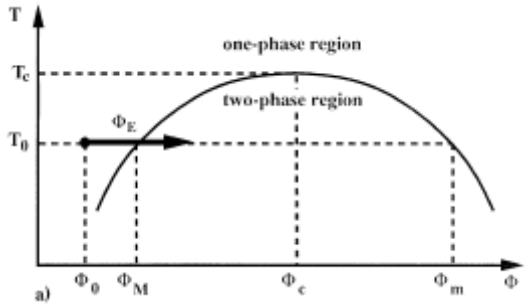
Gregory Eyring and M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305



→ **The laser-induced heating case**

Laser quenching in composition to drive first-order phase transitions?

Field variation of the concentration:



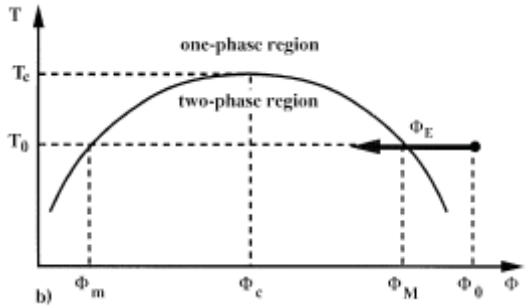
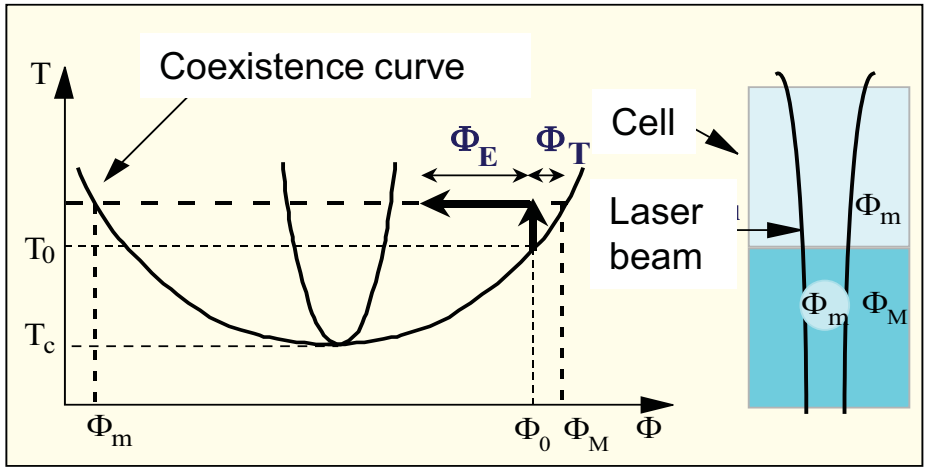


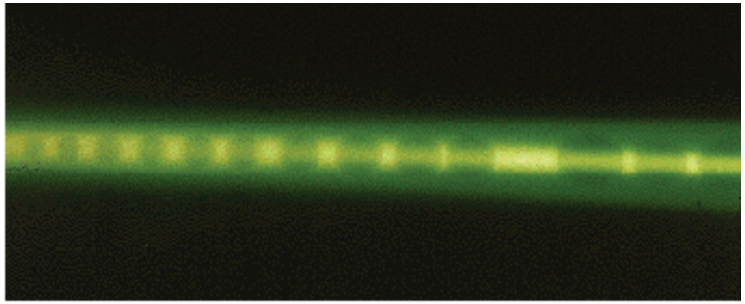
Illustration in a micellar phase of microemulsion:



Quench in temperature: $\tau \sim \frac{\omega_0^2}{2\chi_T}$ → fast

Quench in composition: $\tau \sim \frac{\omega_0^2}{2D}$ → slow

→ **Nucleation and growth of domains**



Laser effect on the critical point

Free-energy per unit volume of a binary mixture according to the Hildebrand description:

$$\frac{\Delta f}{k_B T} = \frac{\Phi}{v_d}\ln\Phi + \frac{(1-\Phi)}{v_c}\ln(1-\Phi) + \frac{\Omega}{2k_B T}\Phi(1-\Phi) \qquad v_d, v_c, \Omega$$

Molecular volumes and two-body coupling

In presence of the field:

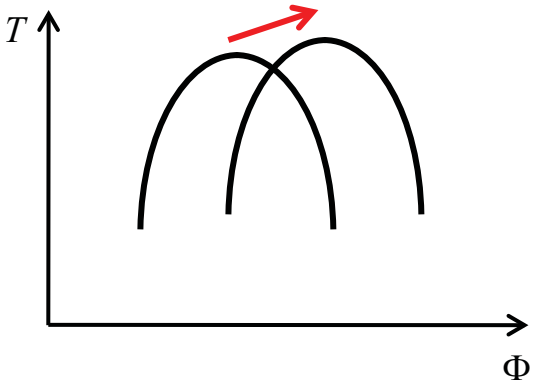
$$d\left(\frac{\Delta f_E}{k_B T}\right) = \left\{\left[\frac{1}{v_d}(1+\ln\Phi) - \frac{1}{v_c}(1+\ln(1-\Phi)) + \frac{\Omega}{2k_B T}(1-2\Phi)\right] + \frac{3}{2}\varepsilon_0 {E_0}^2\left(\frac{\partial\sqrt{\varepsilon}}{\partial\Phi}\right)\right\} d\Phi$$

Definition of the critical point: $\left(\frac{\partial\mu}{\partial\Phi}\right) = \left(\frac{\partial^2\mu}{\partial\Phi^2}\right) = 0$ **with** $\mu = \left(\frac{\partial(\Delta f_E / k_B T)}{\Phi}\right)_T$

$$\begin{cases} \Phi_C^E = \Phi_C^0 + \delta\phi \\ T_C^E = T_C^0 + \delta\tau \end{cases}$$

At first order in perturbation:

$$\begin{cases} \delta\phi = \dfrac{v_d\left(\Phi_C^0\right)^3\left(1-\Phi_C^0\right)}{2}\dfrac{\varepsilon_0 {E_0}^2}{k_B T_C^0}\left(\dfrac{\partial^3\sqrt{\varepsilon}}{\partial\Phi^3}\right)_{\Phi=\Phi_C^0} \\ \delta\tau = \dfrac{\varepsilon_0 {E_0}^2}{\Omega}\left(\dfrac{\partial^2\sqrt{\varepsilon}}{\partial\Phi^2}\right)_{\Phi=\Phi_C^0} \end{cases}$$

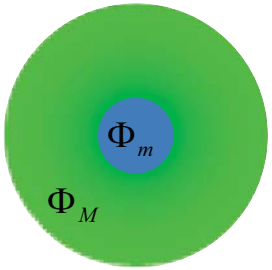


⟶ **Generally a weak effect**

Adapted from: P. Debye et al, J. Chem. Phys. 42, 3155 (1965)

Laser-induced quench in composition

For the sake of simplicity we investigate the growth of a spherical drop in a « spherical » laser wave:



For $t >> \frac{\omega_0^2}{2D}$

$$\begin{cases} \Delta\Phi + \frac{\rho_0}{\rho_p}\frac{k_T}{T_0}\Delta T - \varepsilon_0 \frac{\left(\frac{\partial\sqrt{\varepsilon}}{\partial\Phi}\right)_{T_0}}{\left(\frac{\partial\mu_0}{\partial\Phi}\right)_{T_0}}\Delta E_0^{\,2} = 0 \\ \chi_T \Delta T + \frac{\alpha_a}{\rho_0 c_p} I = 0 \end{cases}$$

Growth: radial flux of solute at the drop interface = drop volume change

$$\longrightarrow \quad \vec{J}_S(r=R) = 4\pi R^2 D\left[\vec{\nabla}\Phi\right]_{r=R} = (\Phi_m - \Phi_M)\frac{d}{dt}\left(\frac{4}{3}\pi R^3\right)\frac{\vec{r}}{r}$$

Concentration field at the drop interface

$$\Delta\Phi(r) = \Delta\Phi_E(r) \qquad \text{with} \qquad \Phi_E(r) = \Phi_{el}(r) \qquad \text{or} \qquad \Phi_E(r) = \Phi_{th}(r)$$

$$\Phi(r \to \infty) = \Phi_0$$

$$\Phi(r=R) = \Phi_R(R) \qquad \text{with} \qquad \Phi_M - \Phi_R(R) = \frac{1}{(\Phi_M - \Phi_m)(\partial\mu/\partial\Phi)_T}\frac{2\sigma}{R} \qquad \text{(Gibbs-Thomson relation)}$$

$$\longrightarrow \quad \Phi(r) = \Phi_0 + \Phi_E(r) + \left[\Phi_R(R) - \Phi_0 - \Phi_E(R)\right]\frac{R}{r}$$

Diffusion-limited droplet growth rate:

$$\longrightarrow \quad \frac{dR}{dt} = \frac{D}{R}\left\{\frac{1}{\Phi_m - \Phi_M}\left[\frac{\partial}{\partial r}\left(r\Phi_E(r)\right)\right]_{r=R} + \frac{\Phi_0 - \Phi_M}{\Phi_m - \Phi_M} - \frac{2d_0}{R}\right\} \qquad \text{where} \quad d_0 = \frac{\sigma}{(\Phi_m - \Phi_M)^2(\partial\mu/\partial\Phi)_T}$$

« capillary length »

Droplet Growth Rate in a "spherical" beam

$$\frac{dR}{dt} = \frac{D}{R}\left\{\frac{1}{\Phi_m - \Phi_M}\left[\frac{\partial}{\partial r}\left(r\Phi_E(r)\right)\right]_{r=R} + \frac{\Phi_0 - \Phi_M}{\Phi_m - \Phi_M} - \frac{2d_0}{R}\right\}$$

Electrostrictive growth rate

$$I(r) = \frac{P}{4\pi a_0^{\,2}}\exp\left(-\frac{r^2}{a_0^{\,2}}\right) \longrightarrow \Phi_{el}(r) = (\Phi_{el})_0 \exp\left(\frac{r^2}{a_0^{\,2}}\right)$$

$$\longrightarrow \frac{dR}{dt} = \frac{D}{R}\left\{\frac{(\Phi_{el})_0}{\Phi_m - \Phi_M}\left(1 - 2\frac{R^2}{a_0^{\,2}}\right)\exp\left(-\frac{R^2}{a_0^{\,2}}\right) - \frac{2d_0}{R}\right\}$$

Thermodiffusive growth rate

$$T_E(r) = \frac{\sqrt{\pi}}{2}\left(\frac{\alpha_a P}{8\pi\Lambda}\right)\frac{erf(r/a_0)}{r/a_0} \longrightarrow \Phi_{th}(r) = (\Phi_{th})_0\left[\frac{\sqrt{\pi}}{2}\frac{erf(r/a_0)}{r/a_0}\right]$$

$$\longrightarrow \frac{dR}{dt} = \frac{D}{R}\left\{\frac{(\Phi_{th})_0}{\Phi_m - \Phi_M}\exp\left(-\frac{R^2}{a_0^{\,2}}\right) - \frac{2d_0}{R}\right\}$$

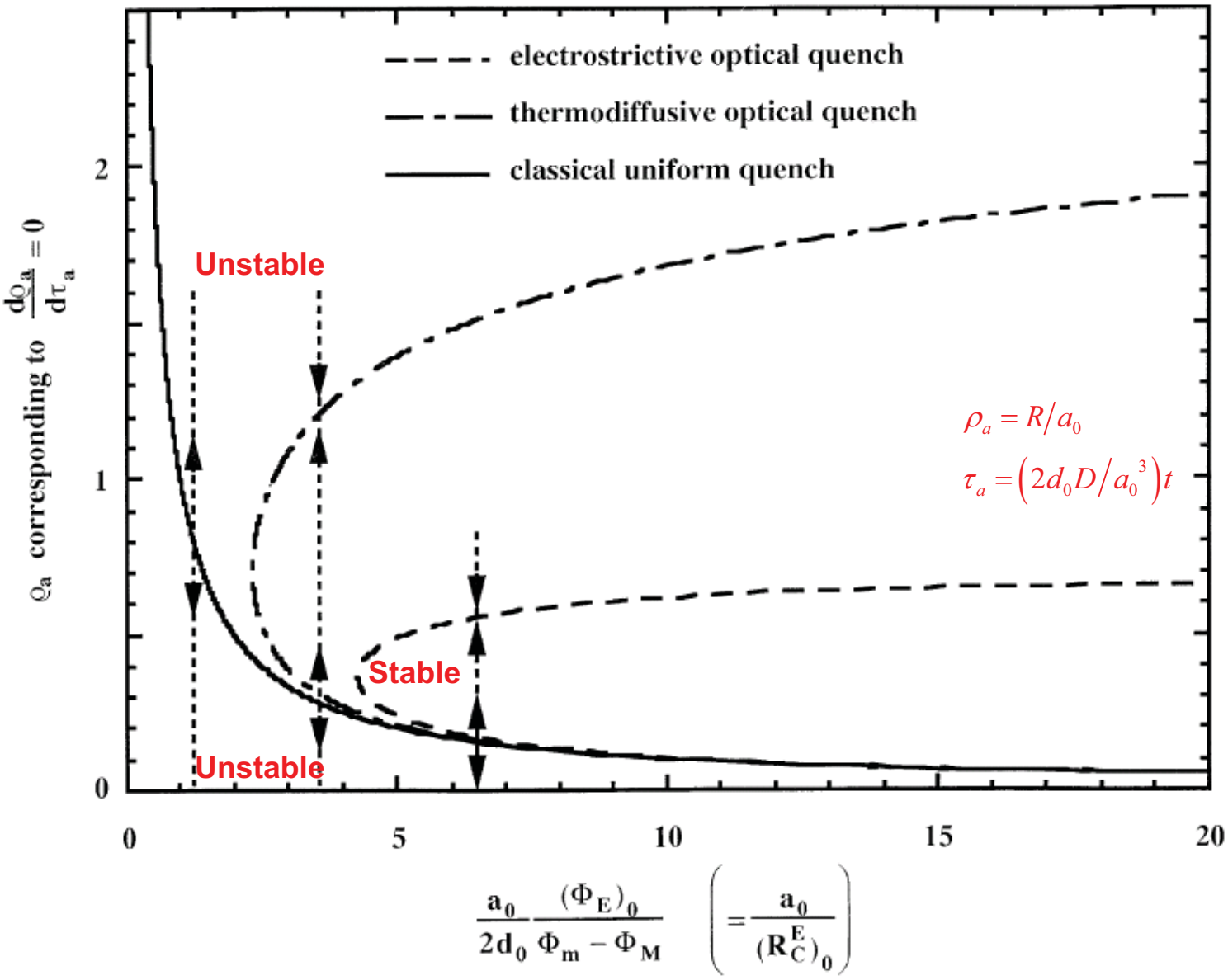
« classical » growth: $R << a_0$

$$\longrightarrow \frac{dR}{dt} = \frac{D}{R}\left\{\frac{(\Phi_E)_0}{\Phi_m - \Phi_M} - \frac{2d_0}{R}\right\}$$

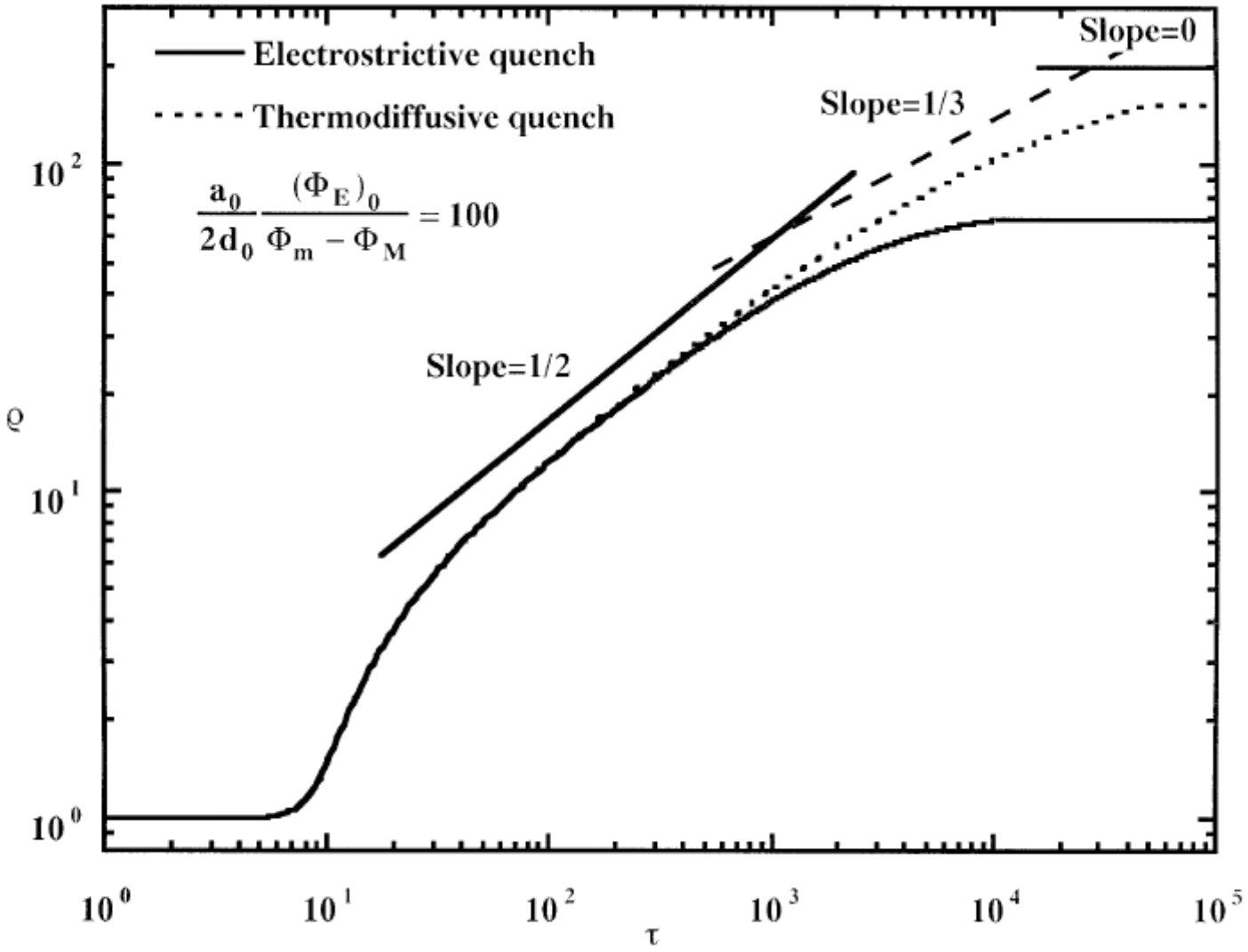
Critical radius: $\left(R_C^E\right)_0 = 2d_0\left(\frac{\Phi_m - \Phi_M}{(\Phi_E)_0}\right)$

J. P. Delville et al, Physica A 262, 40 (1999)

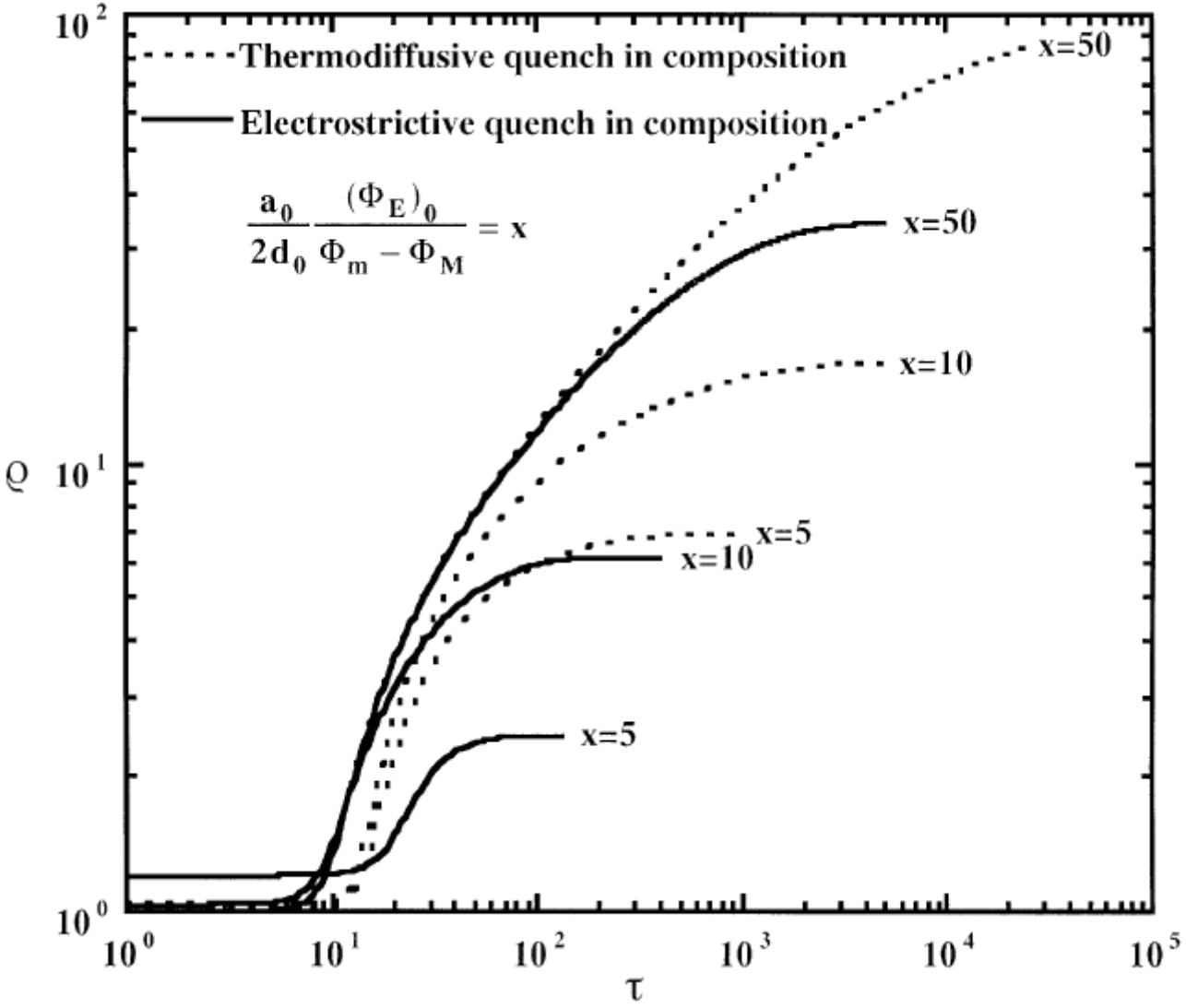
Finite Size effects due to the beam

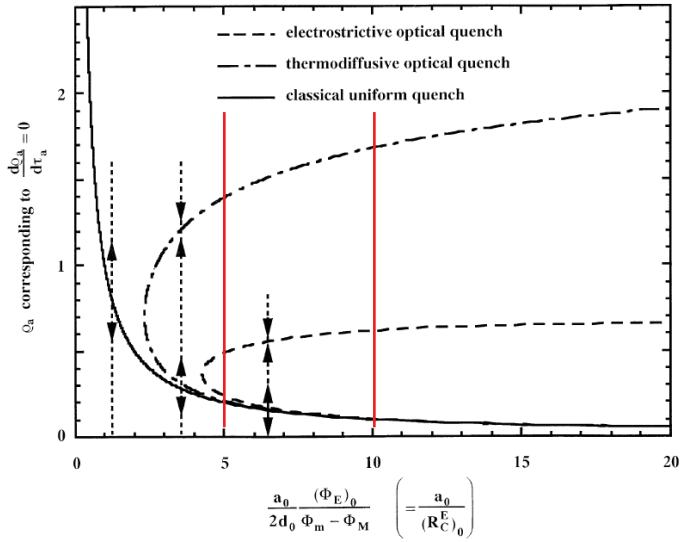


Droplet Growth law



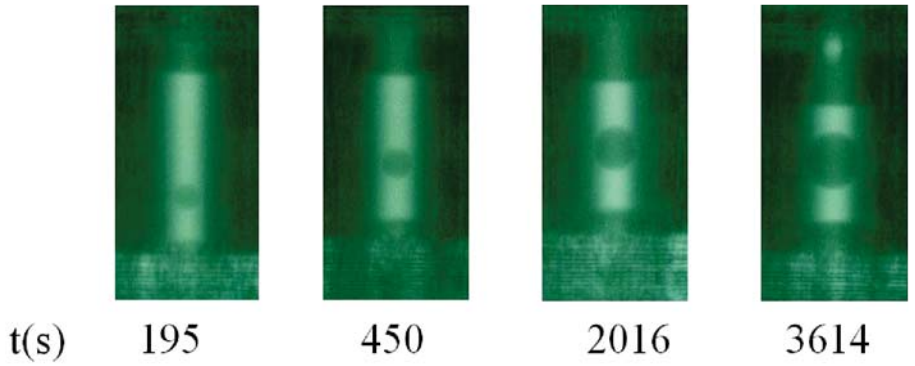
Influence of finite size effects on droplet growth

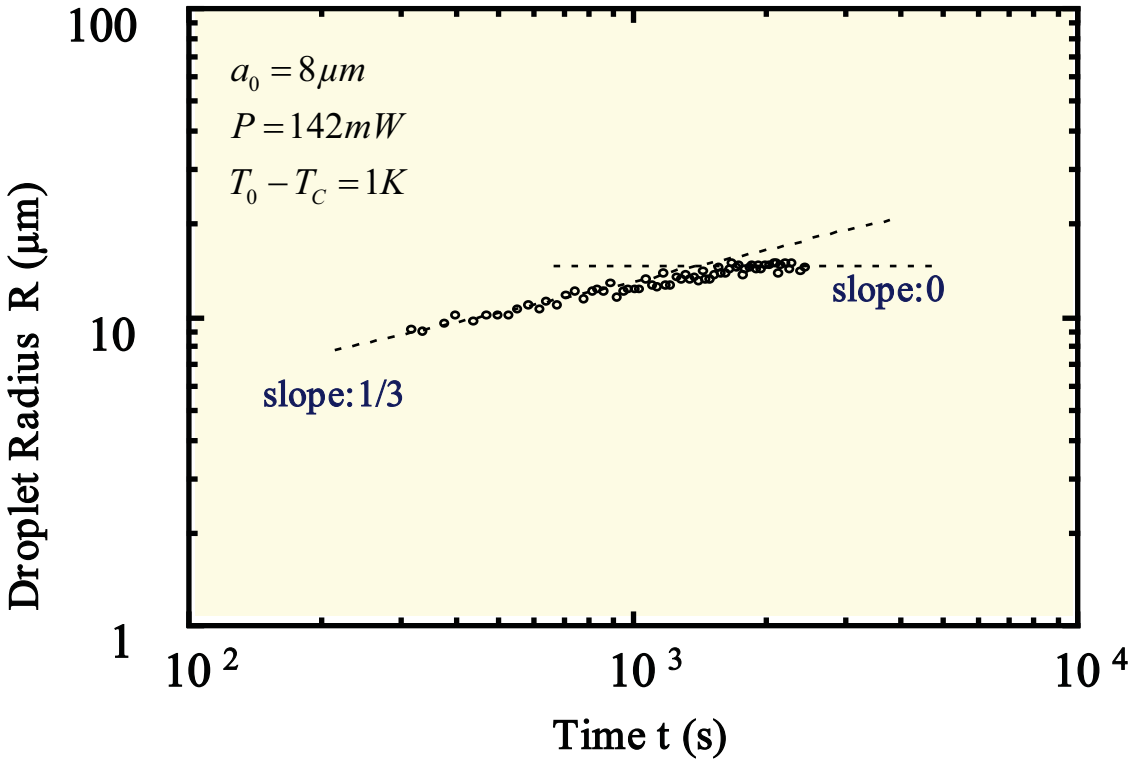




Confrontation to experiments: the optical bottle

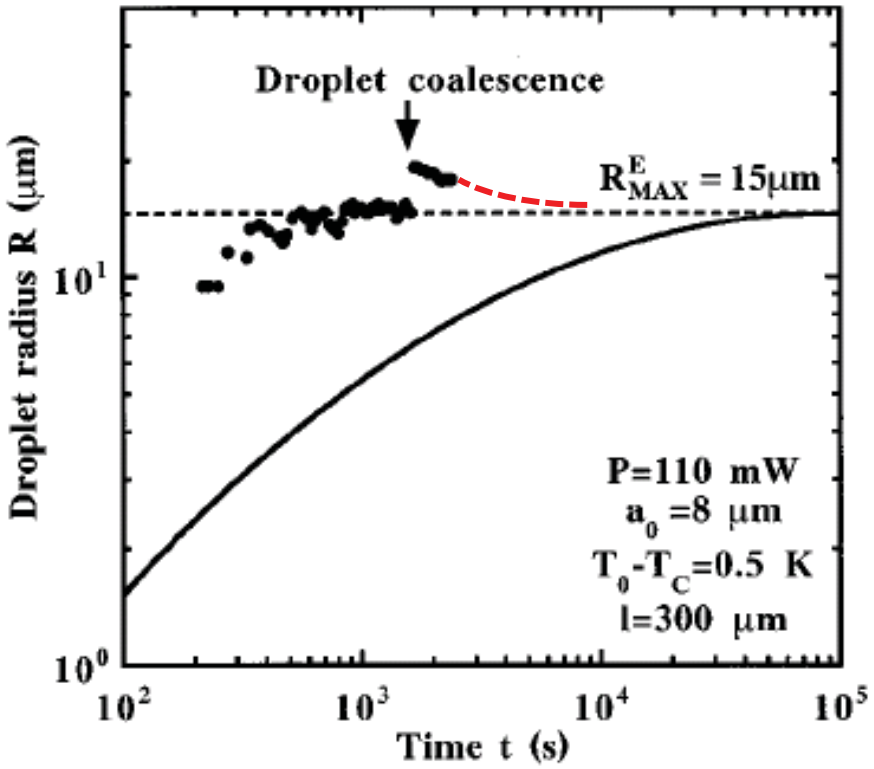
Gaussian beam of Cylindrical symmetry





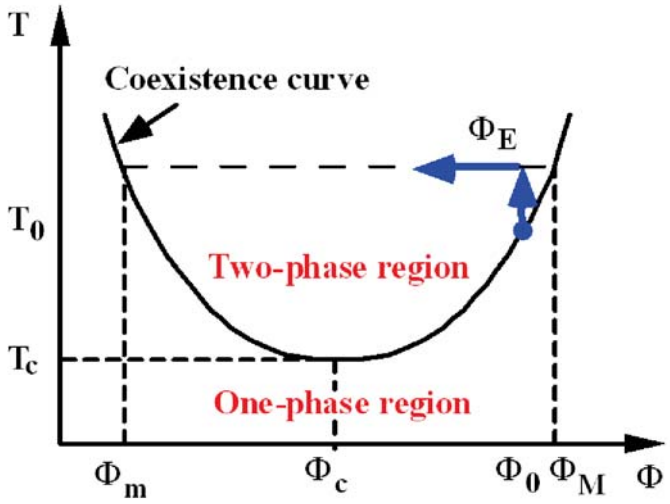
C. Lalaude et al, PRL 78, 2156 (1997)

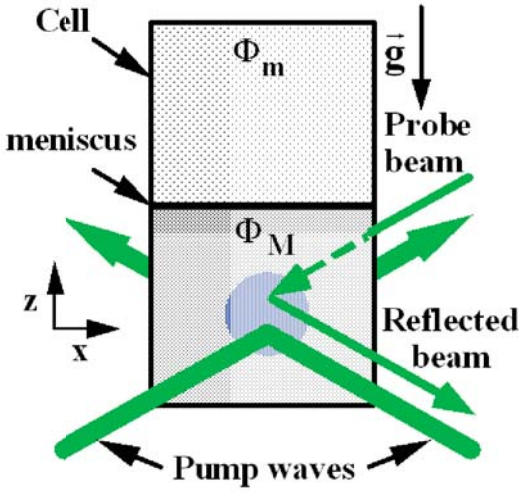
Stability of the final droplet radius



J. P. Delville et al, PRE 59, 5804 (1999)

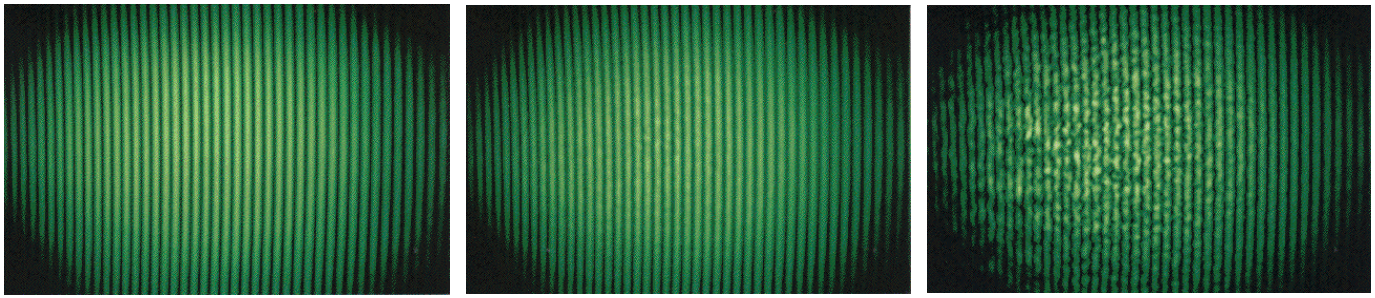
Early stage growth





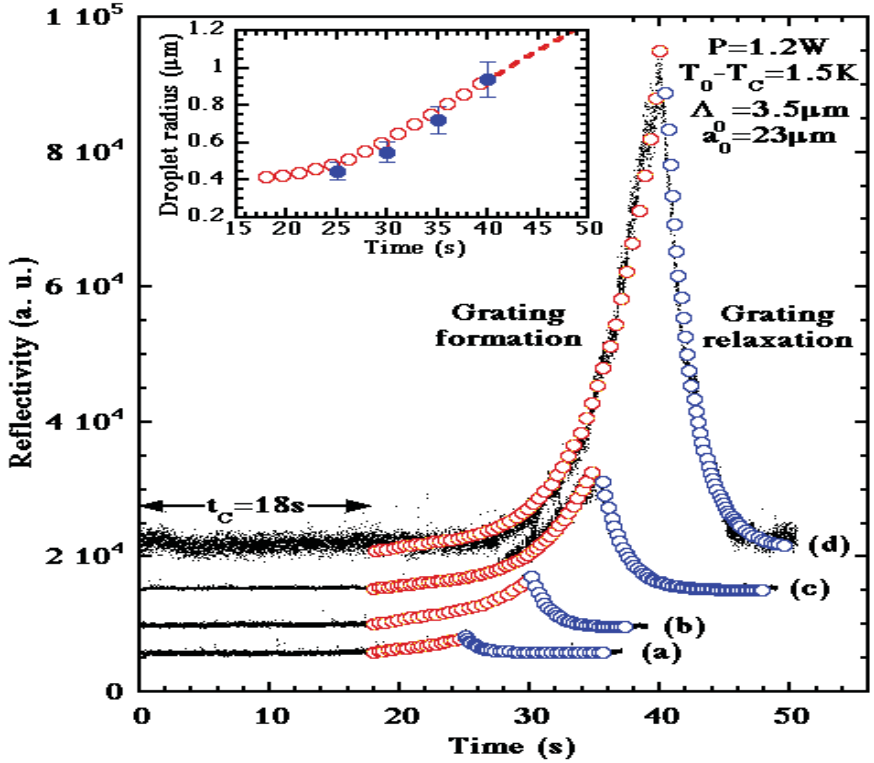
⟶ **Formation of a droplet grating**

$\Lambda_0 = 5\mu m, P = 1W, T_0 - T_C = 0.5K$



t=0s t=240s t=600s

Growth law at early stage



Droplet grating formation

$$\Re\left(t_c < t < t_1\right) \propto \left(\varepsilon_E\right)^2 \propto \left|\Phi_D\left(t\right)\right|^2$$

$$\frac{\partial \Phi_D}{\partial t} = -D_R\left(t\right) q_0^2 \left[\Phi_D\left(t\right) + AR\left(t\right)^3 I\left(q_0\right)\right]$$

$$\frac{\partial R}{\partial t} = \frac{D^-}{R\left(t\right)} \frac{\left(\Phi_E\right)_0 \left(x=0, t=t_C\right)}{\Phi_m - \Phi_M} \left(1 - \frac{R_C}{R\left(t\right)}\right)$$

$$D_R\left(t\right) = \frac{k_B T}{6\pi\eta R\left(t\right)}$$

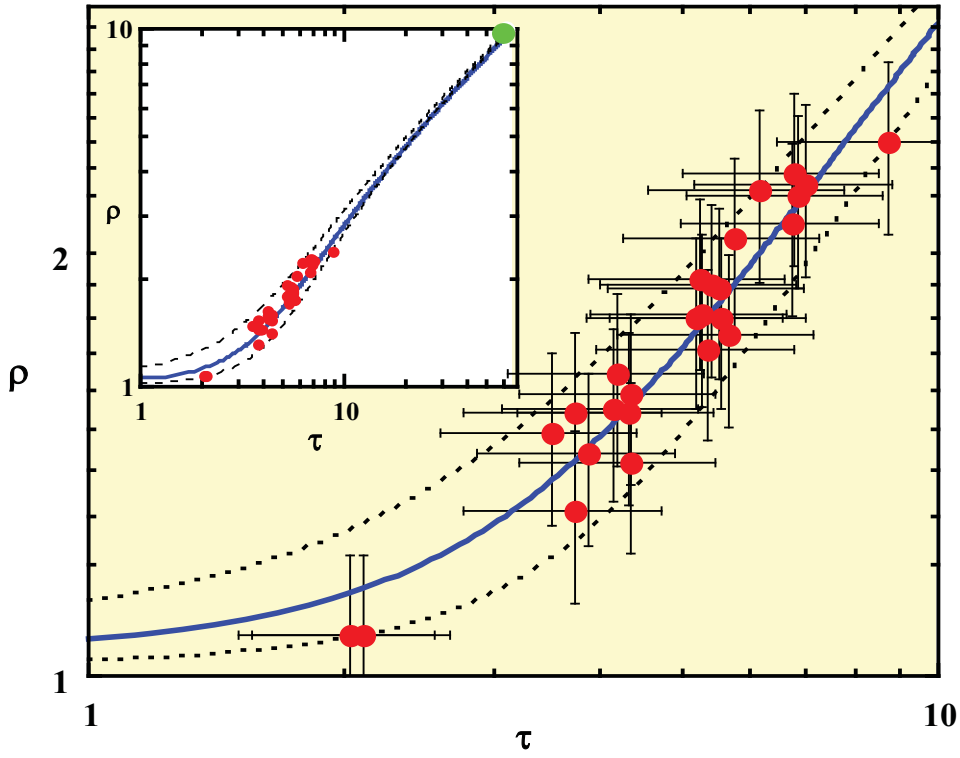
$$R_C = 2d_0 \left(\frac{\Phi_m - \Phi_M}{\left(\Phi_E\right)_0}\right)$$

Droplet grating relaxation

$$\Re\left(t > t_1\right) \propto \exp\left[-2D_R\left(t_1\right) q_0^2 \left(t - t_1\right)\right]$$

S. Buil et al, PRE 63, 1504 (2001)

Universal behavior at early stage



$$\rho = \frac{R}{R_C} \qquad \tau = \left[\frac{D}{R_C^2}\frac{\left(\Phi_E\right)_0\left(x=0,t=t_C\right)}{\Phi_m - \Phi_M}\right]\left(t-t_C\right)$$

$$\longrightarrow \quad \frac{d\rho}{dt} = \frac{1}{\rho}\left(1-\frac{1}{\rho}\right) \qquad \longrightarrow \quad \tau = \rho + \frac{\rho^2}{2} + \ln\left(\rho-1\right) + K$$

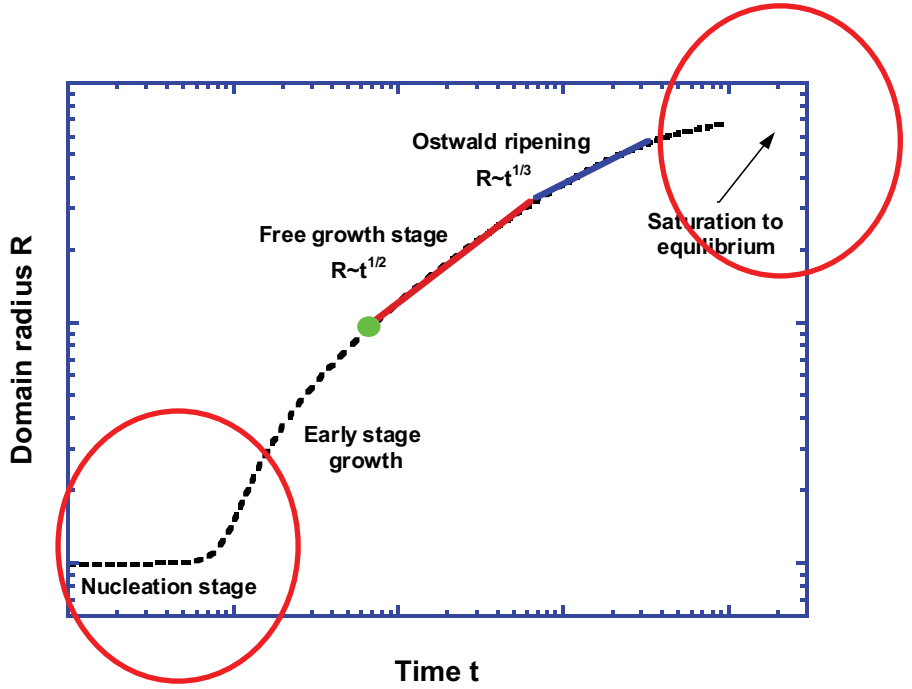
K=4.16±0.26, ρ_c=1.005 ±0.001, Polydispersity 2.5%

S. Buil et al, PRL 82, 1895 (1999)

In Summary

The optical bottle with soft walls

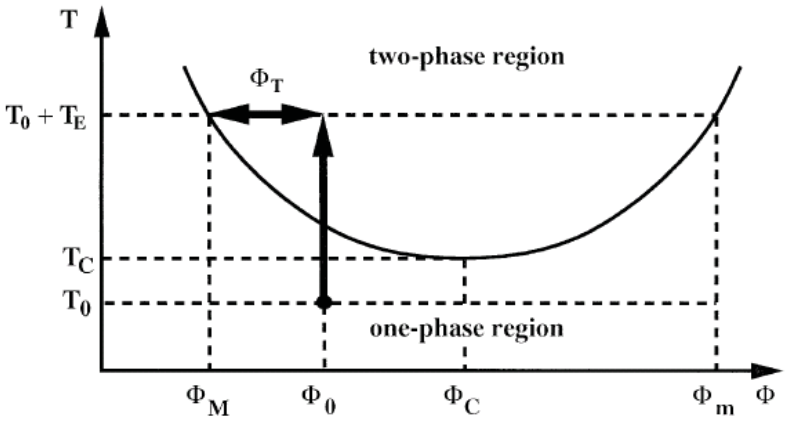
Gravity wetting



Too many droplets polydispersity

The optical bottle with huge confinement

Laser-induced quench in temperature



Coexistence curve: $\left|\Phi_m - \Phi_M\right| = \left(\Delta\Phi\right)_0 \left|1 - T_0/T_C\right|^\beta$

Quench depth $\left|\dfrac{\Phi_T(r)}{\Phi_m - \Phi_M}\right| = \left(1 + \dfrac{T_E(r)}{T_0 - T_C}\right)^\beta - 1 \underset{T_E(r) << T_0 - T_C}{\approx} \dfrac{\beta}{2}\dfrac{T_E(r)}{T_0 - T_C}$

Thermal growth rate: $\dfrac{dR}{dt} = \dfrac{D}{R}\left\{\dfrac{\left(\Phi_T\right)_0}{\Phi_m - \Phi_M}\exp\left(-\dfrac{R^2}{{a_0}^2}\right) - \dfrac{2d_0}{R}\right\}$

$\longrightarrow$ **Same behavior as in the thermodiffusive case**

Related works

Laser-Controlled Association of Poly(*N*-vinylcarbazole) in Organic Solvents: Radiation Pressure Effect of a Focused Near-Infrared Laser Beam

Pawel Borowicz,† Jun-ichi Hotta, Keiji Sasaki,* and Hiroshi Masuhara*

Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan

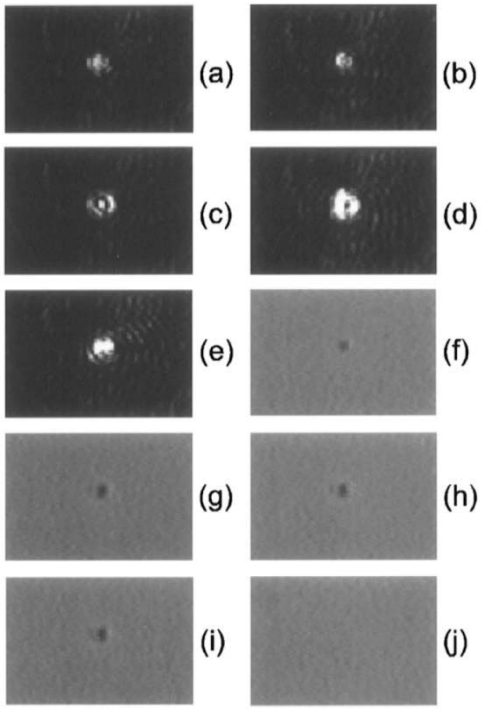
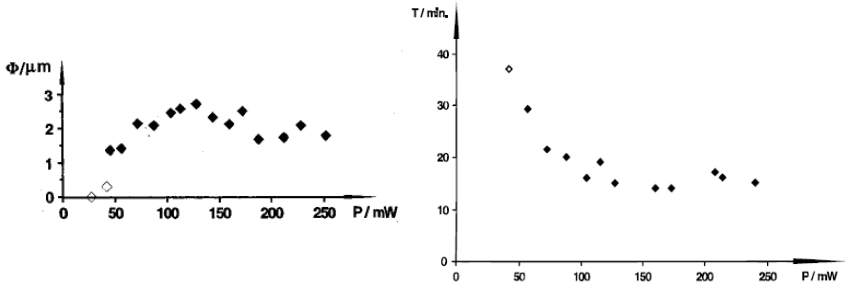


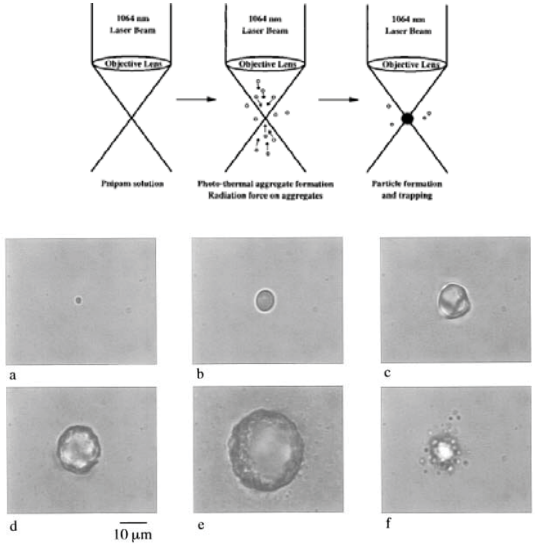
Figure 1. Microscope pictures of a single-particle formation of PVCz in DMF, concn of 3.5 wt %: (a) 270, (b) 600, (c) 1380, (d) 1440, (e) 1560, (f) 1570, (g) 1740, (h) 2040, and (i) 2330 s after introducing the near-infrared laser beam; (j) 2340 s after switching off the beam. Photographs a−e were obtained with backscattering of the He−Ne laser, while f−j were obtained with the optical transmission image.



Molecular Assembling by the Radiation Pressure of a Focused Laser Beam: Poly(*N*-isopropylacrylamide) in Aqueous Solution

J. Hofkens,†,‡ J. Hotta,† K. Sasaki,† H. Masuhara,*,† and K. Iwai§

Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan, and Department of Chemistry, Nara Women's University, Nara 630, Japan



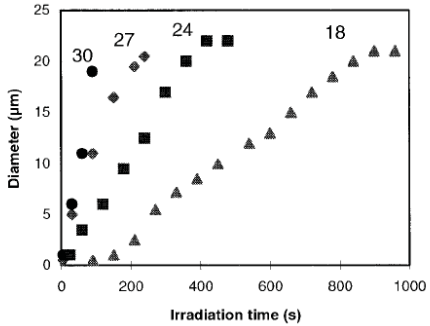


Figure 5. Diameter of the observed particle as function of time for a 3.6 wt % aqueous PNIPAM solution at different initial temperatures (P_{1064} = 230 mW; a, T_{init} = 18 °C (▲); b, T_{init} = 24 °C (■); c, T_{init} = 27 °C (◆); d, T_{init} = 30 °C (●)).

Recent developments 1

Journal of Applied Polymer Science, Vol. 105, 2083–2090 (2007)

Phase Separation of Poly(*N*-isopropylacrylamide) Solutions and Gels Using a Near Infrared Fiber Laser

Michael E. DeRosa,[1] Rebecca L. DeRosa,[2] Lisa M. Noni,[1] Erin S. Hendrick[3]

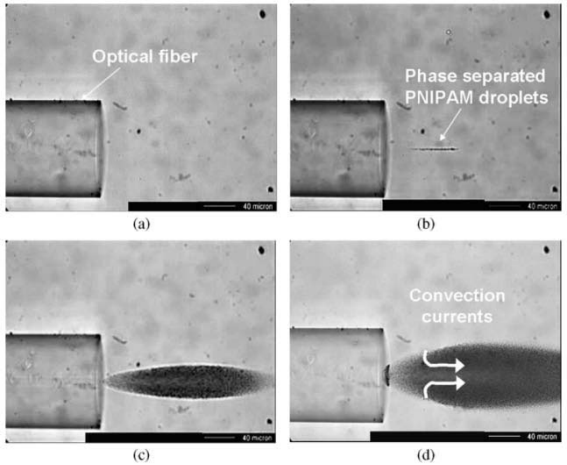


Figure 6 Photothermal phase separation of 6 wt % PNIPAM solution at 1533 nm at (a) 0 mW, (b) 9 mW, (c) 14.5 mW, and (d) 20 mW. Images were taken at 500× magnification.

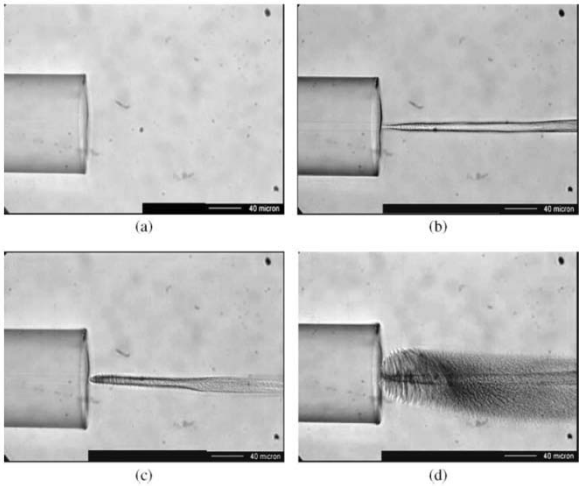


Figure 12 Photothermal phase change behavior at 1533 nm of PNIPAM gel with 0.0039 BIS/NIPAM crosslinker/monomer ratio. Optical powers at the end of the fiber are (a) 0 mW, (b) 12 mW, (c) 13 mW, and (d) 21.5 mW.

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Rhythmic oscillation and dynamic instability of micrometer-size phase separation under continuous photon flux by a focused laser

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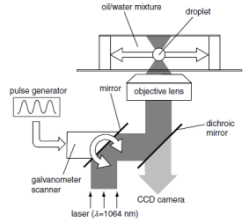
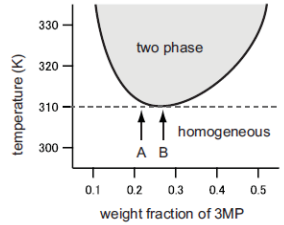
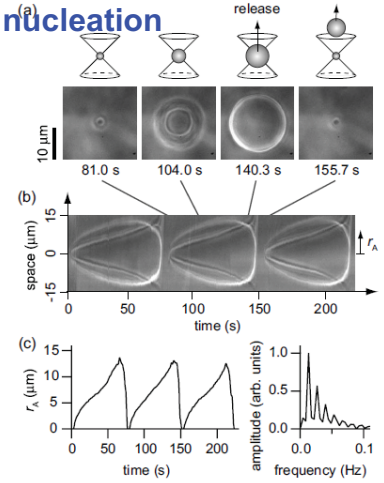
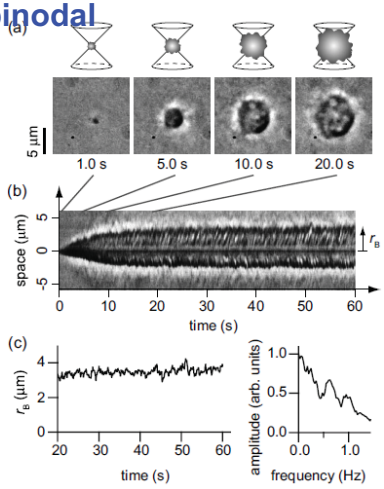




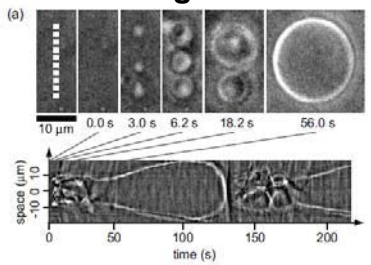
nucleation

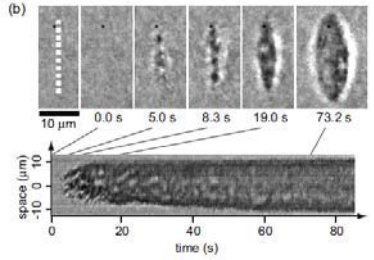


spinodal



scanning





Recent developments 2

PRL 94, 214501 (2005) PHYSICAL REVIEW LETTERS week ending 3 JUNE 2005

Thermal Patterning of a Critical Polymer Blend

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(Received 14 September 2004; published 2 June 2005)

Patterning by thermodiffusion driven by laser close to a critical point $(k_T > 0)$

one-phase

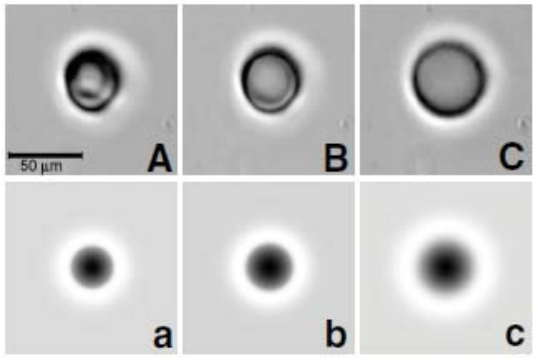

FIG. 1. Temporal development of structure after laser exposure at $T = 38.5\,^{\circ}\mathrm{C}$, $0.8\,^{\circ}\mathrm{C}$ above T_c. Laser exposure starts at $t = 0$ and ends at $t = 200$ s. Images are taken at $t = 200$ s (A), $t = 300$ s (B), and $t = 1100$ s (C). The lower images (a)–(c) show simulations as described in the text.

spinodal

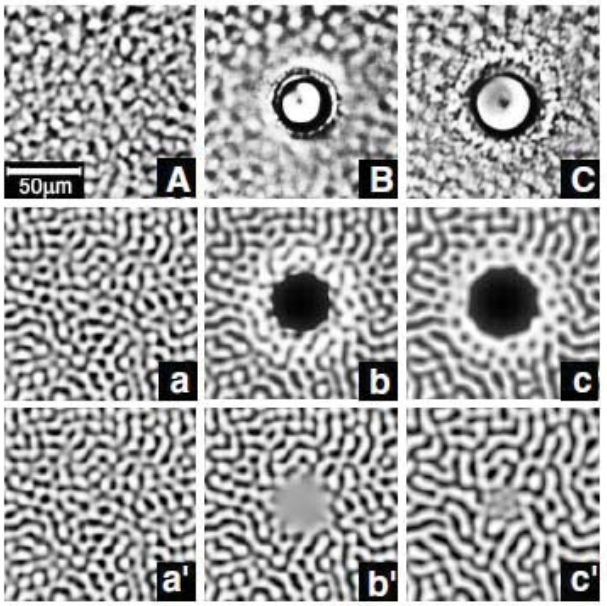

FIG. 2. Temporal development of structure after laser exposure below T_c ($T = 37.2\,^{\circ}\mathrm{C}$). Laser exposure starts at $t = 0$ and ends at $t = 200$ s. Images are taken at $t = 0$ (A), $t = 300$ s (B), and $t = 700$ s (C). Corresponding images of simulations with (a)–(c) and without (a′)–(c′) Soret effect as described in the text.

Concluding remarks

Optical manipulation of liquid mixtures by non resonant laser waves

→ Smoothly to locally vary the composition (applications in NLO, transport)
local/nonlocal couplings (electrostriction/thermodiffusion)

→ intrusively to drive first and second order phase transitions in liquids
(application in surface patterning)

→ to nucleate and grow stable droplets

Should be able to drive flow (illustration in the next lecture)?

Extension to anisotropic liquids (LC)

Extension to resonant fluids

- **generation of new species**
- **photochemical patterning through liquid/solid transition**
- **(photoprecipitation)**

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