Introduction to Optofluidics

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Optical manipulation of binary liquid mixtures

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Optical manipulation of binary liquid mixtures

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II. Field variations of thermodynamic variables

III. Applications of electrostrictive and thermodiffusive variations of concentration

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Light-fluid interaction in a liquid mixture

Electrostriction
Heating
Thermodiffusion

Diffusion

$r << \bar{\lambda}$

Scattering

Flow

Surface Force:
Radiation pressure

Deformation

Dielectric: $n_2 = \sqrt{\varepsilon_2}$

$\bar{p}_2 = n_2 \frac{h \nu}{c} \bar{z}$

Dielectric: $n_1 = \sqrt{\varepsilon_1}$

$n_1 < n_2$

$\bar{p}_1 = n_1 \frac{h \nu}{c} \bar{z}$
**Electrostriction in a binary liquid mixture**

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

\[
\left( \nabla \vec{E} \cdot \vec{E} = 2 \left( \vec{E} \cdot \nabla \vec{E} \right) \vec{E} + 2 \vec{E} \times \left( \nabla \times \vec{E} \right) \nabla \times \vec{E} = 0 \right)
\]

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

\[
\vec{F}_{el}(\vec{r},t) = \frac{\alpha}{2n_p \varepsilon_0 c} \nabla I(\vec{r},t)
\]

where the beam intensity is: \( I(\vec{r},t) = \frac{n_p \epsilon_0 c}{2} |\vec{E}(\vec{r},t)|^2 \)

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

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

Concentration variation:

\[
\delta N = \left( \frac{\partial N}{\partial \Pi} \right) \delta \Pi(\vec{r},t)
\]

\[
\delta N = \left( \frac{\partial N}{\partial \Pi} \right) \frac{\alpha N}{2n_p \varepsilon_0 c} I(\vec{r},t)
\]

\[
\delta N = \frac{\alpha N K}{2n_p \varepsilon_0 c} I(\vec{r},t)
\]

where \( K = \frac{1}{N} \left( \frac{\partial N}{\partial \Pi} \right) \) Osmotic compressibility

\[
K_{\text{gas}} = \frac{1}{N k_B T}
\]
Nonlinear optics in aerosols

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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 ~10⁻¹⁰ 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/cm². 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

Pure Heating:

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

Optical absorption: \( \alpha_d \)

Thermal conductivity: \( \Lambda_T \)

Soret Effect (Thermodiffusion):

\[ \nabla T_E(r) \rightarrow \nabla \Phi_E(r) \]

Soret Coefficient: \( k_T \)
Scattering effects in a binary liquid mixture

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

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

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

Scattering cross section: \( \sigma_{\text{scat}} \)

Work per unit time: \( \dot{W} = f_{\text{Scat}} u \left( \alpha_0^2 L \right) \)

Average suspension velocity: \( u \sim \frac{\alpha_0^2 f_{\text{Scat}}}{\eta} \)

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

\( \eta \): shear viscosity, \( \sigma \): viscous stress

Individual particle:

\( \vec{F}_{\text{drag}}(\vec{r},t) = -6\pi r \eta \vec{u}_p \)

Average particle velocity:

\( u_p \sim \frac{\sigma_{\text{scat}} n L}{c \eta} \)

Collective flow:

\( u_p \ll u \quad \Phi = \frac{4}{3} \pi r^3 N \gg \left( \frac{r}{\alpha_0} \right)^2 \)

Rayleigh scattering:

\( \sigma_{\text{scat}} = \frac{8}{3} \pi (kr)^4 \left( \frac{n_p^2 - n^2}{n_p^2 + 2n^2} \right)^2 \)

\( \tau L \ll 1 \quad (\Delta n)^2 (kr)^4 \left( \frac{r}{\alpha_0} \right)^2 L \ll 1 \)
Bulk versus individual scattering effects in a binary liquid mixture

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

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

→ Optical Chromatography

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

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Hart et al 2007-08
Field variations of thermodynamic variables

Incompressible Fluid mixture: \( dP = 0 \rightarrow df = -s dT - P d \left( \frac{1}{\rho} \right) + \mu dC + \frac{\vec{E} \cdot d\vec{D}}{\rho_0} \) (free energy per mass unit)

Note: \( s \) and \( \mu \) are field modified quantities!

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

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

\[
\rightarrow \quad df = \left( -s + \frac{3}{2} \frac{\varepsilon_0}{\rho_0} E_0^2 \left( \frac{\partial \sqrt{E}}{\partial T} \right) \right) dT + \left( \mu + \frac{3}{2} \frac{\varepsilon_0}{\rho_0} E_0^2 \left( \frac{\partial \sqrt{E}}{\partial C} \right) \right) dC + \frac{\varepsilon_0}{2\rho_0} \sqrt{E} dE_0^2
\]

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

\( s = s_0 + s_E \rightarrow s_E = \frac{\varepsilon_0 E_0^2}{\rho_0} \left( \frac{\partial \sqrt{E}}{\partial T} \right) \)
Mass diffusion in presence of light

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

\[ P_e = \frac{(\vec{u} \cdot \nabla) C}{D \Delta C} = \frac{u \langle x \rangle}{D} = 0 \text{ or } << 1 \quad \text{Peclet number} \]

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

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

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

\[ \frac{\partial C_E}{\partial t} = D \left[ \Delta C_E + \frac{k_T}{T_0} \Delta T_E - \frac{\varepsilon_0}{\rho_0} \left( \frac{\partial \sqrt{E}}{\partial C} \right)_{T_0} \Delta E_0 \right] \]

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

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

Thermal diffusion constant: \[ D_T = D k_T \]

Thermal diffusion in presence of light

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

\[
\left( \frac{\partial S}{\partial t} \right) = \left( \frac{\partial S_v}{\partial T} \right) \left( \frac{\partial T_v}{\partial t} \right) + \left( \frac{\partial S_v}{\partial C} \right) \left( \frac{\partial C_v}{\partial t} \right) + \left( \frac{\partial S_E}{\partial t} \right) = \frac{c_p}{T_0} \left( \frac{\partial S_v}{\partial C} \right) = - \left( \frac{\partial^2 f}{\partial C \partial T} \right) = - \left( \frac{\partial \mu_0}{\partial T} \right), \quad \frac{\partial S_E}{\partial t} = \frac{e_0}{\rho_0} \left( \frac{\partial \sqrt{E}}{\partial T} \right) \frac{\partial E_0^2}{\partial t}
\]

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

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

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

Heat generated by optical absorption: \( Q = \alpha_a I \)

\[
\frac{\partial T_E}{\partial t} - \frac{k_T}{c_p} \left( \frac{\partial \mu_0}{\partial C} \right) \frac{\partial C_E}{\partial t} + \frac{T_0}{\rho_0 c_p} e_0 \left( \frac{\partial \sqrt{E}}{\partial T} \right) \frac{\partial E_0^2}{\partial t} = \chi_T \Delta T_E + \frac{\alpha_a}{\rho_0} I
\]

Thermal diffusivity:
\[
\chi_T = \frac{\Lambda_T}{\rho_0 c_p}
\]

Summary

Per unit mass:

\[
\frac{\partial C_E}{\partial t} = D \left[ \Delta C_E + \frac{k_T}{T_0} \Delta T_E - \frac{\varepsilon_0}{\rho_0} \left( \frac{\partial E}{\partial C} \right)_{T_0} \right] \\
\frac{\partial T_E}{\partial t} = -k_T \left( \frac{\partial \mu_0}{\partial C} \right)_T + \frac{T_0}{\rho_0 c_p} \varepsilon_0 \left( \frac{\partial E}{\partial T} \right)_C \frac{\partial E_0}{\partial t} = \chi_T \Delta T_E + \frac{\alpha_a - \Pi}{\rho_0 c_p} 
\]

Per unit volume:

\[
\mu_{0m} = \frac{1}{\rho_p} \mu_0, \quad \Phi = \frac{V_p}{V_0} = \frac{\rho_0 c_p}{\rho_p} \\
\frac{\partial \Phi_E}{\partial t} = D \left[ \Delta \Phi_E + \frac{\rho_0 k_T}{T_0} \Delta T_E - \varepsilon_0 \left( \frac{\partial E}{\partial \Phi} \right)_{T_0} \right] \\
\frac{\partial T_E}{\partial t} = -k_T \frac{\partial \mu_0}{\partial \Phi} \frac{\partial \Phi}{\partial t} + \frac{T_0}{\rho_0 c_p} \varepsilon_0 \left( \frac{\partial E}{\partial T} \right)_\Phi \frac{\partial E_0}{\partial t} = \chi_T \Delta T_E + \frac{\alpha_a - \Pi}{\rho_0 c_p} 
\]

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

\[
\Pi = -\frac{\partial F}{\partial V} = -f - V \frac{\partial f}{\partial \Phi} \frac{\partial \Phi}{\partial V} = -f + \Phi \mu \quad \frac{\partial \Pi}{\partial \Phi} = \Phi \frac{\partial \mu}{\partial \Phi} \quad \rightarrow \quad K_T = \frac{1}{\Phi} \left( \frac{\partial \Phi}{\partial \Pi} \right) = \frac{1}{\Phi^2} \left( \frac{\partial \Phi}{\partial \mu} \right) \text{ Osmotic compressibility} 
\]
Applications: artificial Kerr media

\[ \varepsilon = \varepsilon_L + \varepsilon_E \]

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

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

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

\[ n_2 = 10^{-8} \text{ cm}^2/\text{W} \]

\[ P = 50mW \]

Wave mixing, nonlinear refraction, …

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

Main features determining thermodiffusion behaviour
- mass
- diameter
- moment of inertia
- interaction with the solvent ($T$, $c$, $p$, ...)
- ionic double layer
- interaction between particles ($T$, $c$, $p$, ...)

Soret coefficient

Detection method: forced Rayleigh scattering

Other methods: Thermal lens, Z-scan
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 3000-fold lower bead concentration in the liquid. (c) Heating along a line leads to the formation of an elongated crystal.
Applications: manipulation in microchannels

**Stretching single molecular DNA by temperature gradient**

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(a)

(b)

(c)

**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 scales 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 depictions 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

Possible Routes in Diffusive Phase Separation

- Nucleation
- Spinodal
- Diffusive Growth
- Ripening
- Break-Up

Gravity wetting

too many droplets polydispersity

Laser-induced first-order phase transitions?

Lutidine/water
Tc=32°C

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

Dieter W. Pohl
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

The laser-induced heating case
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:

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

$$v_d, v_c, \Omega$$

Molecular volumes and two-body coupling

In presence of the field:

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

Definition of the critical point:

$$\left( \frac{\partial \mu}{\partial \Phi} \right) = \left( \frac{\partial^2 \mu}{\partial \Phi^2} \right) = 0 \quad \text{with} \quad \mu = \left( \frac{\partial (\Delta f_E / k_B T)}{\Phi} \right)_T$$

$$\begin{cases} 
\Phi_c^E = \Phi_c^0 + \delta \phi \\
T_c^E = T_c^0 + \delta \tau 
\end{cases}$$

At first order in perturbation:

$$\delta \phi = \frac{v_d \left( \Phi_c^0 \right)^3 (1 - \Phi_c^0) \varepsilon_0 E_0^2}{2} \left( \frac{\partial^3 \sqrt{E}}{\partial \Phi^3} \right)_{\phi = \Phi_c^0}$$

$$\delta \tau = \frac{\varepsilon_0 E_0^2}{\Omega} \left( \frac{\partial^2 \sqrt{E}}{\partial \Phi^2} \right)_{\phi = \Phi_c^0}$$

---

Generally a weak effect

Laser-induced quench in composition

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

$$\frac{\Delta \Phi}{\rho_p T_0} \Delta T - \varepsilon_0 \left( \frac{\partial \sqrt{\varepsilon}}{\partial \Phi} \right)_{T_0} \Delta E_0^2 = 0$$

$$\chi_T \Delta T + \frac{\alpha_a}{\rho_0 c_p} I = 0$$

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

$$\vec{J}_s (r = R) = 4\pi R^2 \mathcal{D} \left[ \mathcal{V} \Phi \right]_{r=R} = (\Phi_m - \Phi_M) \frac{d}{dt} \left( \frac{4}{3} \pi R^3 \right) \hat{f}$$

Concentration field at the drop interface

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

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

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

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

Diffusion-limited droplet growth rate:

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

« capillary length »
Droplet Growth Rate in a “spherical” beam

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

**Electrostrictive growth rate**

\[
I (r) = \frac{P}{4\pi a_0^2} \exp\left(-\frac{r^2}{a_0^2}\right) \quad \rightarrow \quad \Phi_{el} (r) = (\Phi_{el})_0 \exp\left(\frac{r^2}{a_0^2}\right)
\]

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

**Thermodiffusive growth rate**

\[
T_{th} (r) = \frac{\sqrt{\pi}}{2} \left(\frac{\alpha_s P}{8\pi\Lambda}\right) \frac{\text{erf}(r/a_0)}{r/a_0} \quad \rightarrow \quad \Phi_{th} (r) = (\Phi_{th})_0 \left[\frac{\sqrt{\pi}}{2} \frac{\text{erf}(r/a_0)}{r/a_0}\right]
\]

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

« classical » growth: \( R \ll a_0 \)

\[
\frac{dR}{dt} = \frac{D}{R} \left\{ \frac{(\Phi_{E})_0 - 2d_0}{\Phi_m - \Phi_M - R} \right\}
\]

**Critical radius:**

\[
(R_C^E)_0 = 2d_0 \left(\frac{\Phi_m - \Phi_M}{(\Phi_E)_0}\right)
\]

J. P. Delville et al, Physica A 262, 40 (1999)
Finite Size effects due to the beam

\[ \rho_a = \frac{R}{a_0} \]

\[ \tau_a = \left( \frac{2d_0 D}{a_0^3} \right) t \]
Droplet Growth law

\[ \frac{a_0}{2d_0} \frac{(\Phi_E)_0}{\Phi_m - \Phi_M} = 100 \]
Influence of finite size effects on droplet growth

\[
\frac{a_0}{2d_0} \frac{(\Phi_E)_{\infty}}{\Phi_m - \Phi_M} = x
\]

\(x = 50\)

\(x = 10\)

\(x = 5\)
Confrontation to experiments: the optical bottle

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

\[ \Lambda_0 = 5 \mu m, P = 1 W, T_0 - T_c = 0.5 K \]
Growth law at early stage

Droplet grating formation

\[ \Re(t_e < t < t_i) \propto (\varepsilon_E)^2 \propto |\Phi_D(t)|^2 \]

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

\[ \frac{\partial R}{\partial t} = \frac{D^-}{R(t)} \left( \Phi_E(x=0,t=t_C) \right) \left( 1 - \frac{R_c}{R(t)} \right) \]

Droplet grating relaxation

\[ \Re(t > t_i) \propto \exp\left[ -2D_R(t_i)q_0^3(t-t_i) \right] \]

\[ D_R(t) = \frac{k_B T}{6\pi \eta R(t)} \]

\[ R_c = 2d_0 \left( \frac{\Phi_m - \Phi_M}{(\Phi_E)_0} \right) \]

S. Buil et al, PRE 63, 1504 (2001)
Universal behavior at early stage

\[ \rho = \frac{R}{R_c} \]

\[ \tau = \frac{D (\Phi_E) (x = 0, t = t_c)}{R_c^2 \Phi_m - \Phi_M} (t - t_c) \]

\[ \frac{d\rho}{dt} = \frac{1}{\rho} \left( 1 - \frac{1}{\rho} \right) \]

\[ \tau = \rho + \frac{\rho^2}{2} + \ln(\rho - 1) + K \]

K=4.16±0.26, \( \rho_c=1.005\ ±\ 0.001 \), Polydispersity 2.5%

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

- Domain radius $R$
- Time $t$
- Nucleation stage
- Early stage growth
- Free growth stage $R \sim t^{1/2}$
- Ostwald ripening $R \sim t^{1/3}$
- Saturation to equilibrium

Too many droplets polydispersity

- The optical bottle with soft walls
- The optical bottle with huge confinement

Gravity wetting
Laser-induced quench in temperature

Coexistence curve: \[ |\Phi_m - \Phi_M| = (\Delta \Phi)_0 \left| 1 - \frac{T_0}{T_C} \right|^\beta \]

Quench depth \[ \frac{\Phi_T(r)}{\Phi_m - \Phi_M} = \left( 1 + \frac{T_E(r)}{T_0 - T_C} \right)^\beta - 1 \approx \frac{\beta}{2} \frac{T_E(r)}{T_0 - T_C} \]

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

\[ \rightarrow \text{ Same behavior as in the thermodiffusive case} \]
Related works

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

Paweł Borowicz,† Jun-ichi Hotta, Keiji Sasada,† and Hiroshi Masuhara†
Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan

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
Recent developments 1
Patterning by thermodiffusion driven by laser close to a critical point \( (k_T > 0) \)

one-phase

spinodal

FIG. 1. Temporal development of structure after laser exposure at \( T = 38.5^\circ C, 0.8^\circ C \) 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.

FIG. 2. Temporal development of structure after laser exposure below \( T_c \) (\( T = 37.2^\circ C \)). 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.
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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