Stepwise drainage of thin liquid films stabilized by colloidal particles

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and

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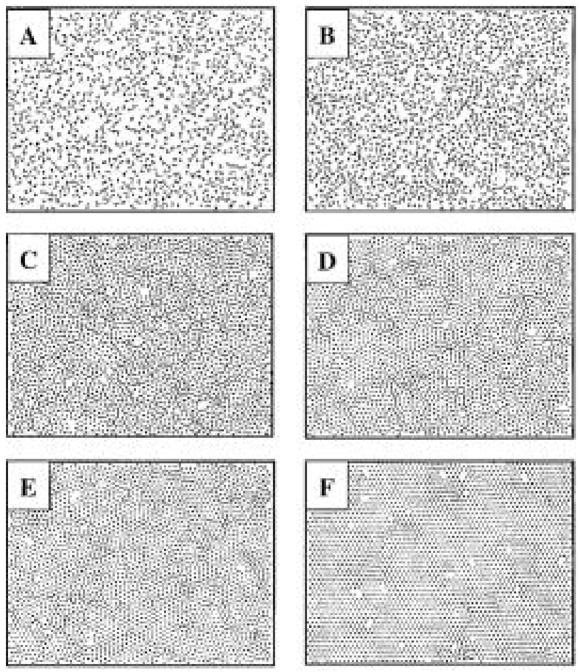
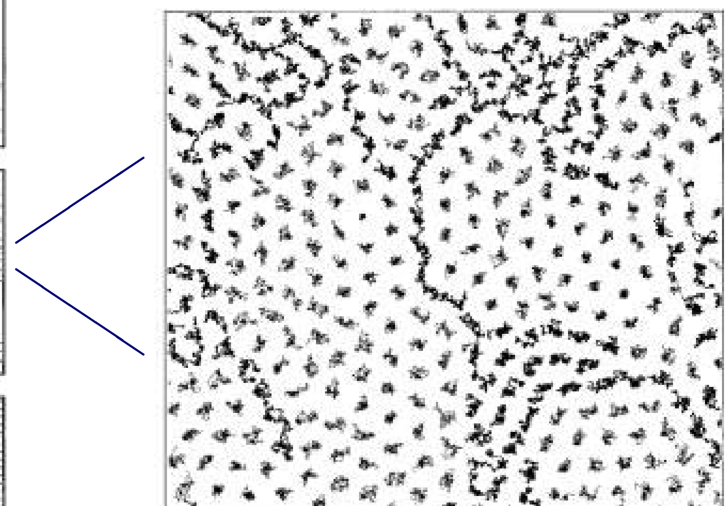
Quasi-two-dimensional colloidal suspension



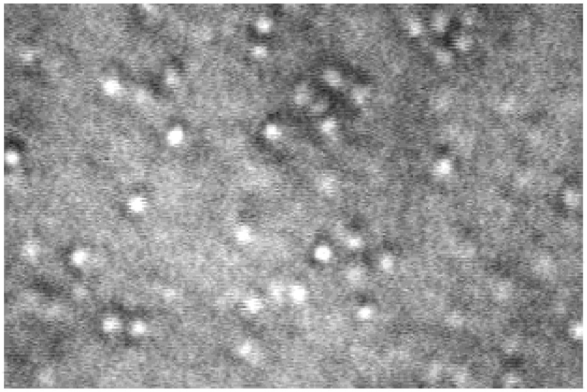
particle trajectories at different area fractions ϕ_{a}



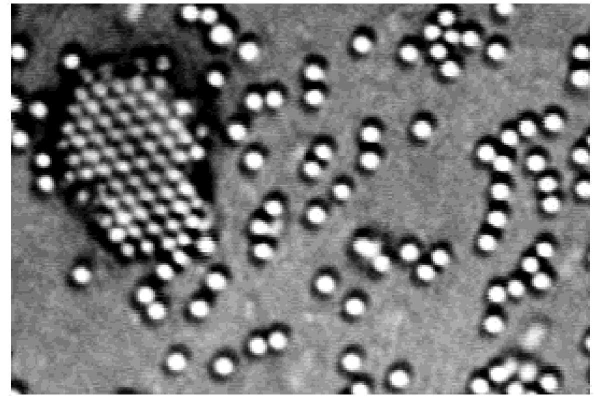
blowup at $\phi_{\mathrm{a}} = 0.64$

Cui, Lin & Rice (2001)

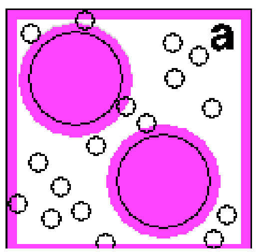
Structural interactions

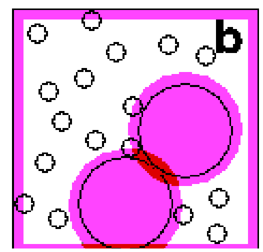


without macromolecules



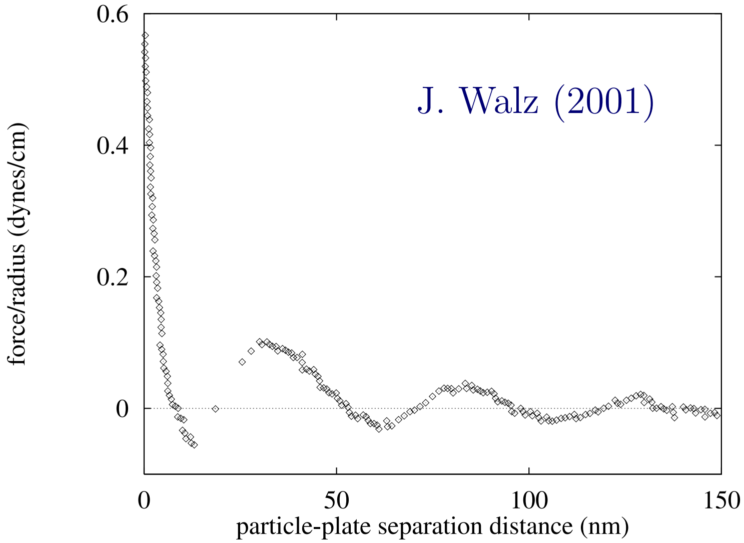
with macromolecules

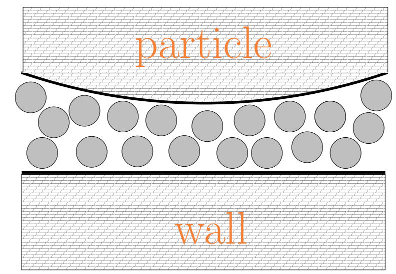




Dinsmore, Yodh, & Pine (2000)

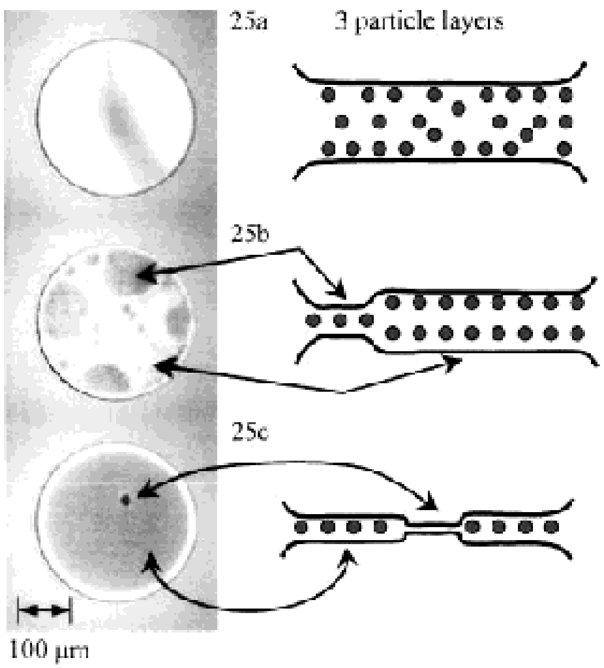
Effective structural force





Stratification of particle-stabilized liquid films

Early observations: Johnot (1906), Perrin (1918)

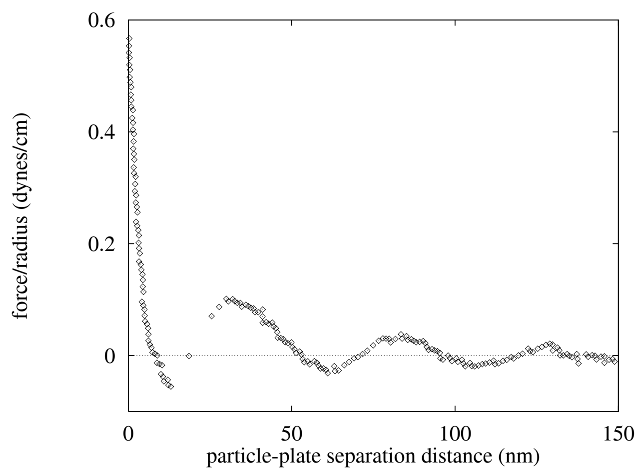


Sethumadhavan,

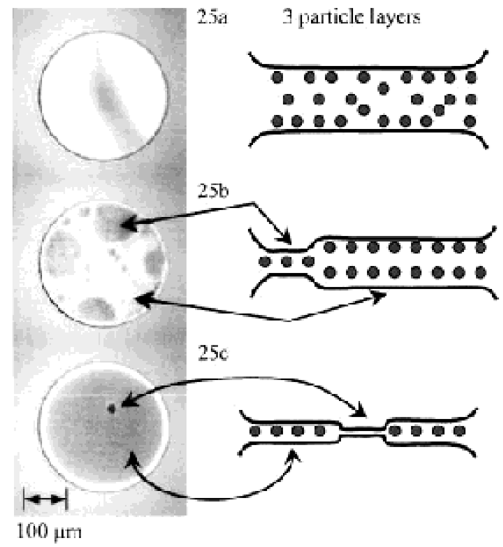
Nikolov & Wasan (2001)

Standard explanation:

normal structural force



$\Longrightarrow$

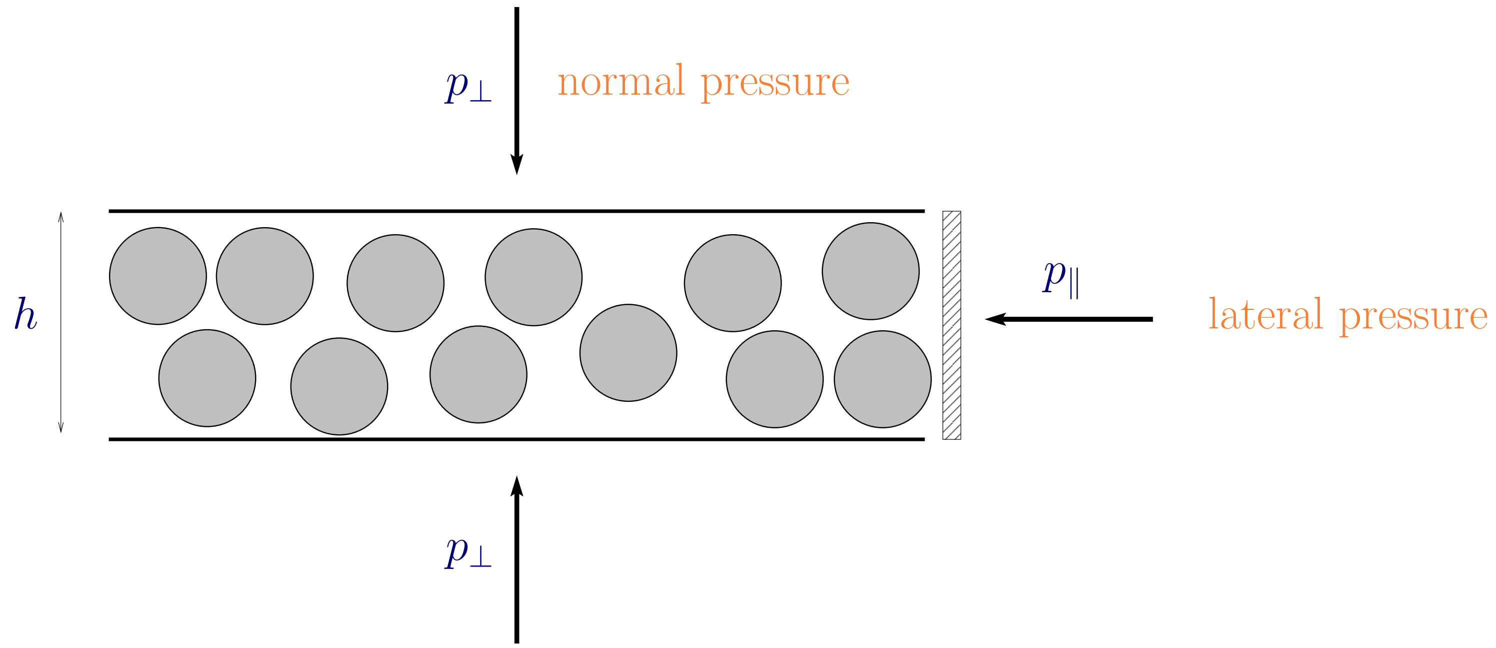


Missing: lateral force balance

Outline

- Normal and lateral structural forces
- Thermodynamics of particle-stabilized films
- Constrained and unconstrained phase equilibria
- Irreversible thermodynamics
- Evaluation of transport coefficients
- Interfaces with different boundary conditions

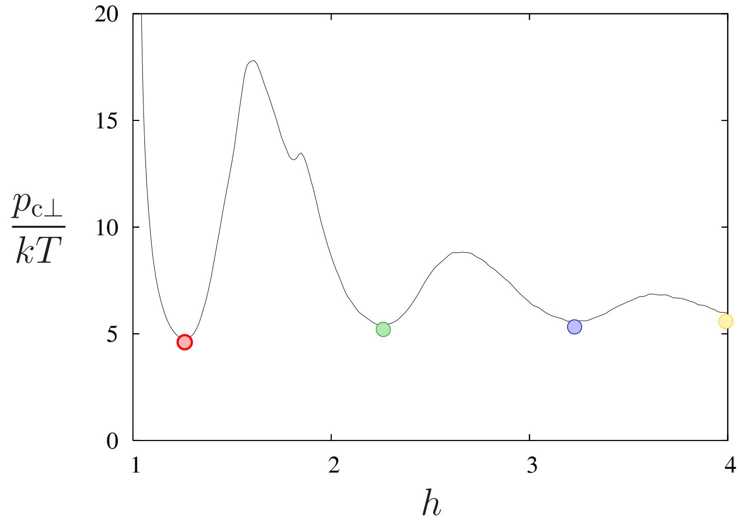
• Normal and lateral structural forces

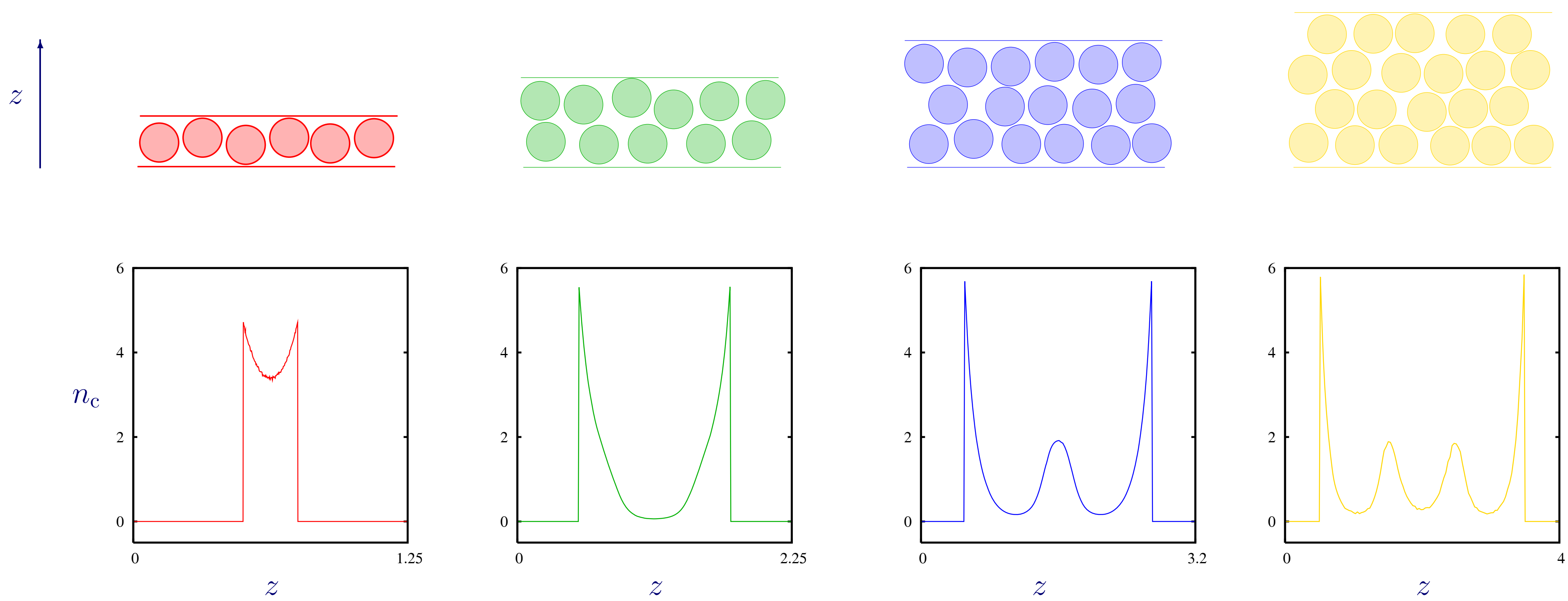


confined suspension of hard spheres

Normal pressure

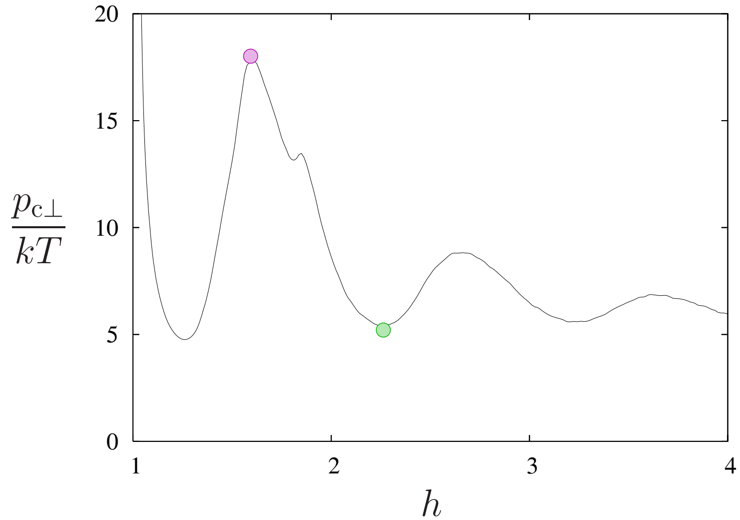
volume fraction $\phi_c = 0.4$

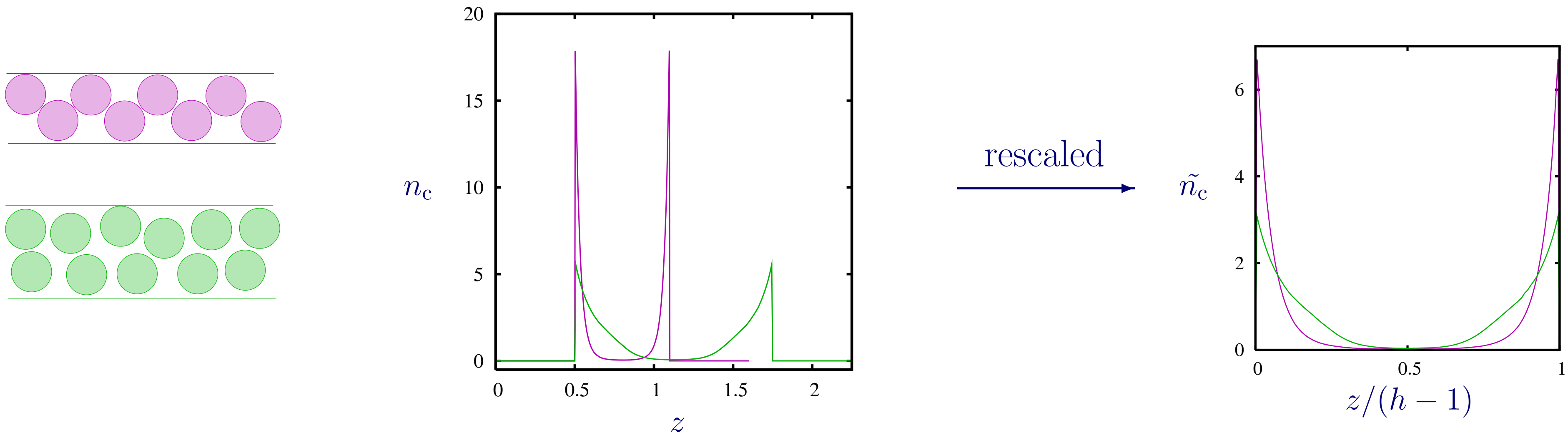




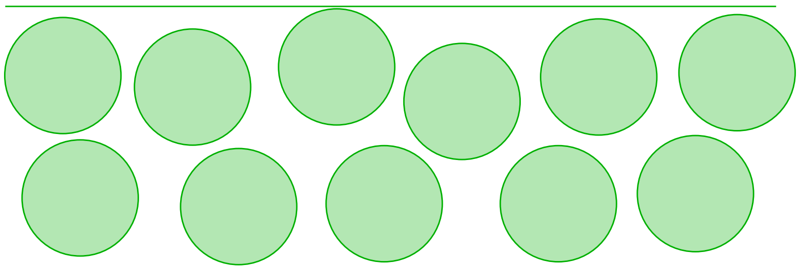
Normal pressure

volume fraction $\phi_c = 0.4$





Lateral pressure

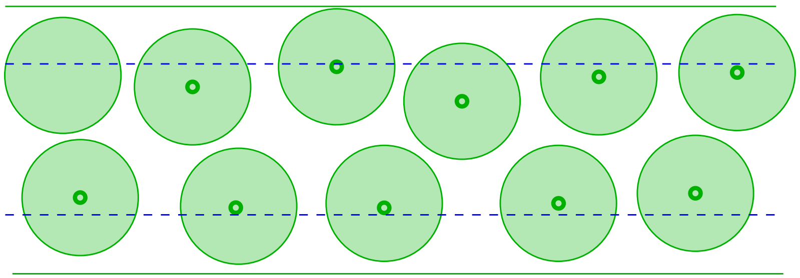


Non-isotropic particle distribution

$$\Longrightarrow \qquad \mathsf{p}_{\rm c} = p_{{\rm c}\perp}\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z + p_{{\rm c}\|}\mathsf{I}_{\rm s}$$

$$\mathsf{I}_{\rm s} = \hat{\mathbf{e}}_x\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y\hat{\mathbf{e}}_y$$

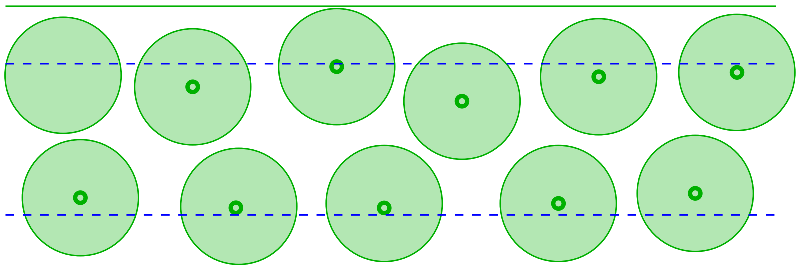
Lateral pressure



$$\Longrightarrow \qquad \mathsf{p}_{\mathrm{c}} = p_{\mathrm{c}\perp}\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z + p_{\mathrm{c}\parallel}\mathsf{I}_{\mathrm{s}}$$

$$\mathsf{I}_{\mathrm{s}} = \hat{\mathbf{e}}_x\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y\hat{\mathbf{e}}_y$$

Lateral pressure



$$\Longrightarrow \qquad \mathsf{p}_\mathrm{c} = p_{\mathrm{c}\perp}\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z + p_{\mathrm{c}\|}\mathsf{I}_\mathrm{s}$$

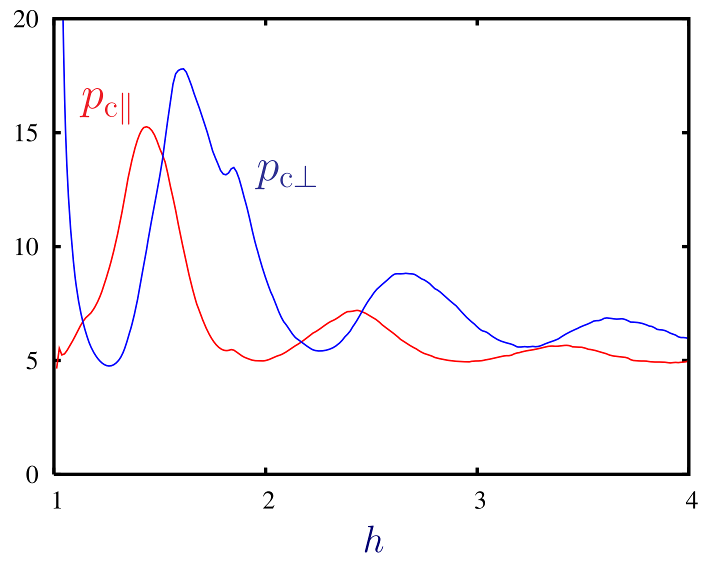
$$\mathsf{I}_\mathrm{s} = \hat{\mathbf{e}}_x\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y\hat{\mathbf{e}}_y$$

$$\mathsf{p}_\mathrm{c} = p_{\mathrm{c}\perp}\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z$$

$$\frac{\mathsf{p}_c}{kT} = n'_c + \tfrac{1}{2}d^3\left\langle \int \mathrm{d}^2\hat{r}\;\hat{\mathbf{r}}\hat{\mathbf{r}}\,n_2^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_1 - d\hat{\mathbf{r}})\right\rangle_{V'}$$

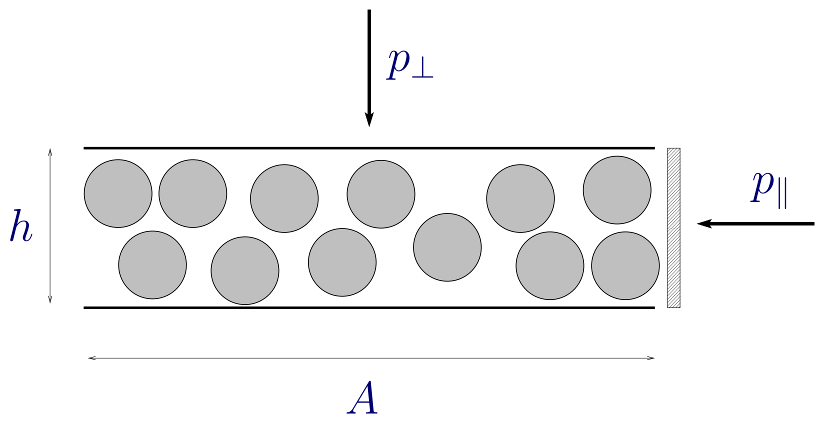
$$\mathsf{p}_\mathrm{c} = p_{\mathrm{c}\perp}\hat{\mathbf{e}}_z\hat{\mathbf{e}}_z$$

Components of pressure tensor



$\phi_{\mathrm{c}} = 0.4$

• Thermodynamic description



Work

$$đW = -Ap_\perp \, \mathrm{d}h + (2\sigma - hp_\parallel)\, \mathrm{d}A$$

$$\Downarrow \qquad \gamma = h(p_\perp - p_\parallel) + 2\sigma \qquad \text{film tension}$$

$$đW = -p_\perp \, \mathrm{d}V + \gamma \, \mathrm{d}A$$

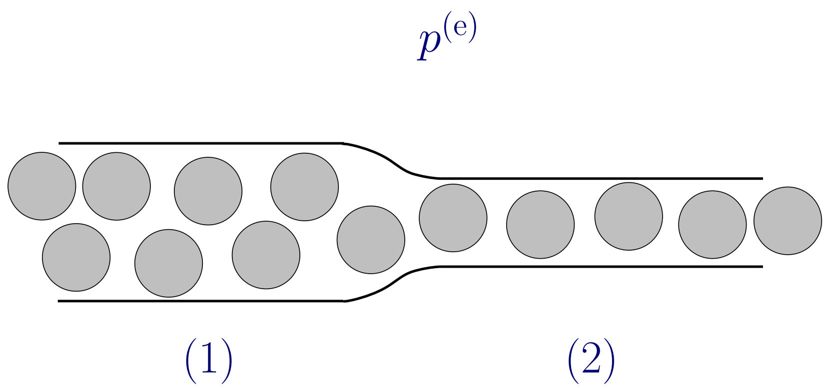
Gibbs free energy

$$\mathrm{d}F = -S\,\mathrm{d}T - p_\perp \, \mathrm{d}V + \gamma \, \mathrm{d}A + \mu_\mathrm{c}\, \mathrm{d}N_\mathrm{c} + \mu_\mathrm{f}\, \mathrm{d}N_\mathrm{f}$$

V, A extensive

$p_\perp, \gamma$ intensive

Phase equilibria



$\mathsf{p} = p_\perp \mathsf{I} + (p_\parallel - p_\perp)\mathsf{I}_s$ inside

$\mathsf{p} = p^{(e)}\mathsf{I}$ outside

$\gamma = h(p_\perp - p_\parallel)$ **excess lateral force**

Equilibrium conditions

mechanical

$$p_\perp^{(1)} = p_\perp^{(2)} = p^{(e)}$$
$$\gamma^{(1)} = \gamma^{(2)}$$

chemical

$$\mu_c^{(1)} = \mu_c^{(2)}$$
$$\mu_f^{(1)} = \mu_f^{(2)}$$

Colloidal contributions

$$\mathsf{p} = p_{\mathrm{f}}\mathsf{I} + \mathsf{p}_{\mathrm{c}}$$

isotropic fluid pressure — nonisotropic osmotic pressure

$\Longrightarrow$

equilibrium conditions

$$p_{\mathrm{c}\perp}^{(1)} = p_{\mathrm{c}\perp}^{(2)}$$

$$\gamma_{\mathrm{c}}^{(1)} = \gamma_{\mathrm{c}}^{(2)}$$

Fundamental relation

$$\mathrm{d}F_{\mathrm{c}} = -p_{\mathrm{c}\perp}\,\mathrm{d}V + \gamma_{\mathrm{c}}\,\mathrm{d}A + \mu_{\mathrm{c}}\,\mathrm{d}N_{\mathrm{c}}$$

$$(T = \mathrm{const})$$

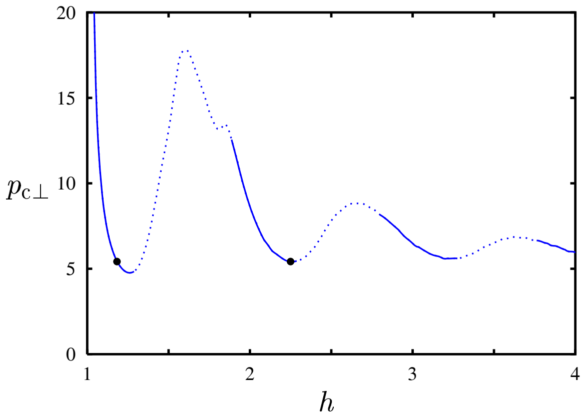
Chemical potential

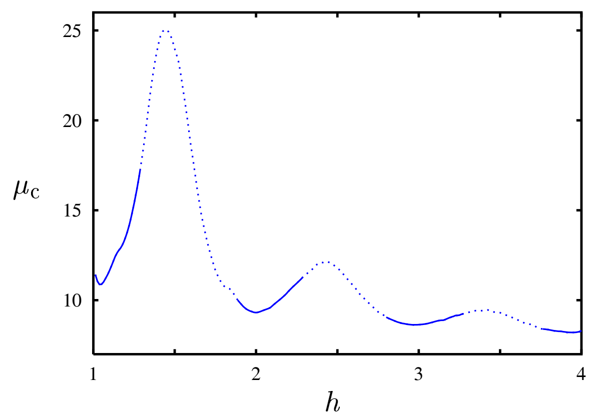
$$\mathrm{d}\mu_{\mathrm{c}} = v\,\mathrm{d}p_{\mathrm{c}\perp} - a\,\mathrm{d}\gamma_{\mathrm{c}}$$

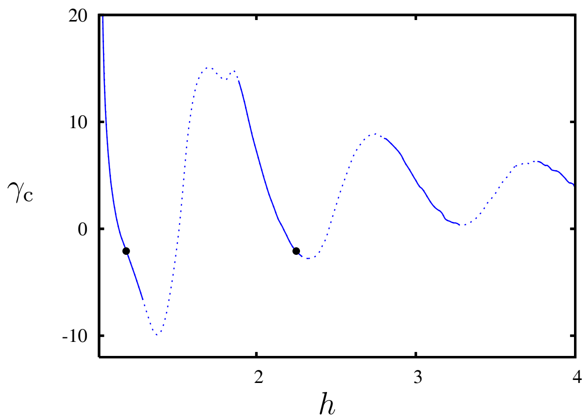
Gibbs–Duhem relation

$v = V/N_c, \qquad a = A/N_c$

Equations of state (Volume fraction $\phi_c = 0.4$)







Stability condition

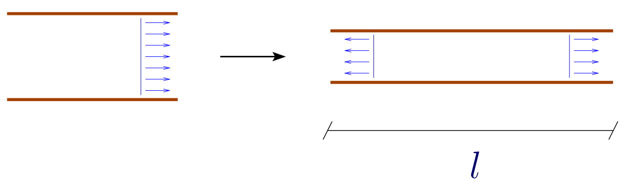
$$(\partial p_{c\perp}/\partial h)_{T\mu_c} < 0$$

• Constrained and unconstrained phase equilibria

Three relaxation mechanisms (surfactant-free film)

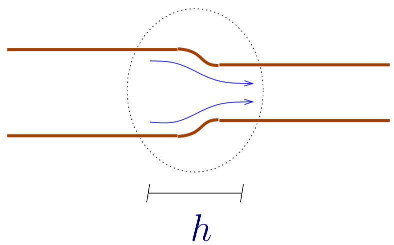
- area exchange

  $\tau_1 \sim \eta/(n_c kT)$



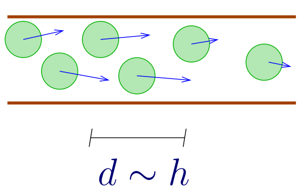
- volume exchange

  $\tau_2 \sim (l/h)\tau_1$



- particle exchange

  $\tau_3 \sim (l/h)\tau_2$



Energy-dissipation argument

$$\eta(\nabla u)^2 V_d \sim n_c kT \frac{dV}{dt}$$

energy dissipation | work of structural force

Anticipated equilibration phases

- **Timescale** τ_1:

  area exchange by film-tension relaxation

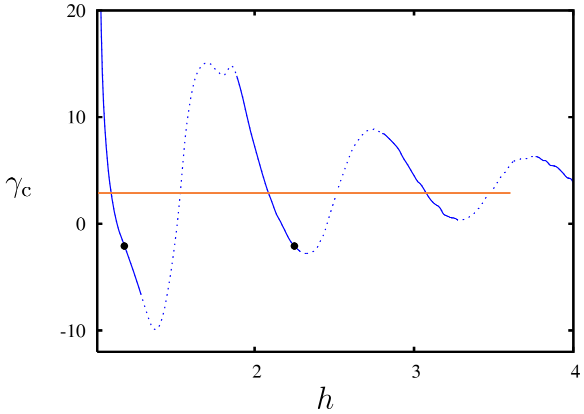
- **Timescale** $\tau_2 \gg \tau_1$:

  normal-pressure relaxation by volume exchange at $\phi_{\mathrm{c}} = \mathrm{const}$

- **Timescale** $\tau_3 \gg \tau_2$:

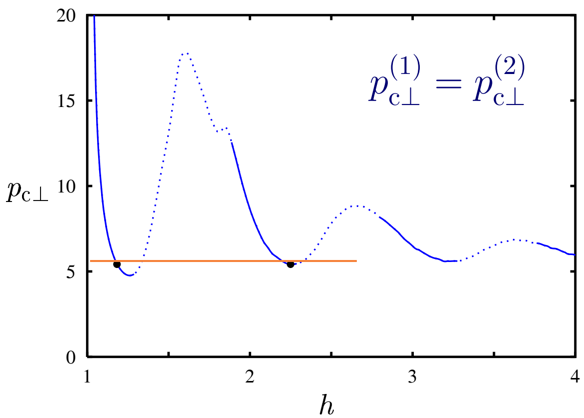
  chemical-potential relaxation by particle exchange

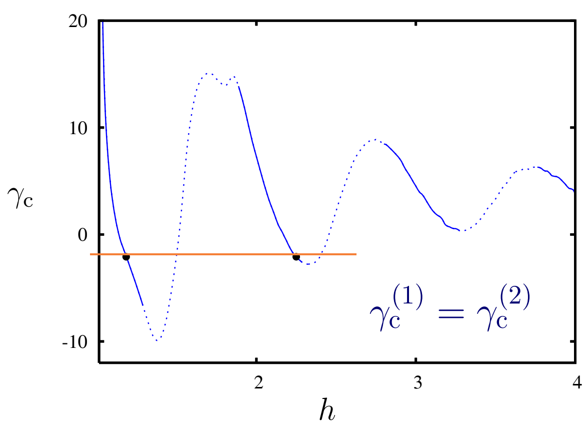
Determination of equilibrium conditions

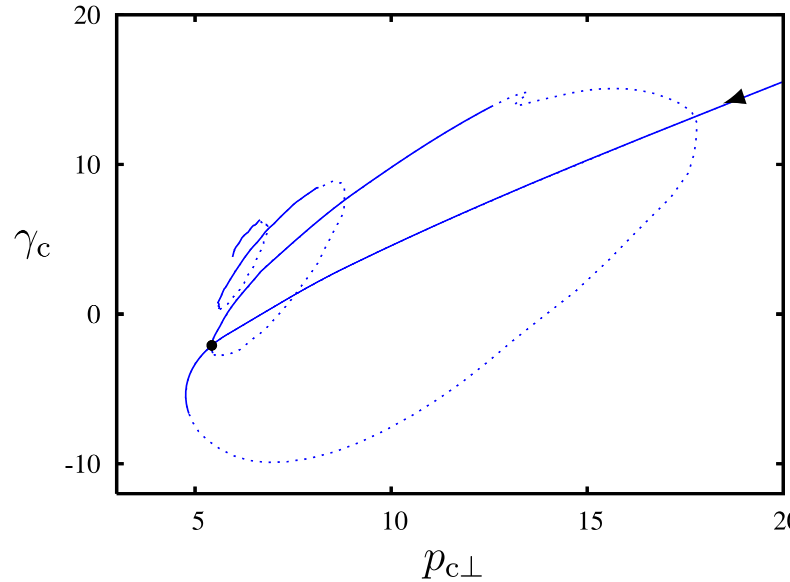


$$\gamma_c^{(1)} = \gamma_c^{(2)} \qquad \text{(partial equilibrium)}$$

$$\phi_c = \text{const}$$

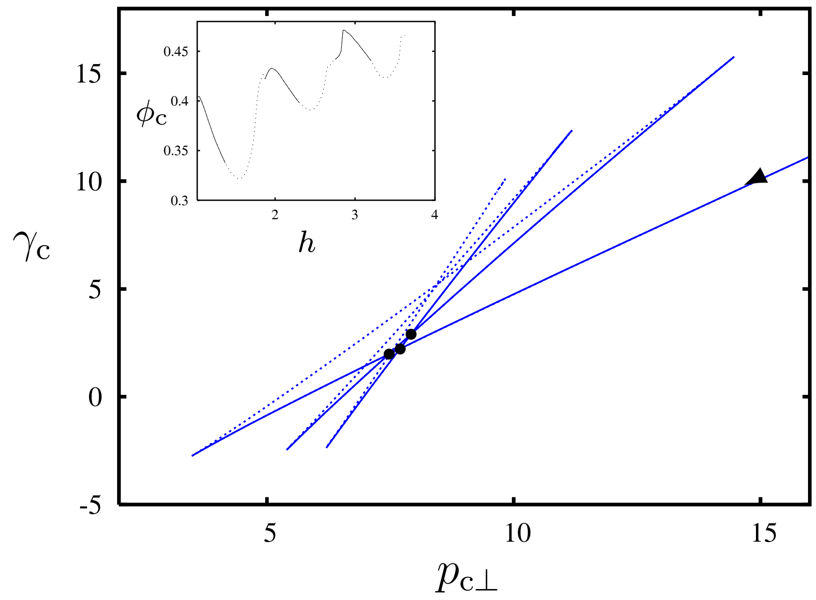






$$\phi_c = \text{const}$$

(partial equilibrium)



$\mu_c = \text{const}$

full equilibrium

Explanation of plot shape:

$$\left(\frac{\partial \gamma_c}{\partial p_{c\perp}}\right)_{T\mu_c} = h,$$

which follows from Gibbs-Duhem relation $\mathrm{d}\mu_c = v\,\mathrm{d}p_{c\perp} - a\,\mathrm{d}\gamma_c$

• Film hydrodynamics

long-wavelength limit ⇒ 2D “compressible” flow

Conservation equations

$$\boldsymbol{\nabla}_{\mathrm{s}} \cdot (\gamma \mathsf{I}_{\mathrm{s}} + \boldsymbol{\tau}_{\mathrm{s}}) = -\mathbf{F}_{\mathrm{s}}$$ momentum

$$\frac{\partial \nu_{\mathrm{c}}}{\partial t} = -\boldsymbol{\nabla}_{\mathrm{s}} \cdot (\nu_{\mathrm{c}} \mathbf{v}_{\mathrm{s}} + \mathbf{j}_{\mathrm{s}})$$ particle number

$$\frac{\partial h}{\partial t} = -\boldsymbol{\nabla}_{\mathrm{s}} \cdot (h \mathbf{v}_{\mathrm{s}})$$ volume

Constitutive relations

$$\boldsymbol{\tau}_{\mathrm{s}} = 2\eta_{\mathrm{s}} \left[\boldsymbol{\nabla}_{\mathrm{s}} \mathbf{v}_{\mathrm{s}}\right]_{\mathrm{d}} + \kappa_{\mathrm{s}} (\boldsymbol{\nabla}_{\mathrm{s}} \cdot \mathbf{v}_{\mathrm{s}}) \mathsf{I}_{\mathrm{s}}$$ stress tensor

$$\mathbf{j}_{\mathrm{s}} = -\nu_{\mu} \boldsymbol{\nabla}_{\mathrm{s}} (\mu_{\mathrm{c}} + \psi_{\mathrm{c}}) - \nu_{\mathrm{p}} \boldsymbol{\nabla}_{\mathrm{s}} (p_{\mathrm{c}\perp} - \psi_{\mathrm{f}})$$ particle flux

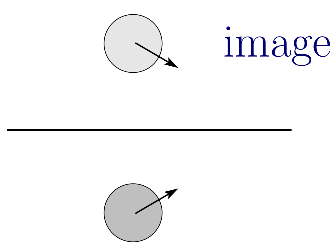
$$\mathbf{f}_{\mathrm{f}} = -\boldsymbol{\nabla}_{\mathrm{s}} \psi_{\mathrm{f}}, \qquad \mathbf{f}_{\mathrm{c}} = -\boldsymbol{\nabla}_{\mathrm{s}} \psi_{\mathrm{c}}$$

$$\mathbf{F}_{\mathrm{s}} = h \mathbf{f}_{\mathrm{f}} + \nu_{\mathrm{c}} \mathbf{f}_{\mathrm{c}}$$

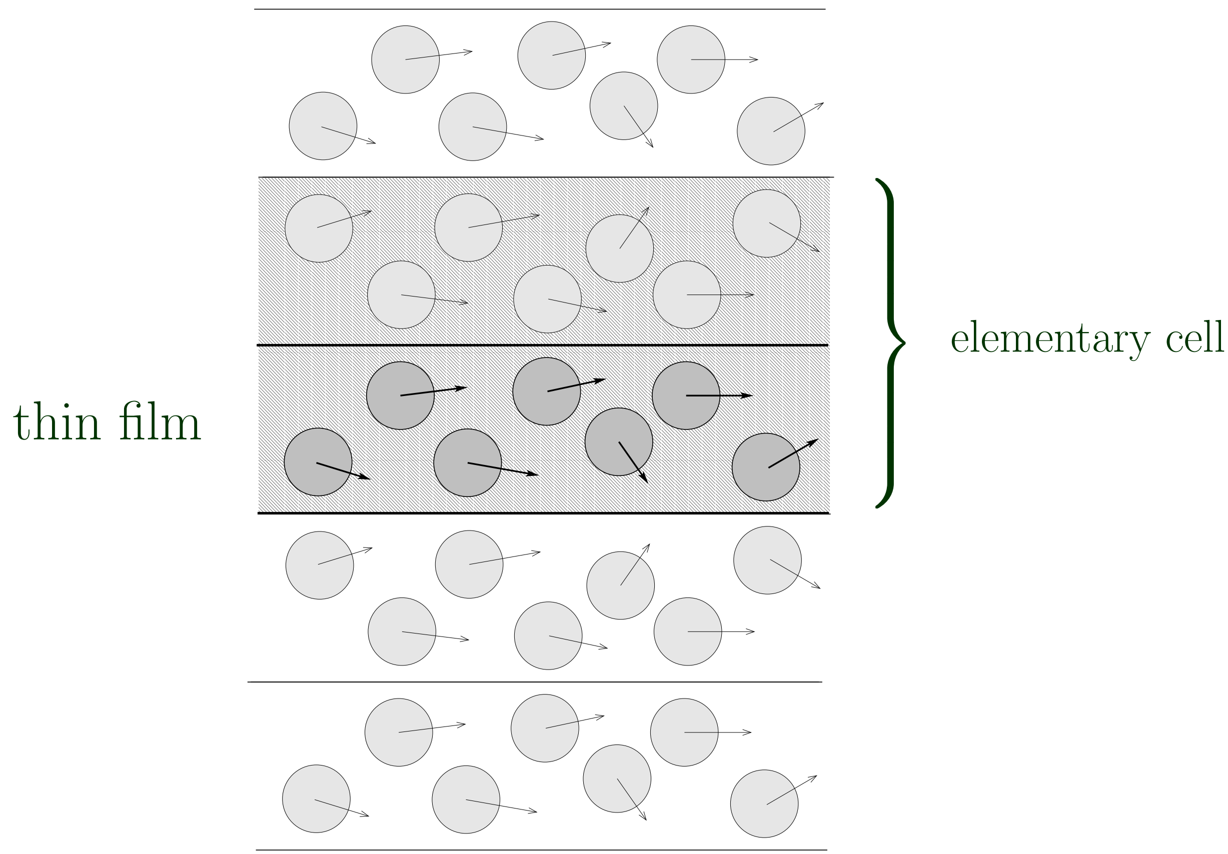
$\nu_{\mathrm{c}} = N_{\mathrm{c}}/A$ (particles per unit area)

• Evaluation of transport coefficients

Multiple-reflection method (free interface)

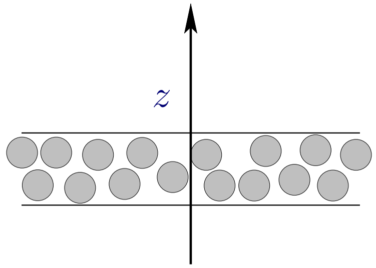


single reflection



periodic representation

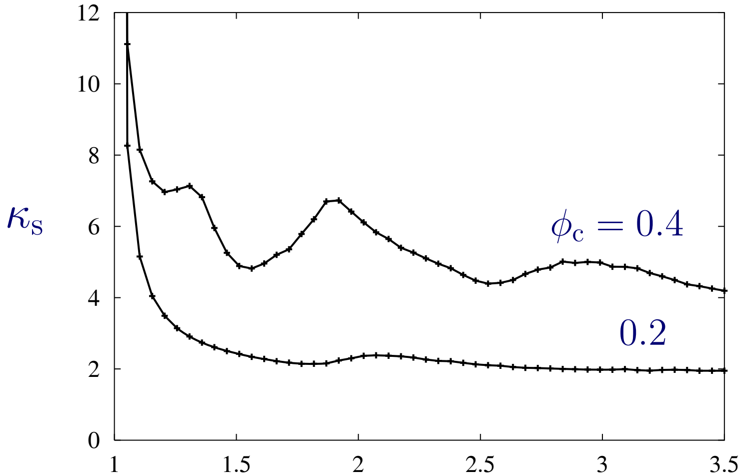
Surface viscosity

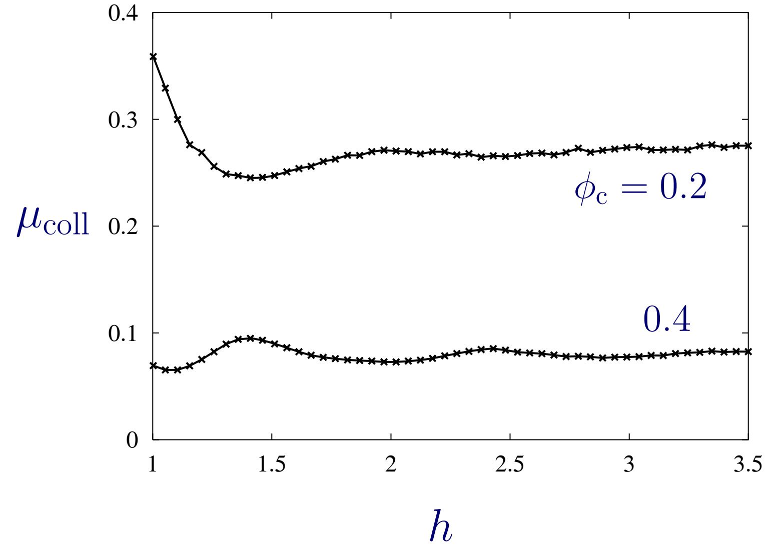


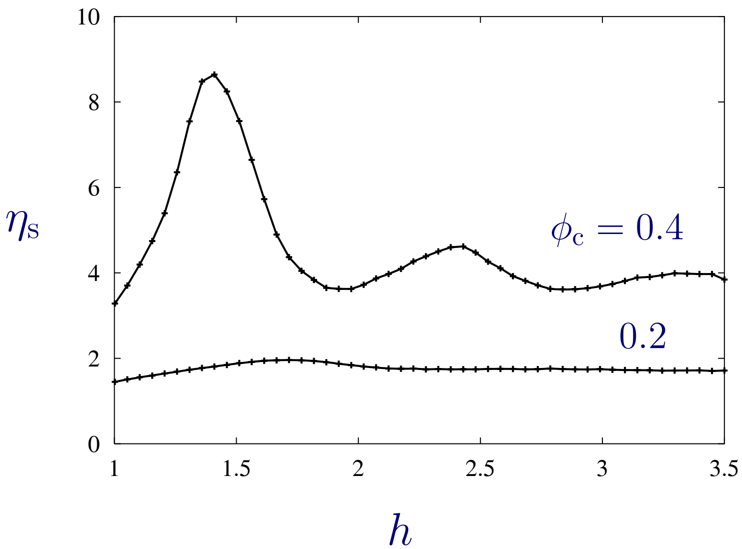
$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \longrightarrow \kappa_s \quad \text{compressional}$$

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \longrightarrow \eta_s \quad \text{shear}$$

Numerical results







$$\mu_{coll} = h^{-1}(\nu_\mu + n_c^{-1}\nu_p)$$

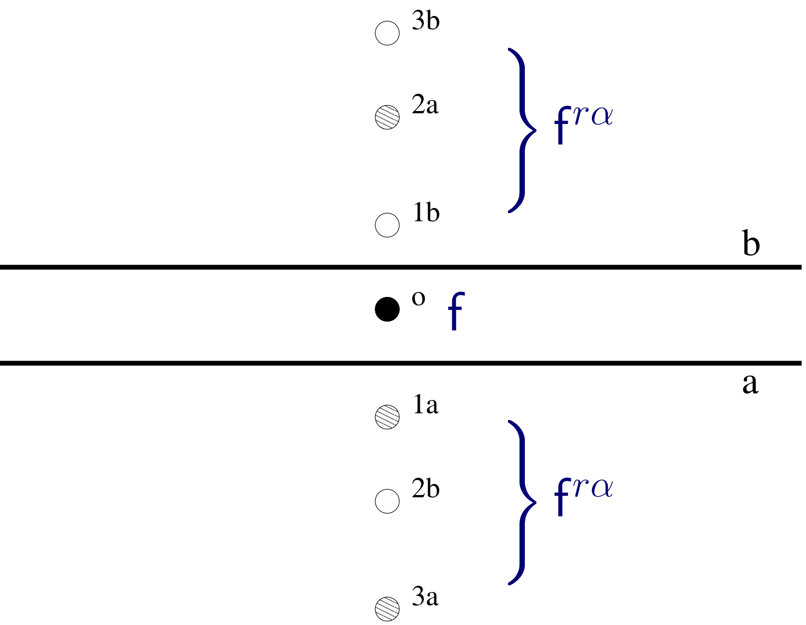
• Different boundary conditions

- surfactant-covered interfaces
- biological membranes
- rigid walls

collaborators: S. Bhattacharya
M. Ekiel–Jeżewska

Image method

Image singularities



Reflection matrix

$$\mathsf{f}^{r\alpha} = \mathsf{R}^{r\alpha} \cdot \mathsf{f} \qquad r = 1, 2, \cdots, \qquad \alpha = a, b$$

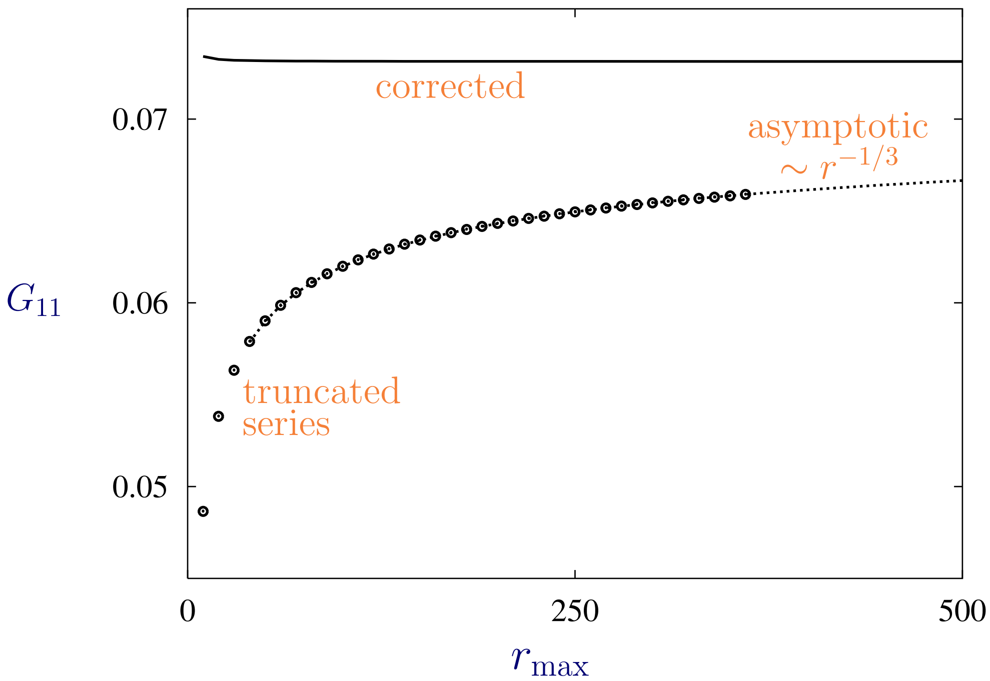
$$\mathsf{R}^{r} = \prod_{i=1}^{r} \mathsf{R}^{\mathrm{sw}}(h^{i})$$ multiple reflections

Rigid wall $\Rightarrow$ order of $\mathsf{f}^{r\alpha} \geq$ order of f

Double reflection identity

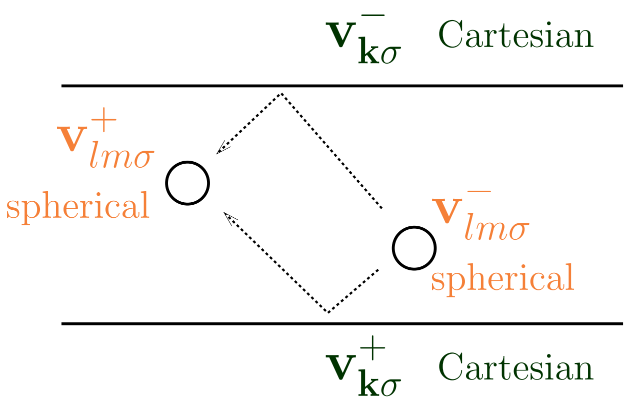
$$\mathsf{R}^{\mathrm{sw}}(h) \cdot \mathsf{R}^{\mathrm{sw}}(-h) = \mathsf{I} \qquad \Longrightarrow \qquad \text{commutation relations}$$

Convergence problem



Cartesian representation method

Spherical and Cartesian basis fields



Spherical: $r^l Y_{lm} \Downarrow \mathbf{v}^+_{lm\sigma}$ $\quad r^{-l-1} Y_{lm} \Downarrow \mathbf{v}^-_{lm\sigma}$

Constructed from scalar potentials

Cartesian: $e^{+kz}\ e^{\mathrm{i}\mathbf{k}\cdot\boldsymbol{\rho}} \Downarrow \mathbf{v}^+_{\mathbf{k}\sigma}$ $\quad e^{-kz}\ e^{\mathrm{i}\mathbf{k}\cdot\boldsymbol{\rho}} \Downarrow \mathbf{v}^-_{\mathbf{k}\sigma}$

σ: potential, vorticity & pressure solutions

$\boldsymbol{\rho} = x\hat{\mathbf{e}}_x + y\hat{\mathbf{e}}_y \qquad \mathbf{k} = k_x\hat{\mathbf{e}}_x + k_y\hat{\mathbf{e}}_y$

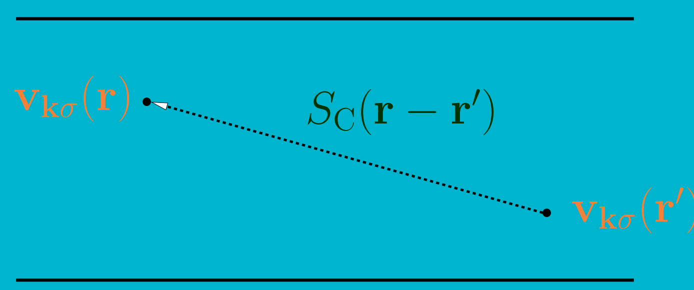
Transformation relations

Spherical $\leftrightarrow$ Cartesian

$$\mathbf{v}^{\pm}_{lm\sigma} = \int \mathrm{d}\mathbf{k}\, T^{\pm\pm}_{\mathrm{SC}}(lm\sigma \mid \mathbf{k}\sigma')\mathbf{v}^{\pm}_{\mathbf{k}\sigma'}$$

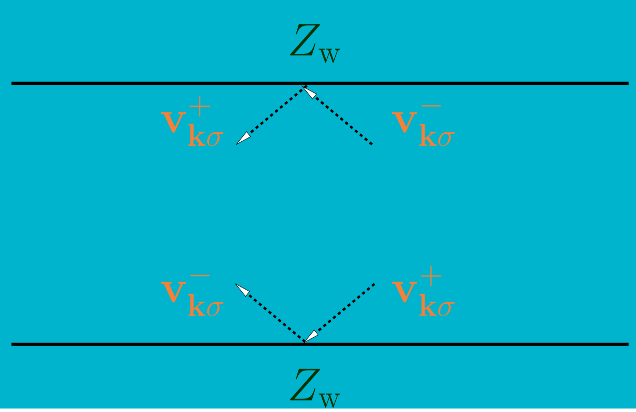
$$\mathbf{v}^{\pm}_{\mathbf{k}\sigma} = \sum_{lm\sigma'}^{\pm} T^{\pm\pm}_{\mathrm{CS}}(\mathbf{k}\sigma \mid lm\sigma')\mathbf{v}^{\pm}_{lm\sigma'}$$

Displacement relations



$$\mathbf{v}^{\pm}_{\mathbf{k}\sigma}(\mathbf{r}) = \sum_{\sigma'} S^{\pm\pm}_{\mathrm{C}}(\sigma \mid \sigma'; \mathbf{r} - \mathbf{r}')\mathbf{v}^{\pm}_{\mathbf{k}\sigma'}(\mathbf{r}')$$

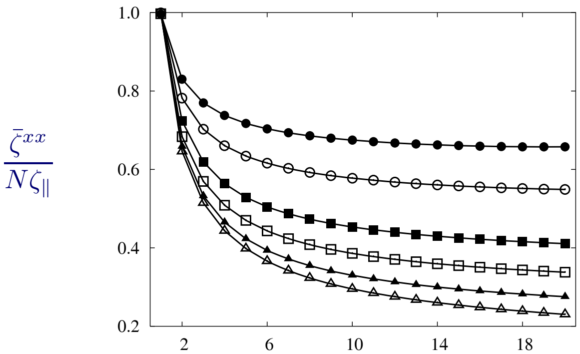
Wall reflection



$$\mathbf{v}^{\pm}_{\mathbf{k}\sigma} \Longrightarrow \sum_{\sigma'} Z_w(\sigma \mid \sigma')\ \mathbf{v}^{\mp}_{\mathbf{k}\sigma'}$$

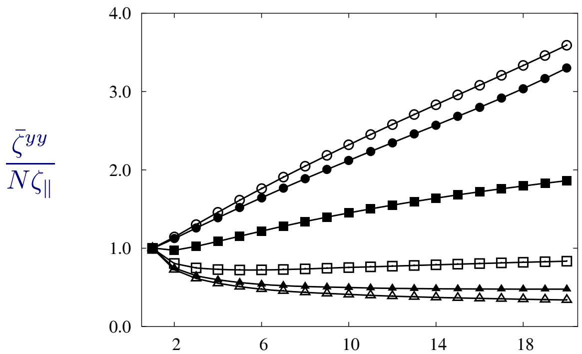
incident reflected

Linear polymer chains



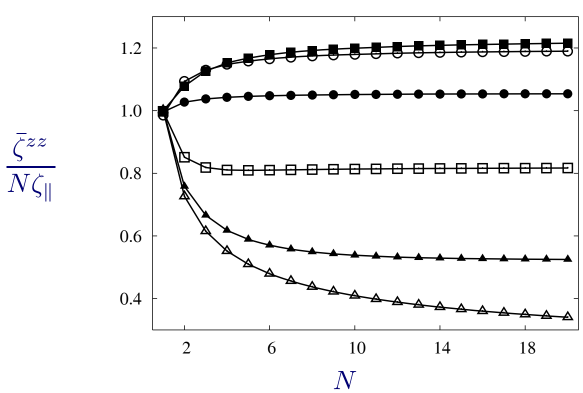
narrow gap

infinite space



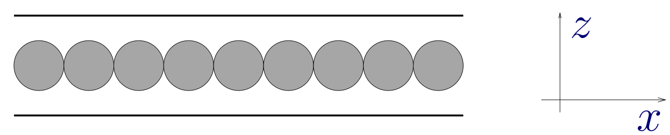
narrow gap

infinite space

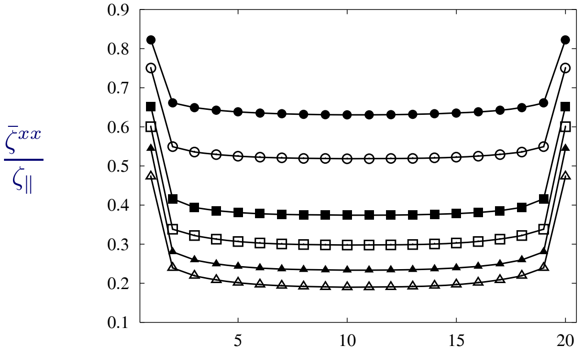


narrow gap

infinite space

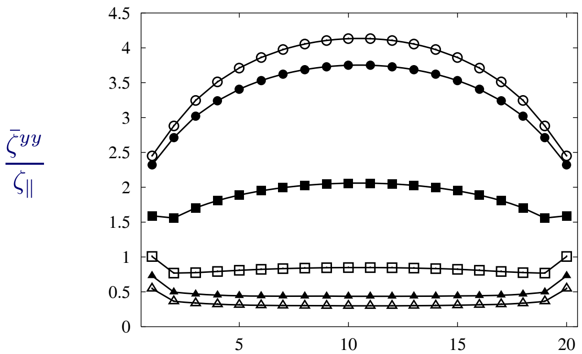


Forces on individual spheres



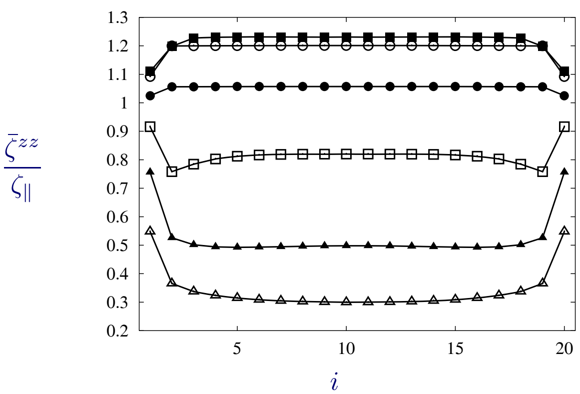
narrow gap

infinite space



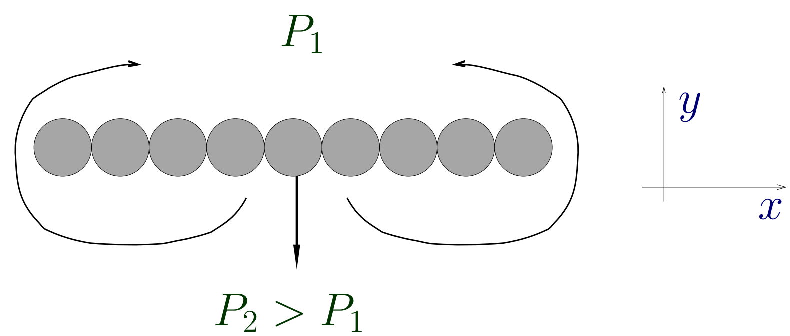
narrow gap
(pressure effect)

infinite space



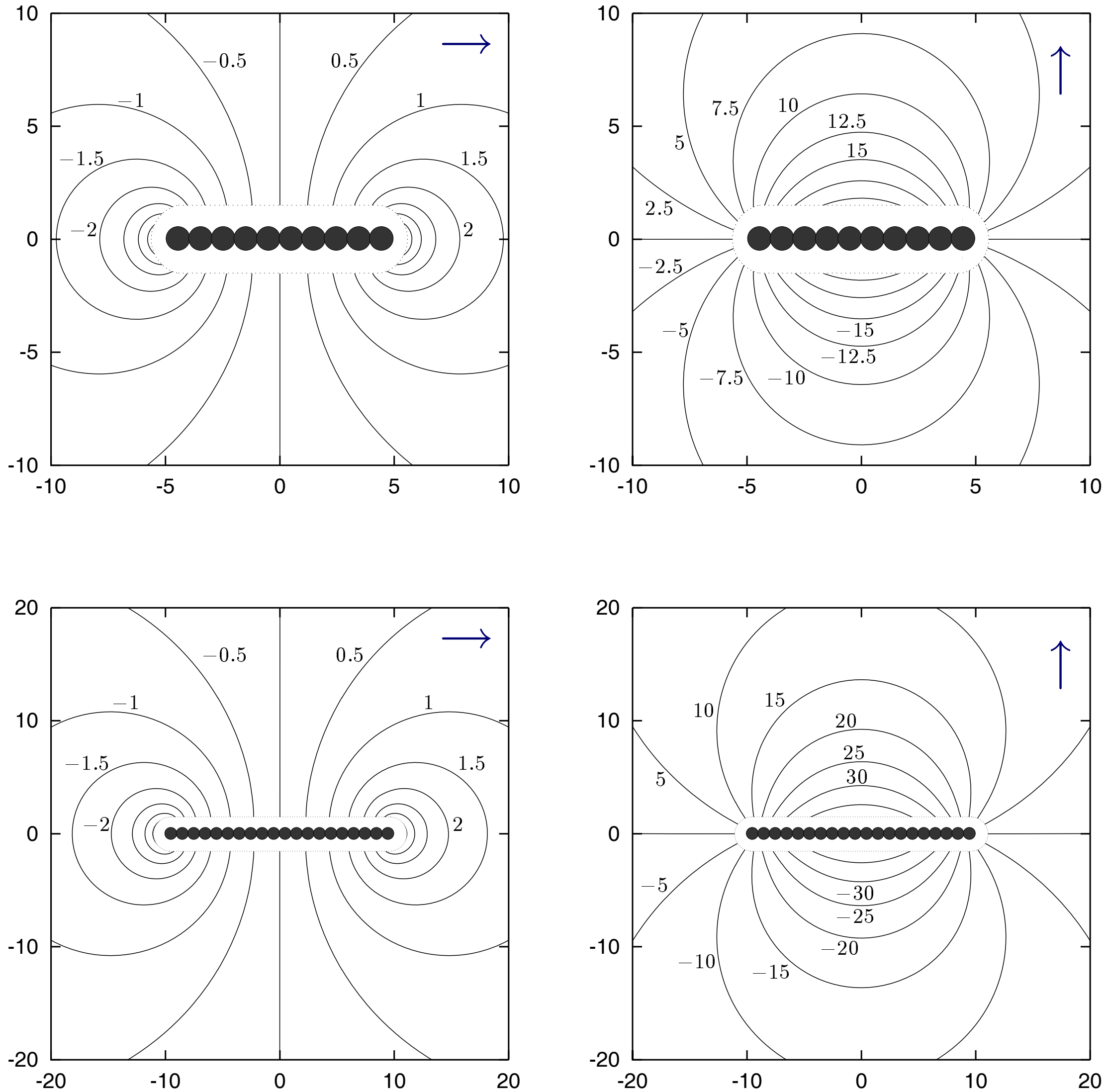
narrow gap

infinite space



Pressure effect

Far-field pressure



$$h = 1.05d$$

Far-field approximation

Hele–Shaw flow

$$\mathbf{v}^{\mathrm{as}} \sim z(H-z)\boldsymbol{\nabla} p^{\mathrm{as}}$$
$$\nabla^2 p^{\mathrm{as}}(x,y) = 0$$

flow determined by scalar field

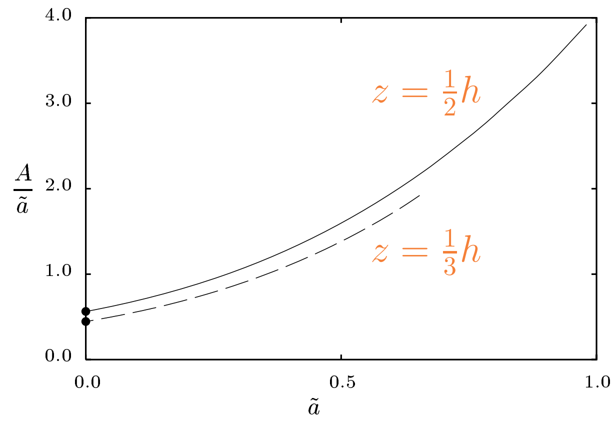
Mutual friction matrix

$$p^{\mathrm{as}} \sim \rho^{-1}\cos\phi$$ far-field pressure

$$\Downarrow$$

$$\zeta_{12}^{yy} \approx -\zeta_{12}^{xx} = A\tilde{\rho}^{-2} + O(\tilde{\rho}^{-4})$$

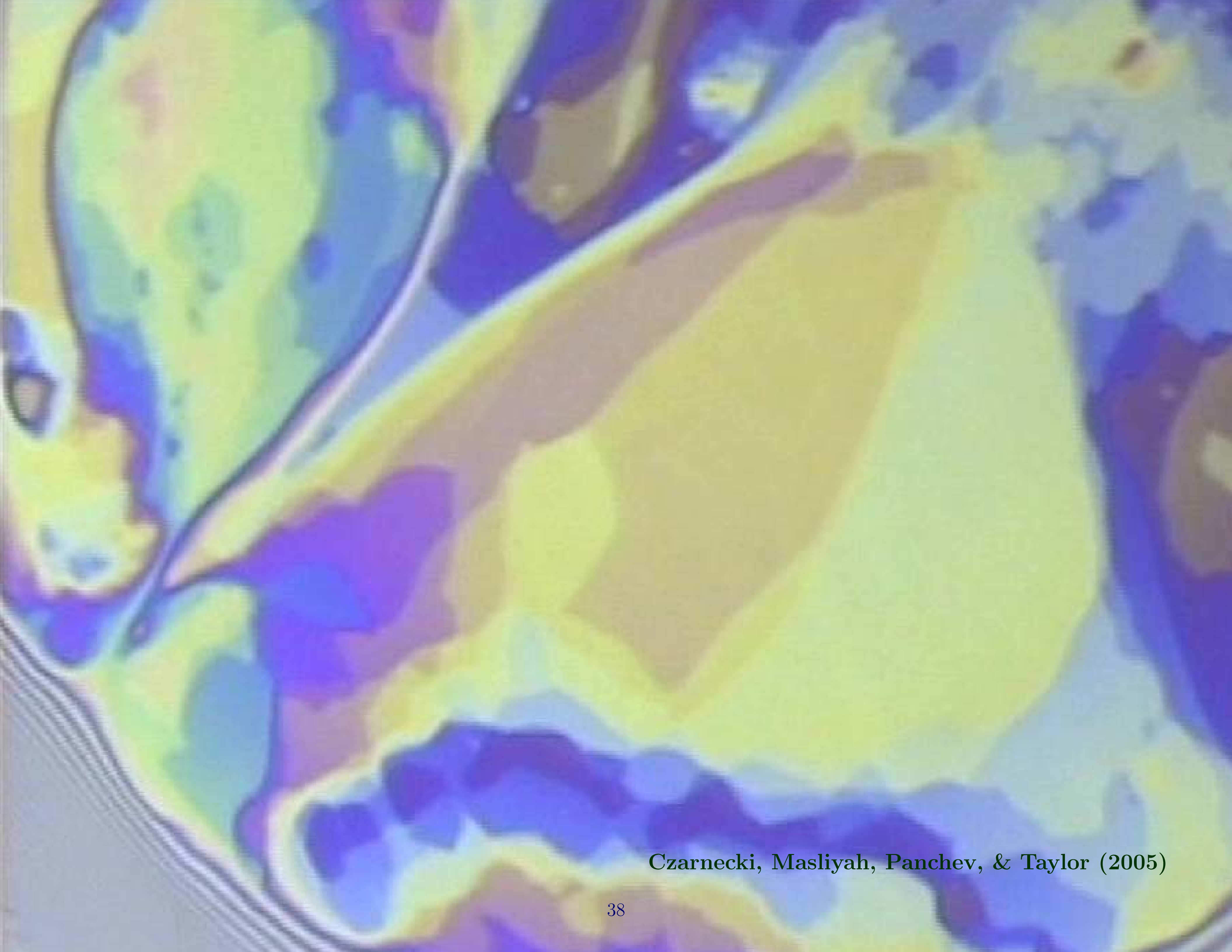
In free space $\zeta_{12}^{xx}, \zeta_{12}^{yy} = O(\tilde{\rho}^{-1}) > 0$



$\tilde{a} = a/h$
$\tilde{\rho} = \rho/h$

Conclusions and future work

- Phase transitions in thin films
  - More realistic potentials
  - Transport through junction between regions of different thickness
  - Dynamics in presence of surfactants
  - Experimental: construct two-phase system in full equilibrium
- Development of hydrodynamic algorithms
  - Periodic systems
  - Iterative solvers
  - Fast-multipole or PPPM methods
- Cylindrical geometry: Blood microcirculation!



Czarnecki, Masliyah, Panchev, & Taylor (2005)