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Structure Formation in Soft Matter by Solvent Evaporation

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Drying is not simple

Solvent evaporation induces

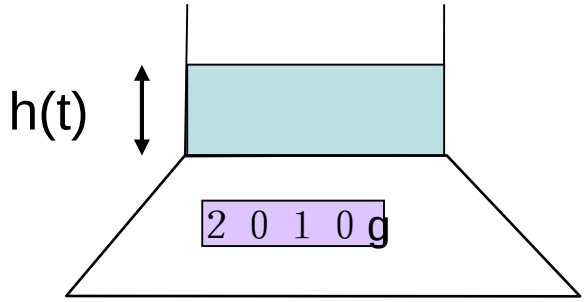
- Liquid flow
- Deformation
- Structural change (phase separation, gelation etc)

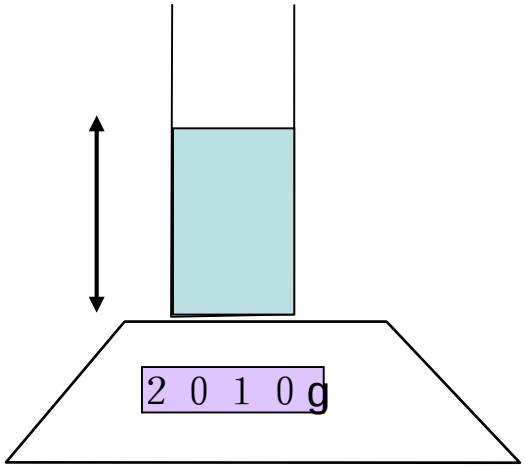
Outline

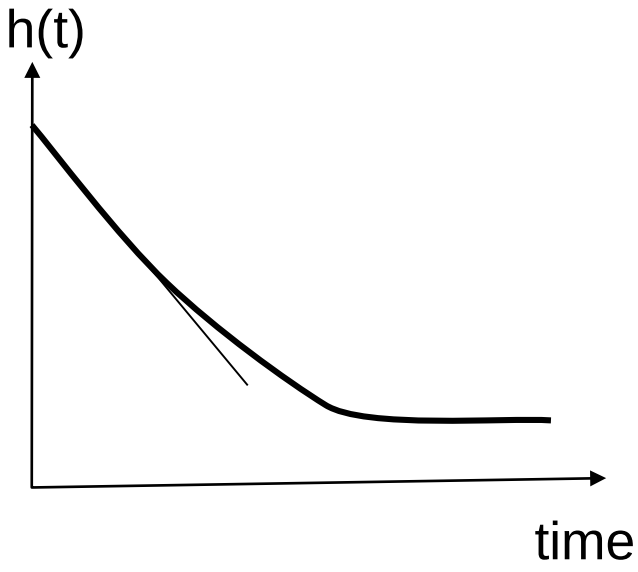
- Evaporation rate
  - What determines the evaporation rate
- Flow induced by evaporation
  - Coffee ring effect
- Structural formation
  - Skin formation
- Summary

Evaporation rate

Measurement of evaporation rate



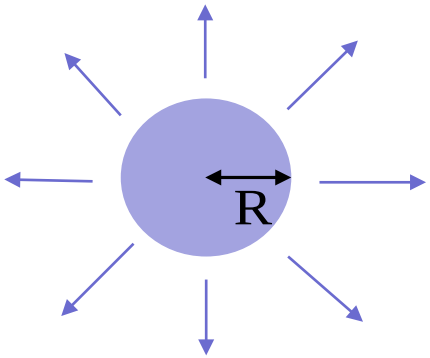




Evaporation rate depends on

Temperature
Humidity
Original volume
Shape of the container

Evaporation of a droplet



$$\frac{\partial c}{\partial t} = D_g \nabla^2 c$$

$$\nabla^2 c = 0$$

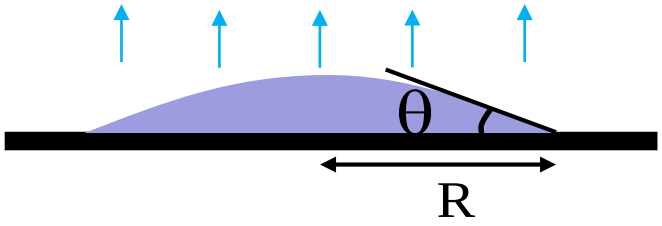
$$c(R) = c_v$$

$$c(\infty) = c_a = c_v H$$

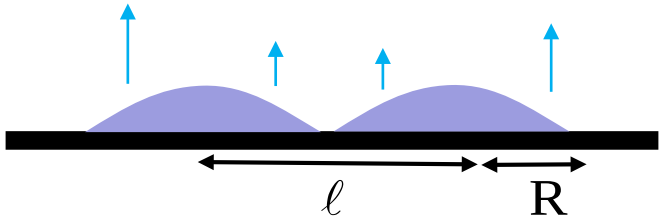
$$J = v_s D_g \frac{\partial c}{\partial r} \quad \Rightarrow \quad J = D_g v_s \frac{c_v(T)(1-H)}{R}$$

Calculation of evaporation rate

Kobayashi, Makino,
Okuzono, MD JPSJ 2010

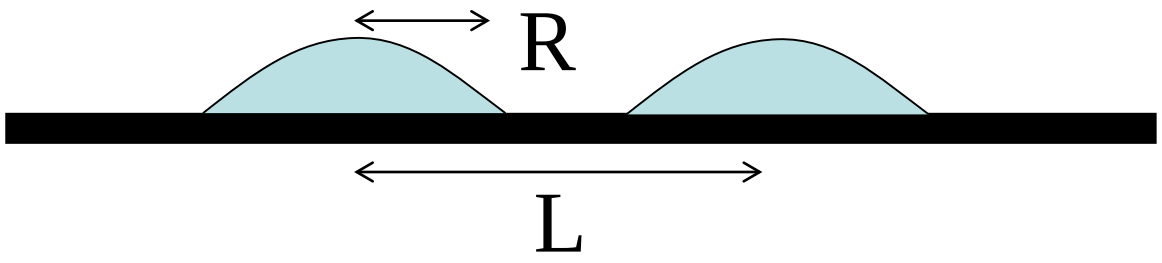


$$\overline{J} = D_g v_s \frac{c_v - c_a}{R}\left(0.65 + 0.135\theta^2\right)$$

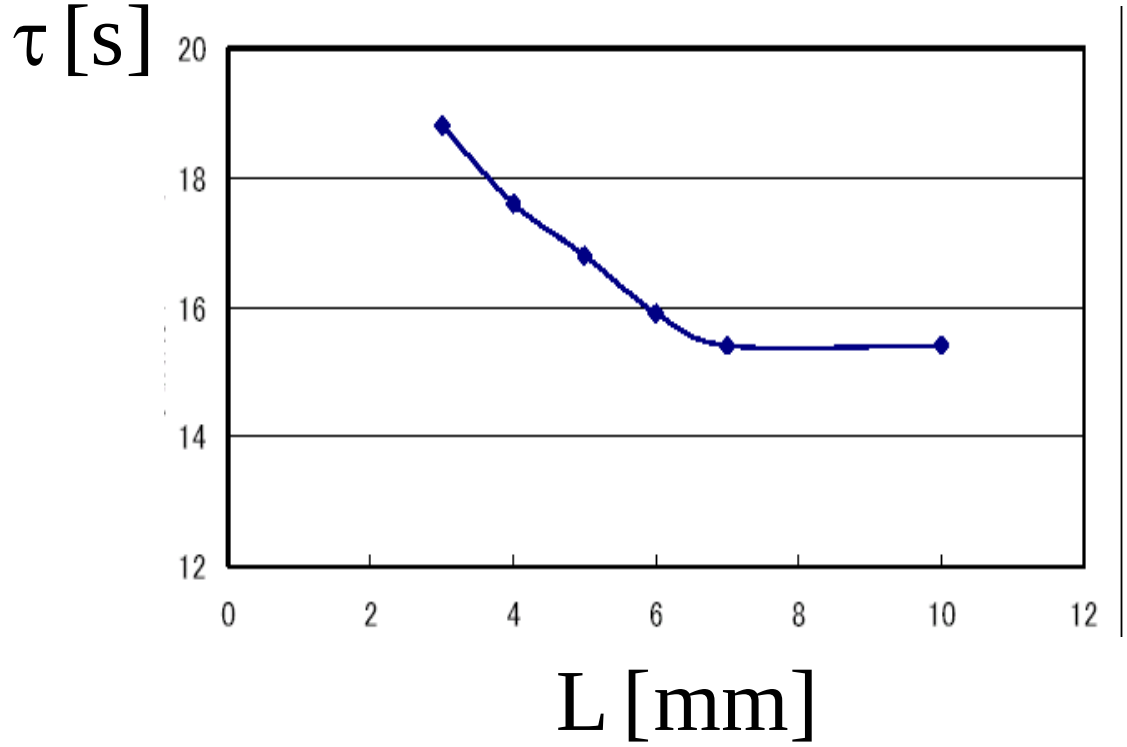


$$\overline{J} \approx \frac{J_0}{1 + (R/\ell)}$$

Experiments



Kobayashi, Makino, Okuzono, MD JPSJ 2010



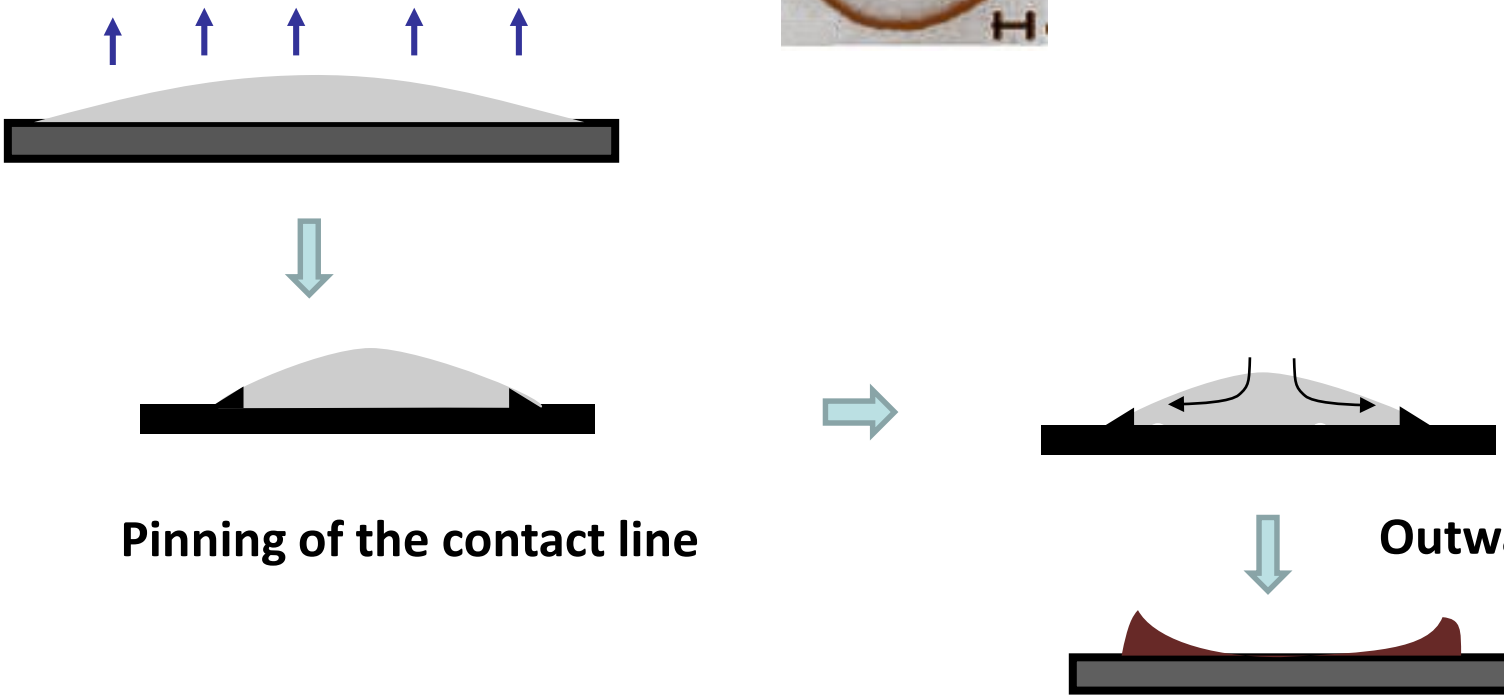
Interference is long range

$$J \approx J_0 \frac{L}{L+R}$$

Flow induced by evaporation

Coffee ring effect

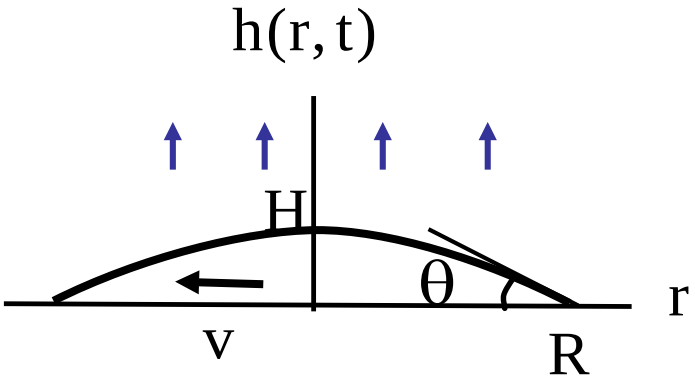
Coffee ring



Pinning of the contact line

Outward flow

Calculation of the outward flow



Assume $$h(r,t) = H(t)\left(1 - \frac{r^2}{R(t)^2}\right)$$

$$H = \frac{1}{2}\theta R \qquad V = \frac{\pi}{4}\theta R^3$$

$$\frac{\partial h}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(hrv) - \bar{J}$$

$$\bar{J} = -\frac{\dot{V}}{\pi R^2}$$

$$v = r\left(\frac{\dot{R}}{R} - \frac{\dot{V}}{4V}\right)$$

When contact line is pinned $$v(r) > 0$$

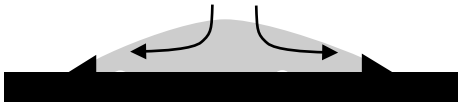
The outward flow brings coffee particles to the edge, making the ring

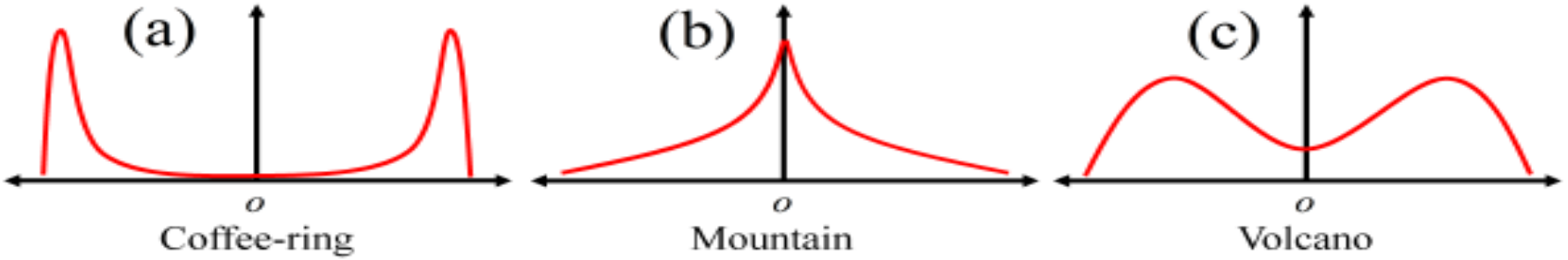
Contact line can move

Xingkun Man, MD PRL (2016)

When contact line is pinned

When contact line is not pinned



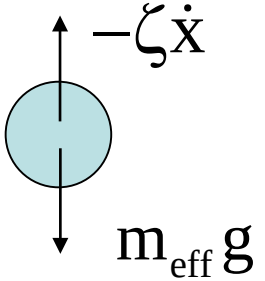


Use Onsager principle for contact line motion

State variables specifying the non-equilibrium state

$$x = (x_1, x_2, ...x_f)$$

$A(x)$ Free energy



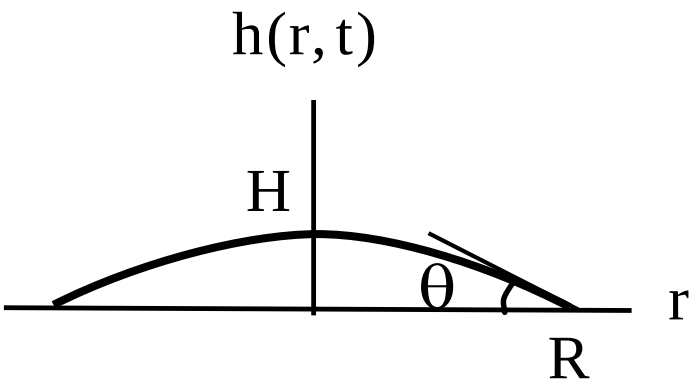
Kinetic equation $$\sum_j \zeta_{ij}(x)\dot{x}_j = -\frac{\partial A}{\partial x_i}$$

Minimize $$R = \Phi + \dot{A}$$

$$\Phi = \frac{1}{2}\sum \zeta_{ij}(x)\dot{x}_i\dot{x}_j$$ Energy dissipation function $$\Phi = \frac{1}{2}\zeta\dot{x}^2$$

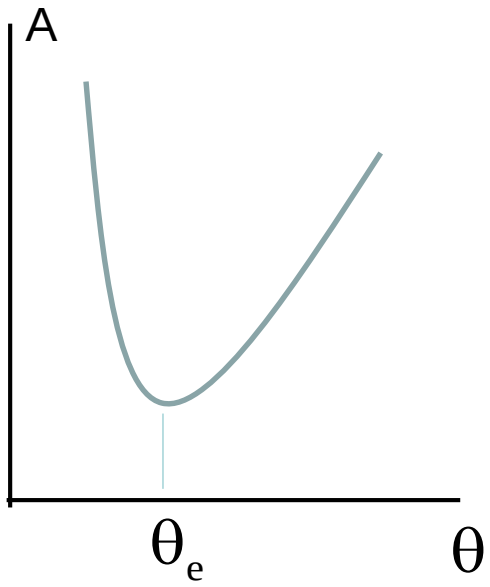
$$A = \sum_i \frac{\partial A}{\partial x_i}\dot{x}_i$$ Free energy change rate $$A = m_{eff}\,g x$$

Free energy



$$A = \int_0^R dr\, 2\pi r \left(\gamma \sqrt{1 + h'^2} - \gamma_{sv} + \gamma_{sl} \right)$$

$$h(r,t) = H(t)\left(1 - \frac{r^2}{R(t)^2}\right)$$



$$A = \gamma \left(\frac{4V^2}{\pi R^4} + \frac{1}{2}\pi R^2 \theta_e^2 \right)$$

$$\gamma_{sv} - \gamma_{sl} = \gamma \cos\theta_e$$

Dissipation function

Energy dissipation function
(lublication approximation)

$$\Phi = \frac{1}{2}\int_0^R dr\, 2\pi r \frac{3\eta}{h} v^2$$

$$v = r\left(\frac{\dot{R}}{R} - \frac{\dot{V}}{4V}\right)$$

$$h(r,t) = H(t)\left(1 - \frac{r^2}{R(t)^2}\right)$$

$$\Phi = 2\pi R\left[\frac{1}{2}\xi_{hydro}\left(\dot{R} - \frac{\dot{V}}{4V}R\right)^2 + \frac{1}{2}\xi_{cl}\dot{R}^2\right]$$

$$\xi_{hydro} = \frac{3\eta}{\theta}\ln\left(\frac{R}{a}\right)$$

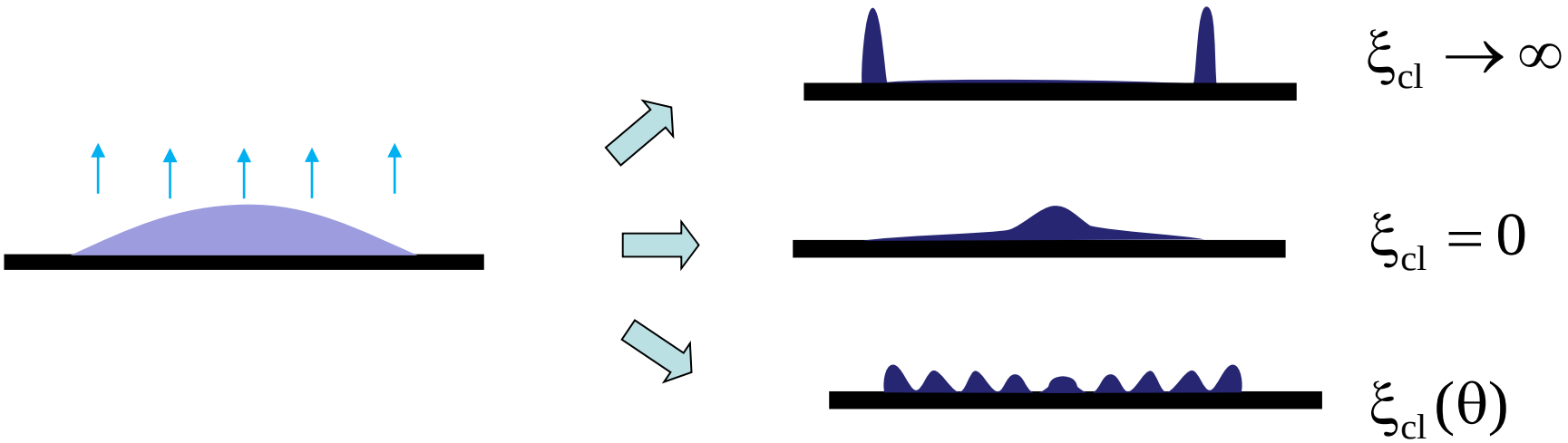
ξ_{cl} phenomenological parameter

Evolution equation

$$\left(1+\frac{\xi_{cl}}{\xi_{hydro}}\right)\dot{R}=\frac{\dot{V}R}{4V}+\frac{\gamma\theta(\theta^2-\theta_e^2)}{6\eta\ln(R/a)}$$

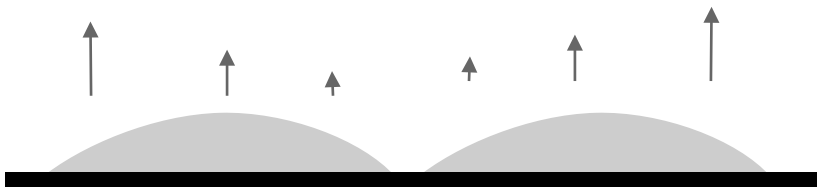
Xingkun Man, MD PRL (2016)

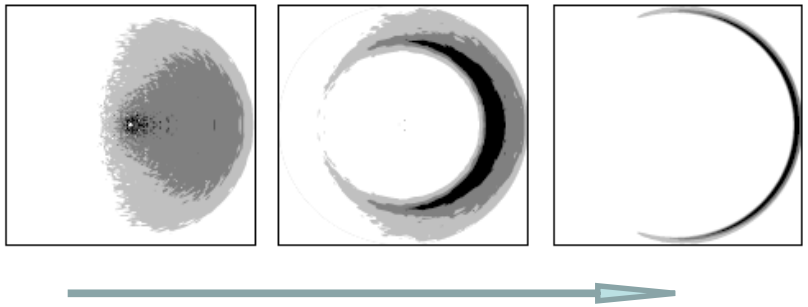
$$v(R)=\dot{R}-\frac{\dot{V}R}{4V}$$



Deposit pattern in two neighbouring droplets

Shiyuan Hu, Yuhan Wang, Xingkun Man and MD Langmuir (2017)





Stronger pinning

Structural formation in droplets

Evaporation creates inhomogeneity

Drying of a film of colloidal solution

Okuzono, Ozawa MD PRL 2006

$$h(t) = h_0 - Jt$$

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z}\left(D(\phi) \frac{\partial \phi}{\partial z} \right)$$

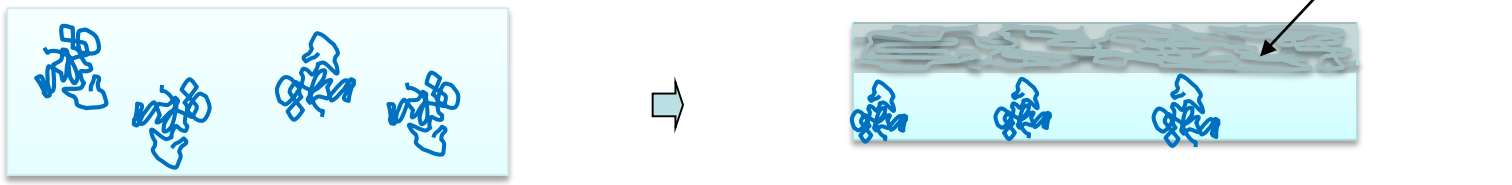
$$D \frac{\partial \phi}{\partial z} = J\phi \quad \text{at} \quad z = h(t)$$

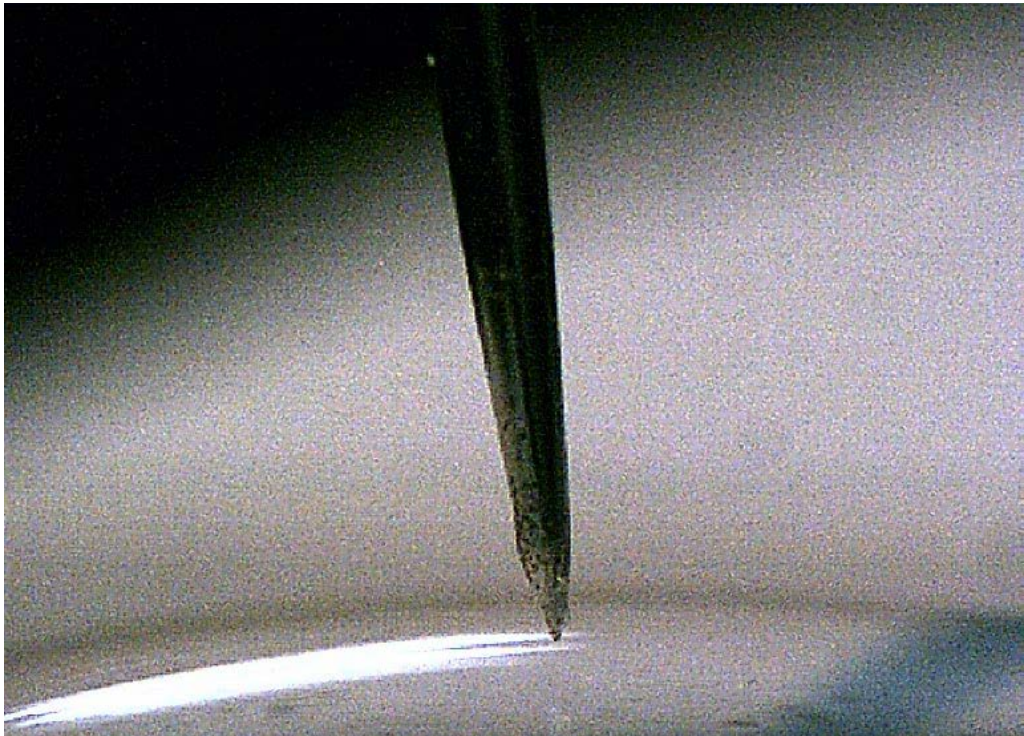
$$D \frac{\partial \phi}{\partial z} = 0 \quad \text{at} \quad z = 0$$

$$\frac{Jh_0}{D} << 1$$

$$\frac{Jh_0}{D} >> 1$$

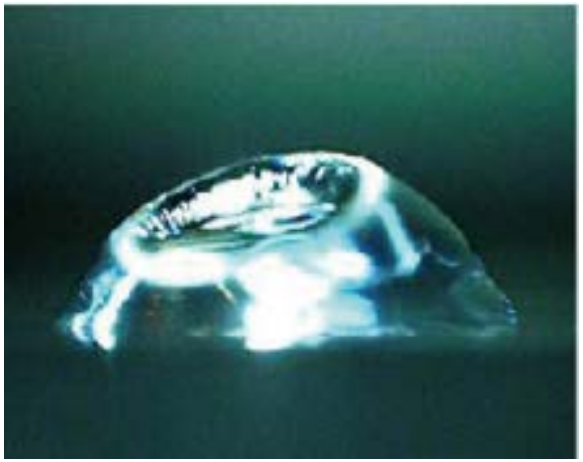
Skins





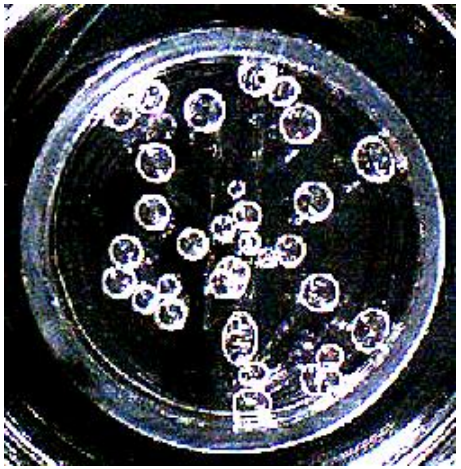
Skins cause problems

Dimples



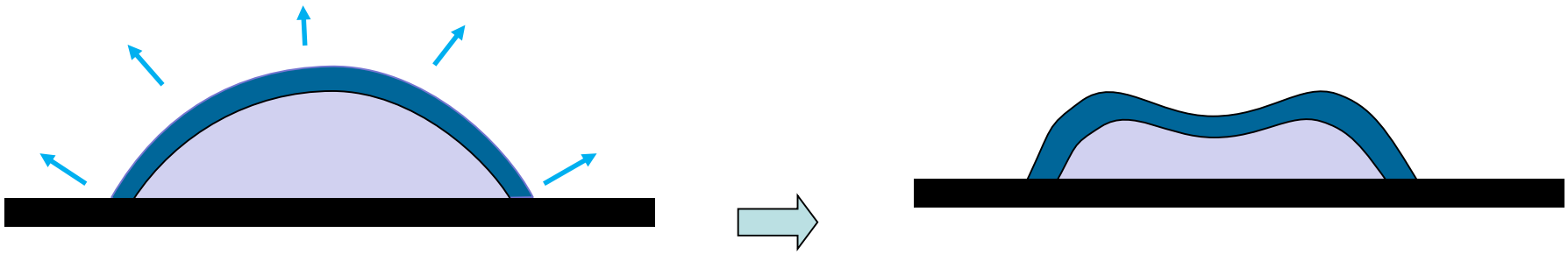
Pauchard et al (2003), Kajya et al (2006)

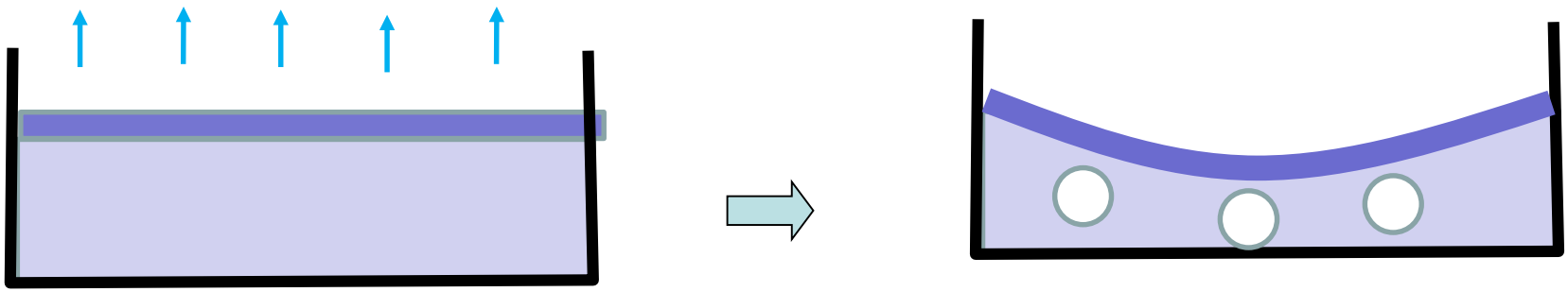
Cavitues



Arai et al (20013)

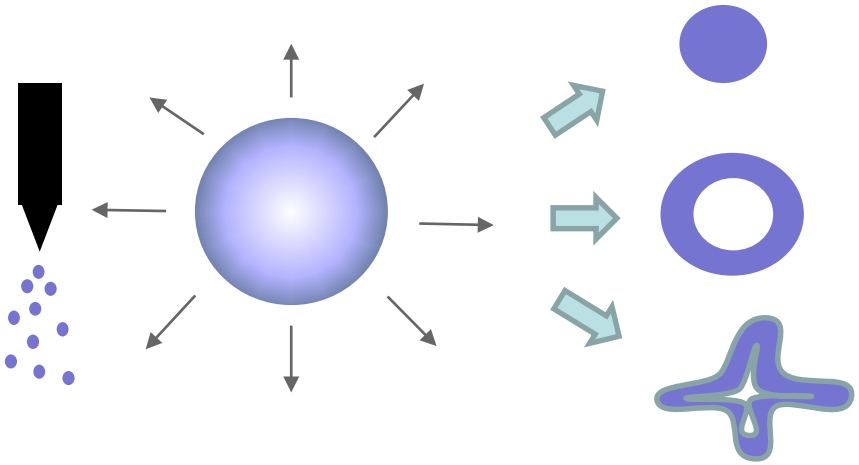
Dimples and Cavities





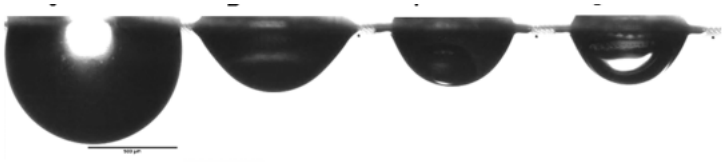
Cavity formation

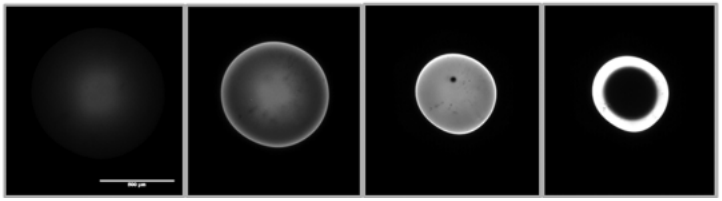
Spray drying

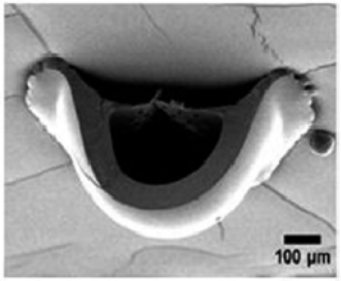


Protein suspensions (milk)

Sadek et al Langmuir 2013

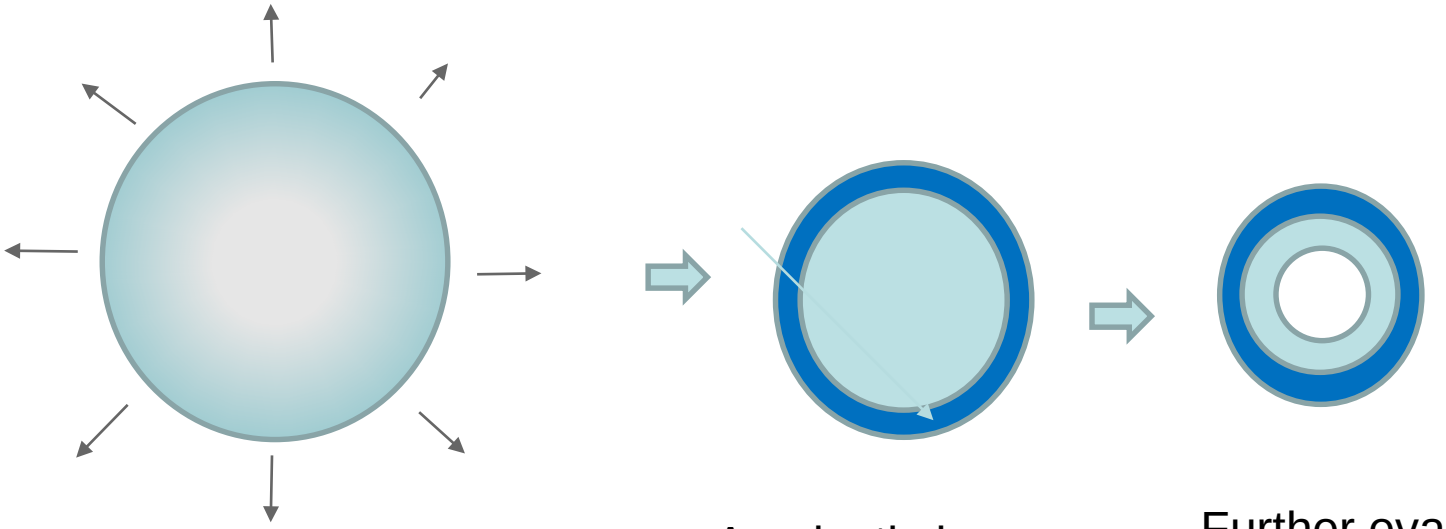






Mechanism of cavity formation

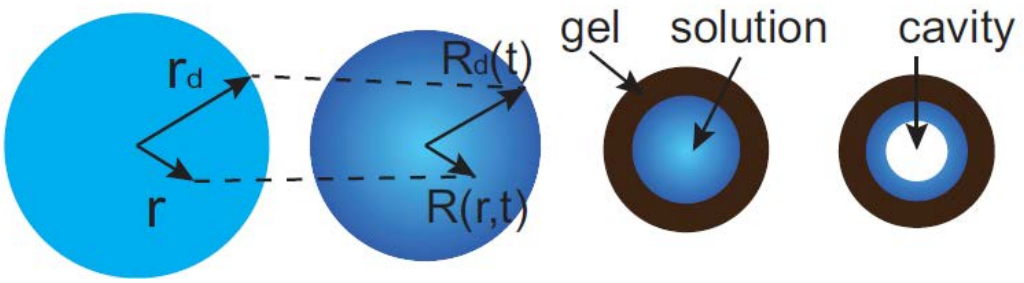
F. Meng MD, Z. OuYang PRL (2014)



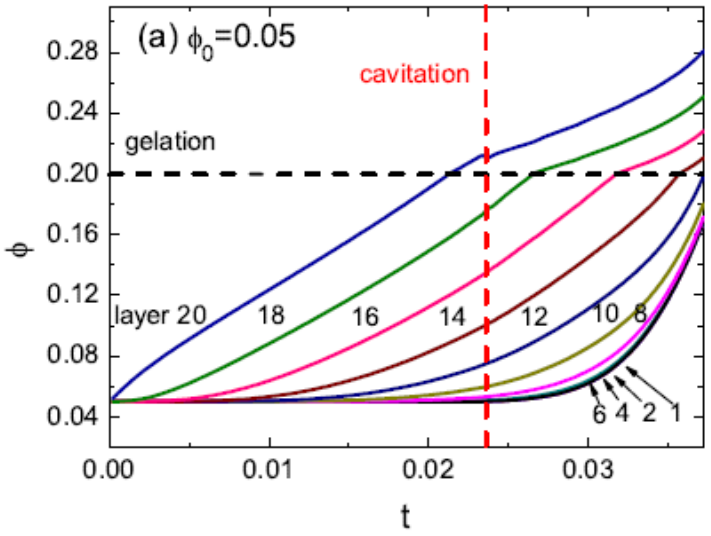
An elastic layer is created at the surface

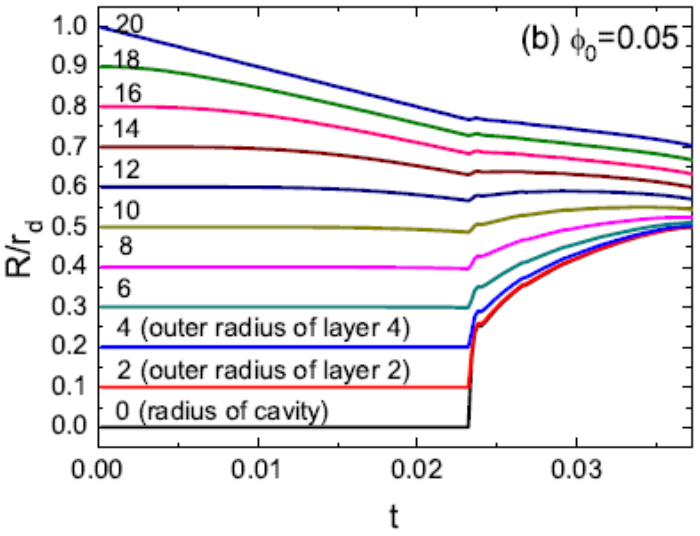
Further evaporation creates contractile stress, and negative pressure

Simulation



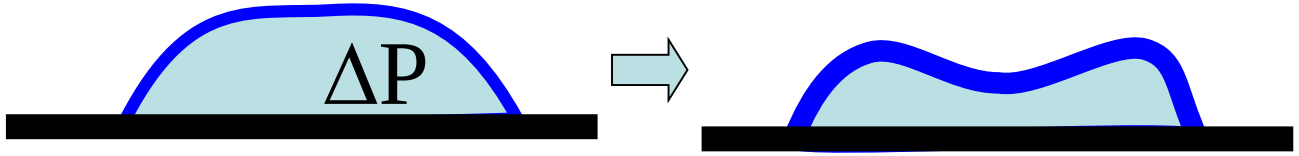
F. Meng et al EPJE (2015)

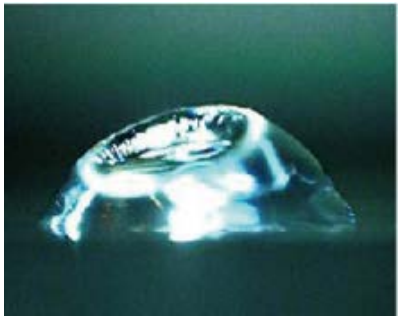




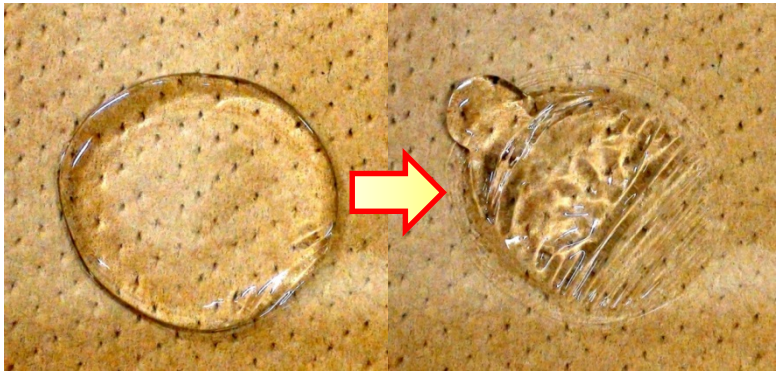
Skins in sessile droplet

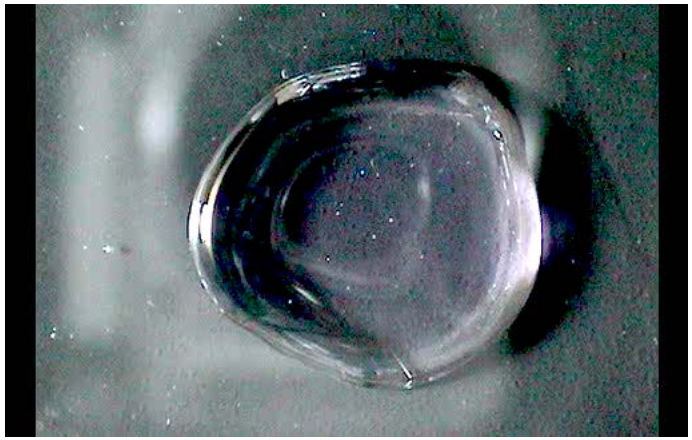
Arai Doi, EPJE 2013





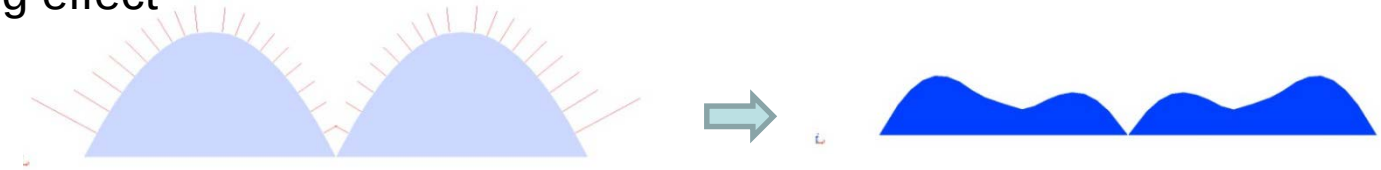
But there are phenomena which indicates that it must be positive.



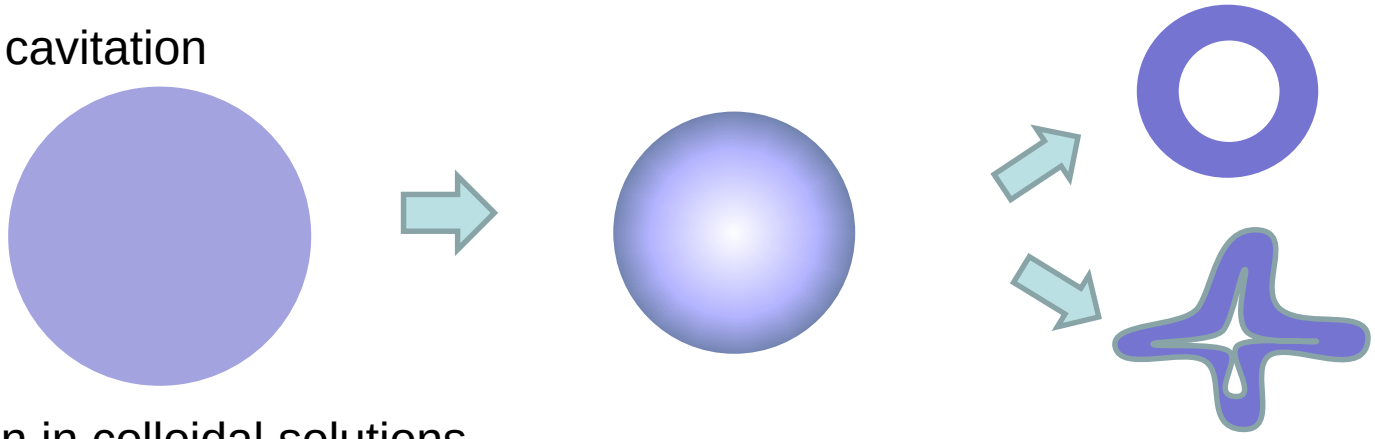


Summary

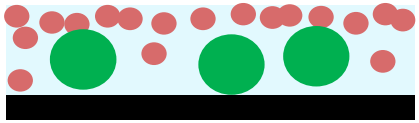
Coffee ring effect



Skin and cavitation



Stratification in colloidal solutions



Molecular configuration, crystallization kinetics