Molecular hydrodynamics of the moving contact line

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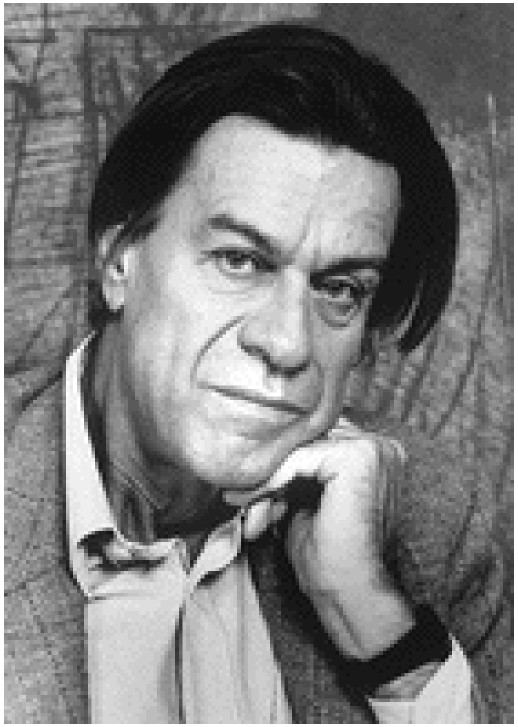
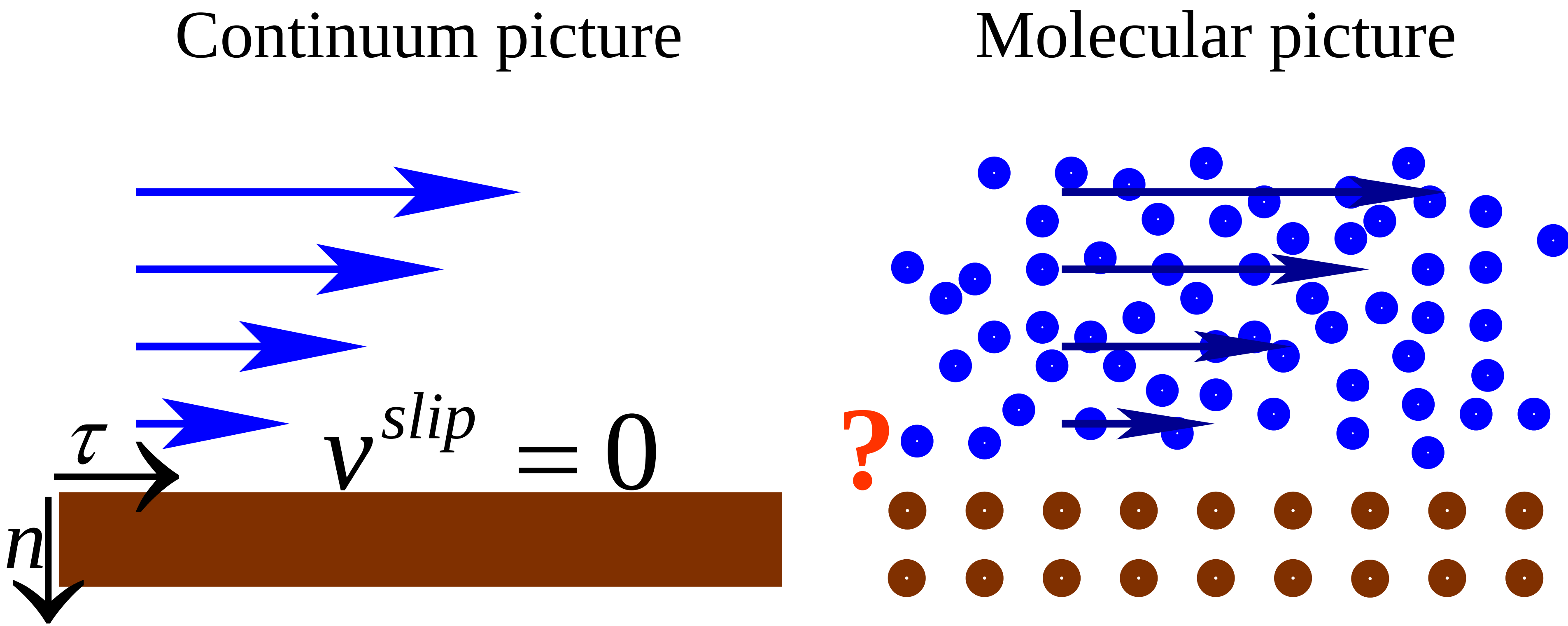
The borders between great empires are often populated by the most interesting ethnic groups. Similarly, the interfaces between two forms of bulk matter are responsible for some of the most unexpected actions.

----- P.G. de Gennes, Nobel Laureate in Physics,
in his 1994 Dirac Memorial Lecture: Soft Interfaces

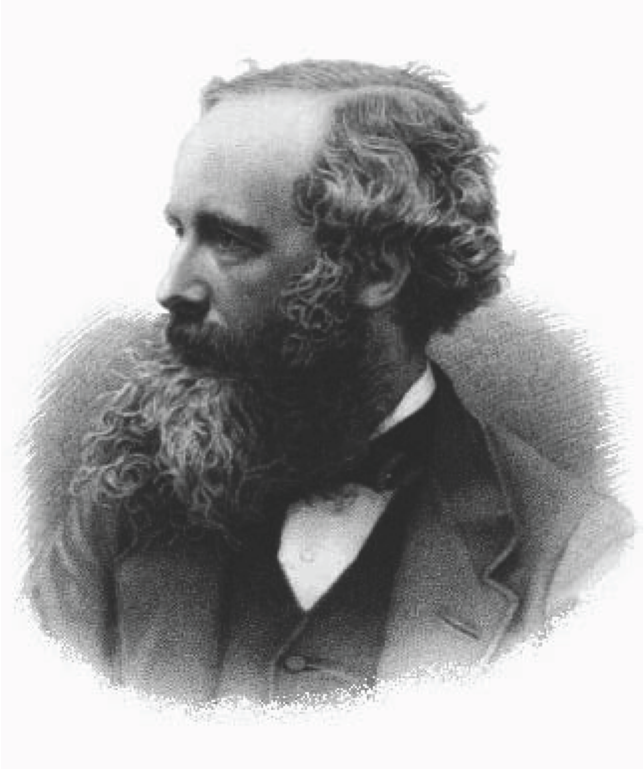


- The no-slip boundary condition and the moving contact line problem
- The generalized Navier boundary condition (GNBC) from molecular dynamics (MD) simulations
- Implementation of the new slip boundary condition in a continuum hydrodynamic model (phase-field formulation)
- Comparison of continuum and MD results
- A variational derivation of the continuum model, for both the bulk equations and the boundary conditions, from Onsager's principle of least energy dissipation

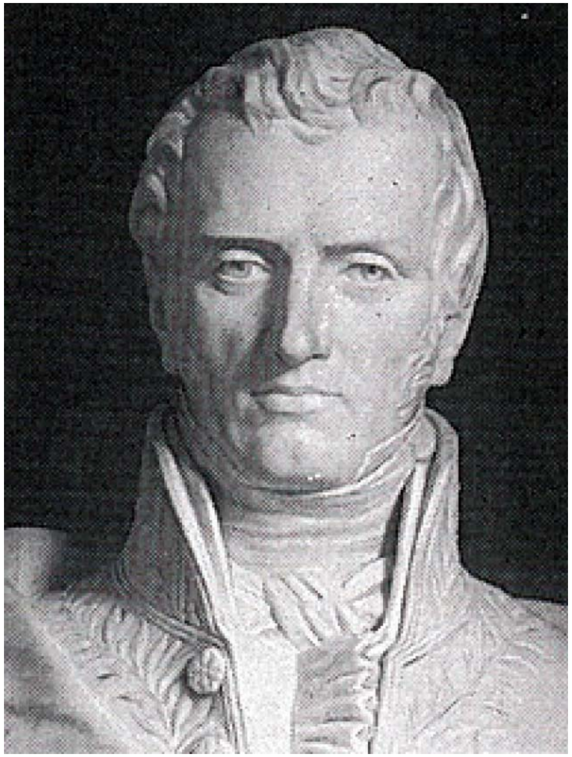


No-Slip Boundary Condition, **A Paradigm**

$$v_{\tau}^{slip} = 0$$



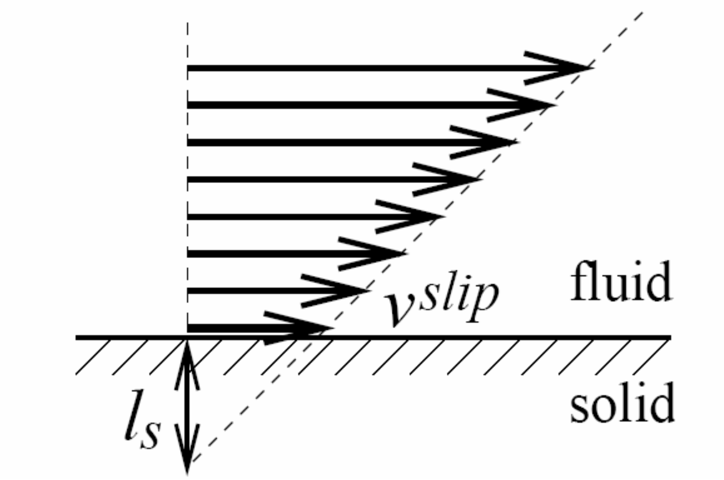
James Clerk Maxwell



Claude-Louis Navier

Many of the great names in **mathematics** and **physics** have expressed an opinion on the subject, including Bernoulli, Euler, Coulomb, Navier, Helmholtz, Poisson, Poiseuille, Stokes, Couette, Maxwell, Prandtl, and Taylor.

from **Navier** Boundary Condition **(1823)**
to **No-Slip** Boundary Condition



$$v_\tau^{slip} = l_s \cdot \dot{\gamma}$$

$\dot{\gamma}$: ***shear rate at solid surface***

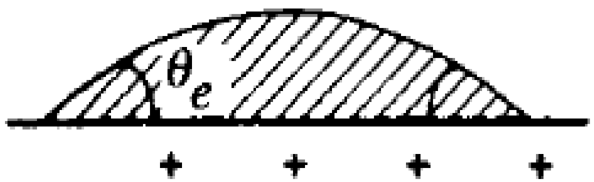
l_s: ***slip length***, from nano- to micrometer

Practically, **no slip** in macroscopic flows

$$\dot{\gamma} \approx U / R \rightarrow \; v^{slip} / U \approx l_s / R \rightarrow 0$$

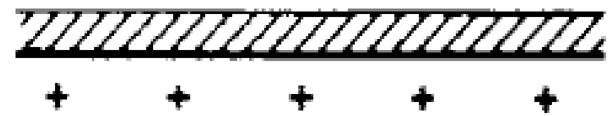
Static wetting phenomena

Partial wetting



(a)

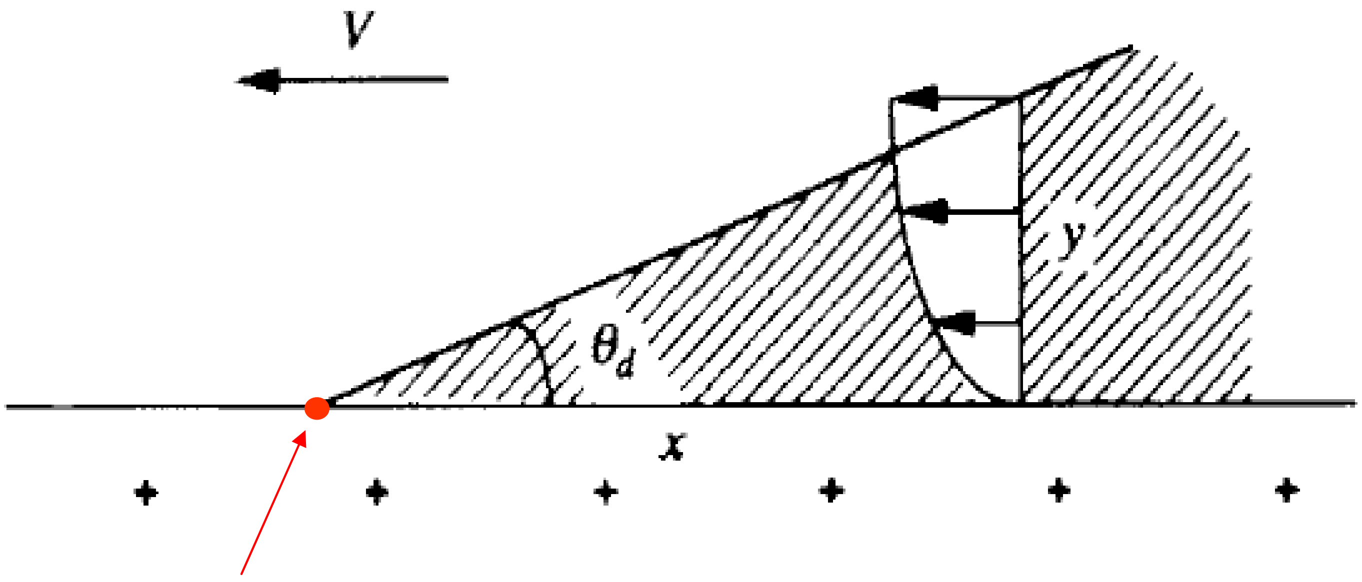
Complete wetting



(b)

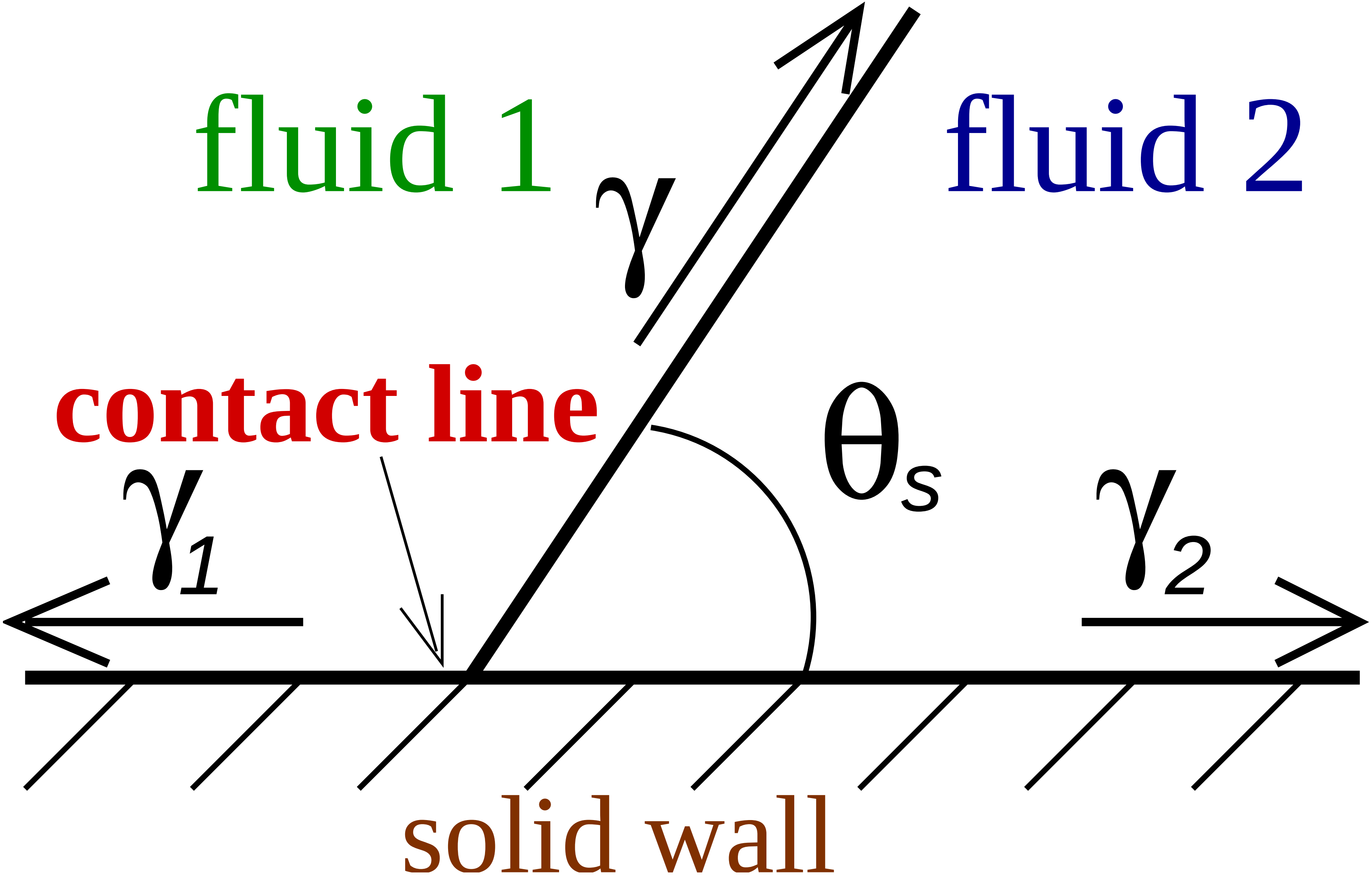
Plant leaves after the rain

Dynamics of wetting



Moving Contact Line

What happens near the moving contact line had been an unsolved problems for decades.

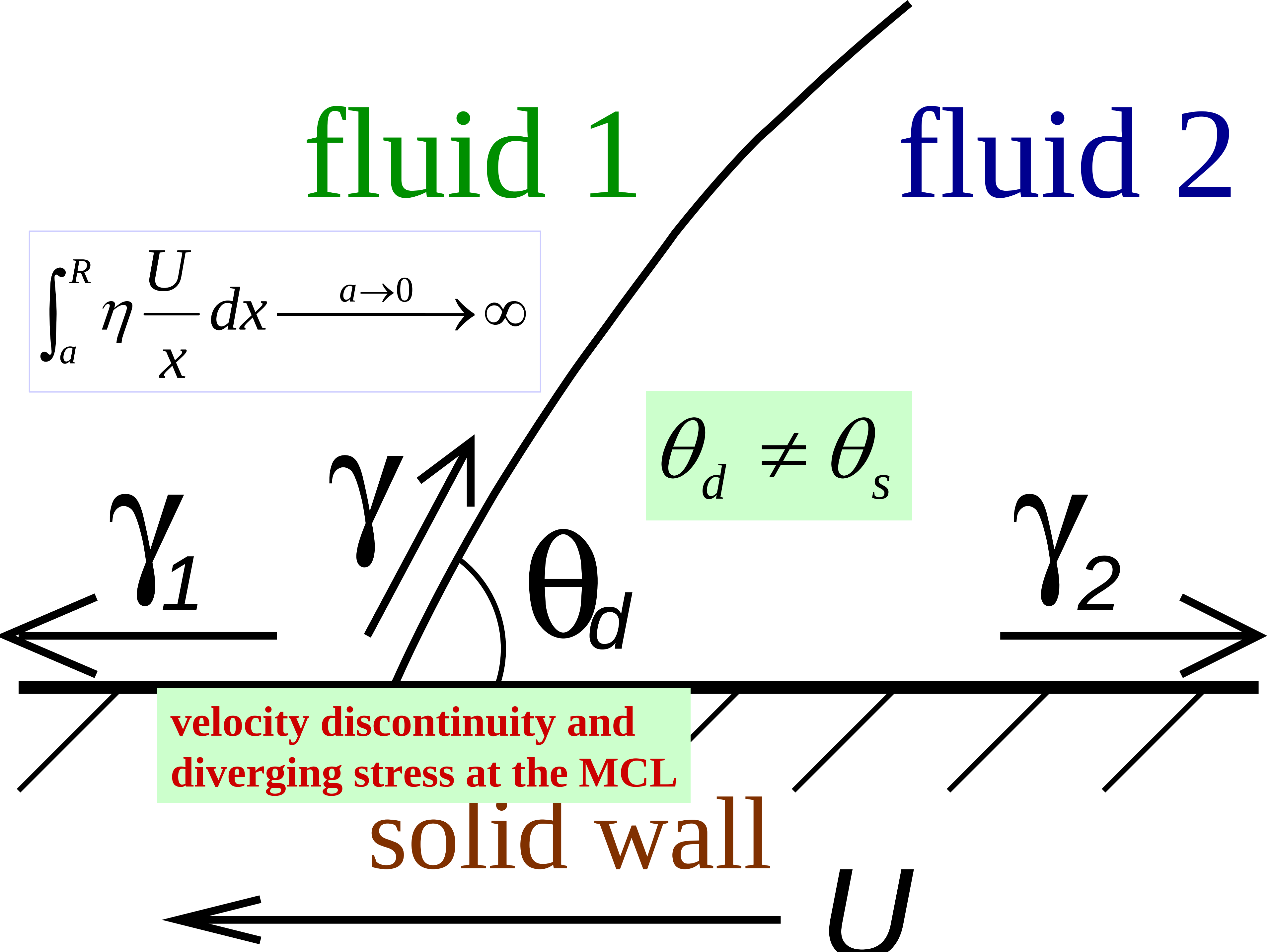


Young's equation: $\gamma \cos\theta_s + \gamma_2 = \gamma_1$

Manifestation of the contact angle:
From partial wetting (droplet) to complete wetting (film)

(a) (b)

Thomas Young (1773-1829) was
an English polymath, contributing to
the scientific understanding of vision, light,
solid mechanics, physiology, and Egyptology.


fluid 1
fluid 2
$\int_a^R \eta \frac{U}{x} dx \xrightarrow{a \to 0} \infty$
$\theta_d \neq \theta_s$
γ
γ_1
θ_d
γ_2
velocity discontinuity and
diverging stress at the MCL
solid wall
U

No-Slip **Boundary Condition ?**

1. **Apparent Violation** seen from the ***moving/slipping*** contact line
2. **Infinite Energy Dissipation** (unphysical singularity)

G. I. Taylor
Hua & Scriven
E.B. Dussan & S.H. Davis
L.M. Hocking
P.G. de Gennes
Koplik, Banavar, Willemsen
Thompson & Robbins

No-slip B.C. breaks down !

- **Nature of the true B.C.** ? **(microscopic *slipping* mechanism)**

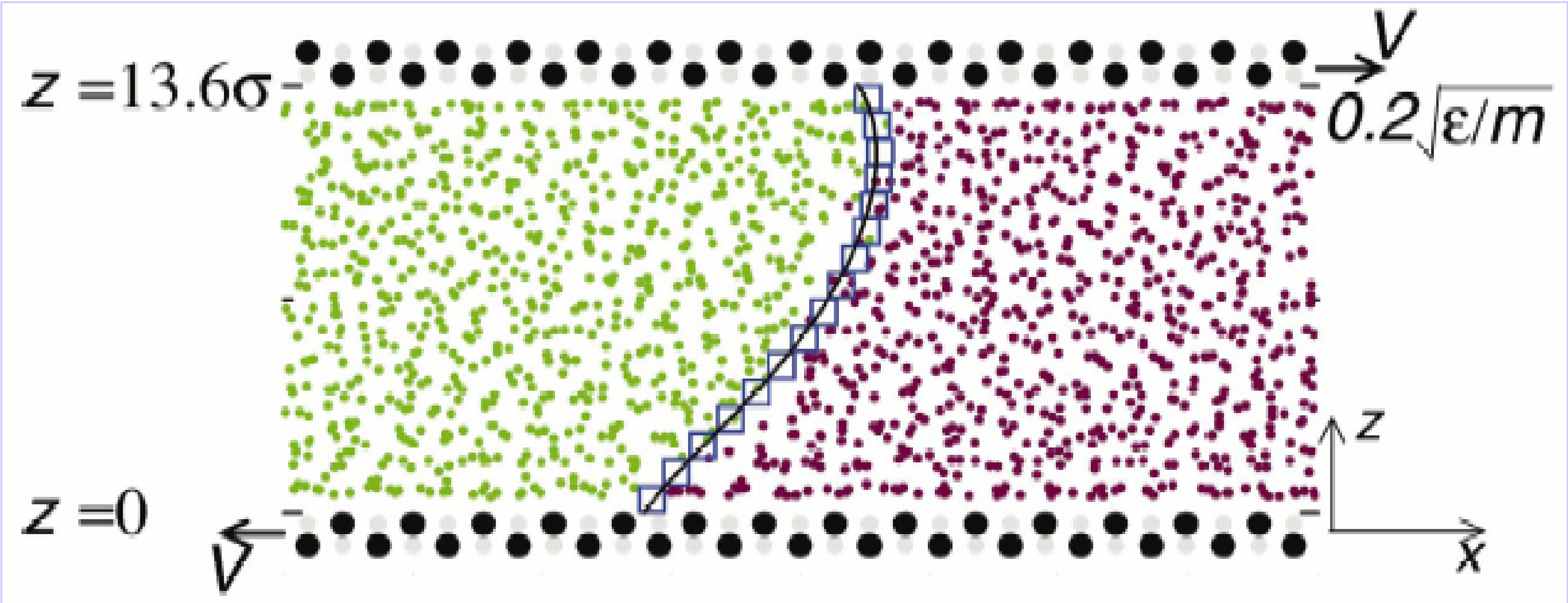
Qian, Wang & Sheng, PRE **68**, 016306 (2003)

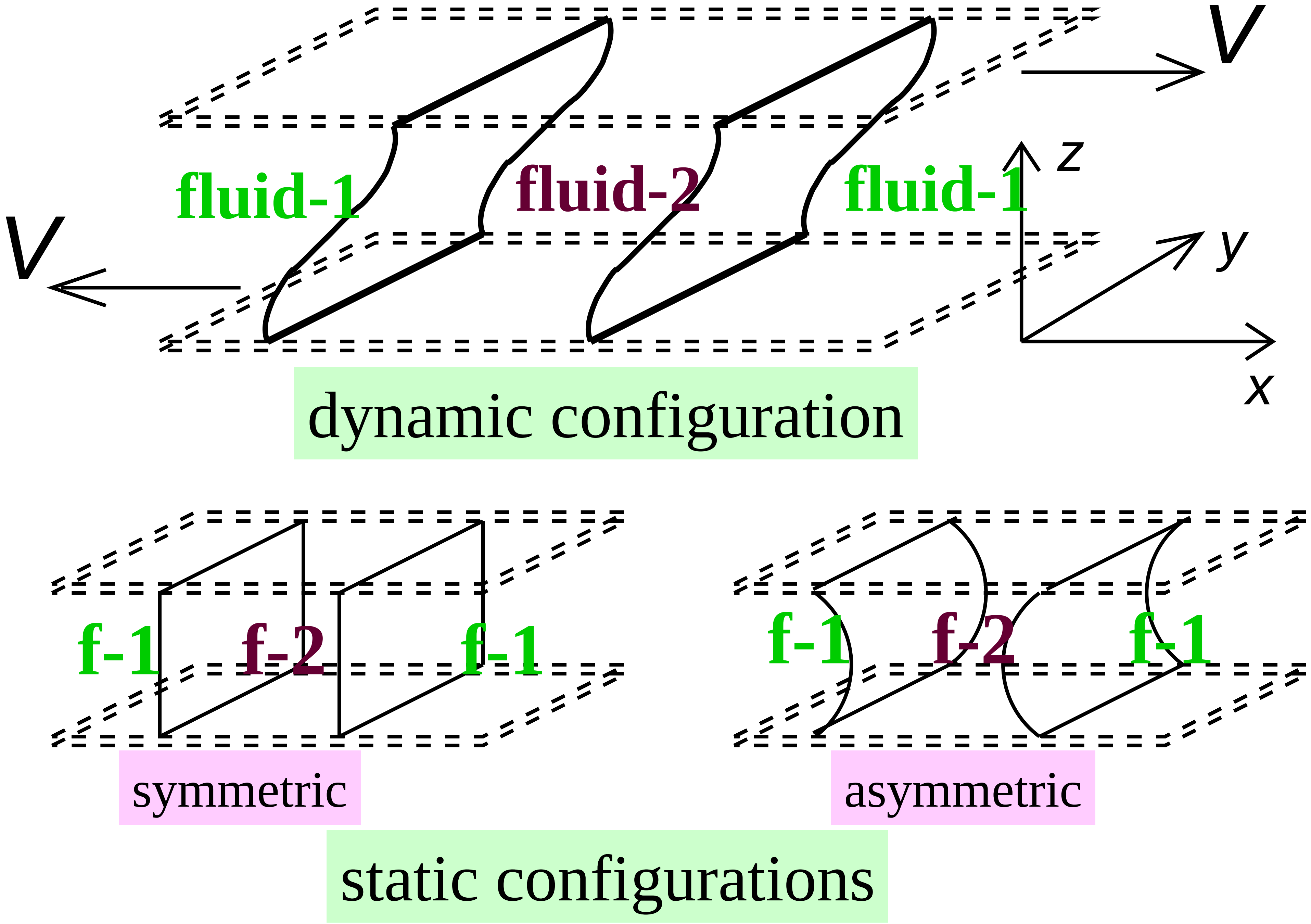
- If ***slip*** occurs within a length scale S in the <u>vicinity</u> of the contact line, then what is the magnitude of S ?

Qian, Wang & Sheng, PRL **93**, 094501 (2004)

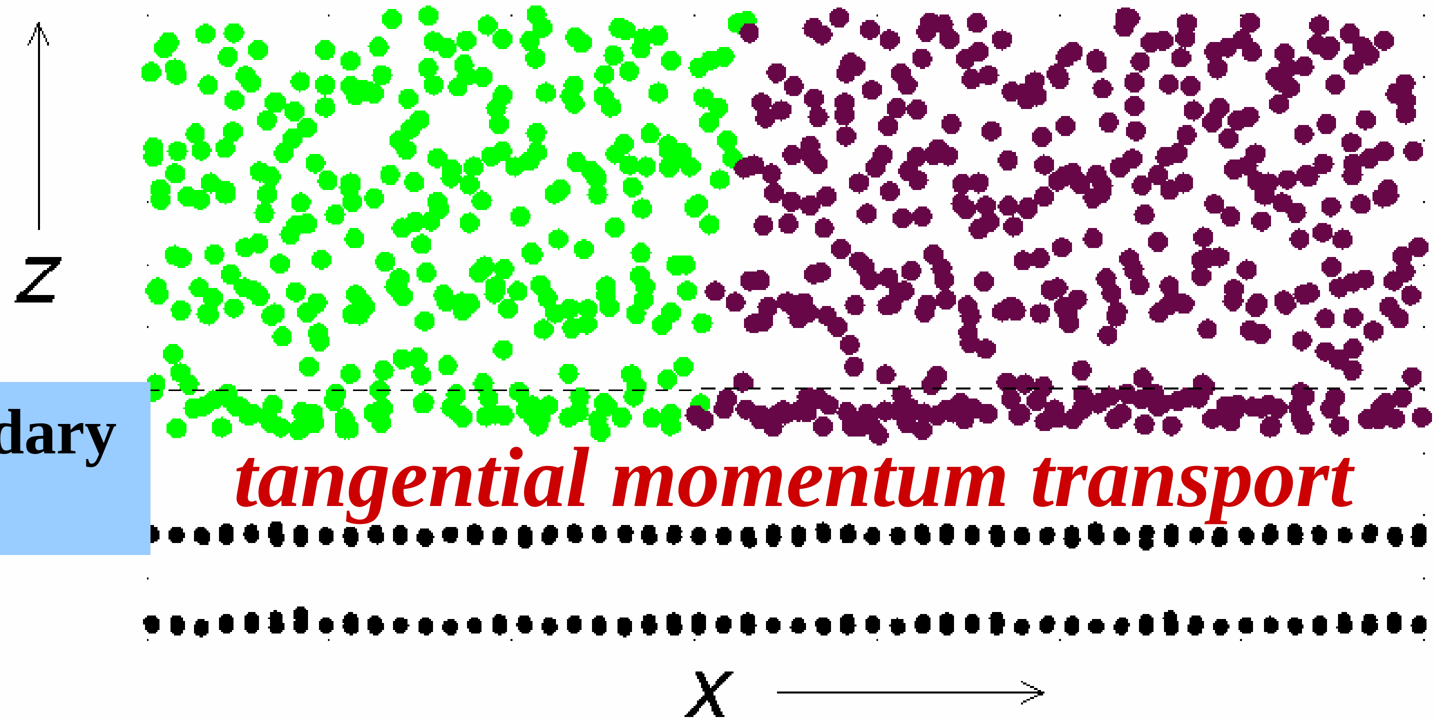
Molecular dynamics simulations for two-phase Couette flow

- **Fluid-fluid molecular interactions**
- **Fluid-solid molecular interactions**
- **Densities (liquid)**
- **Solid wall structure (fcc)**
- **Temperature**
- ***System size***
- ***Speed of the moving walls***




V
V
z
y
x
fluid-1
fluid-2
fluid-1
dynamic configuration
f-1
f-2
f-1
symmetric
f-1
f-2
f-1
asymmetric
static configurations

Measurement at Solid–Fluid Boundary



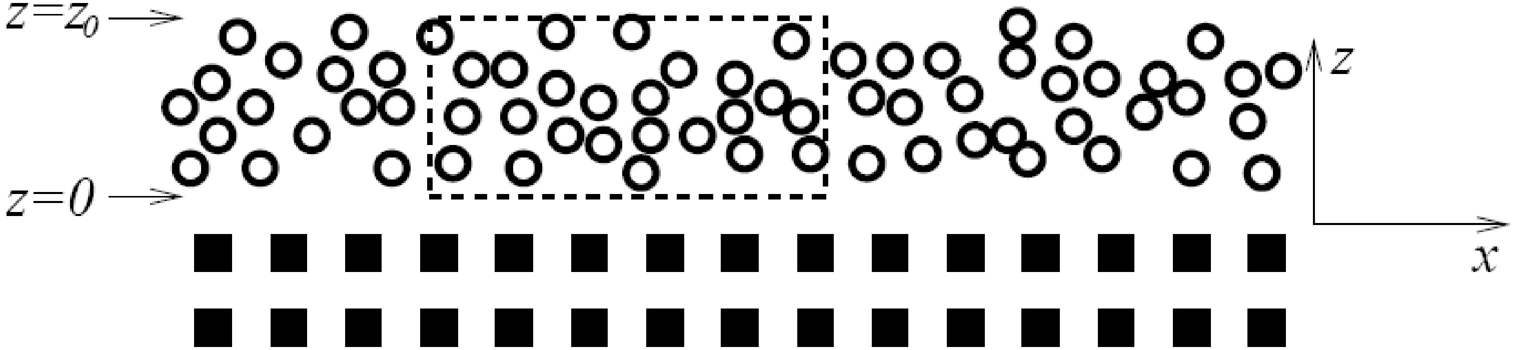
boundary layer

tangential momentum transport

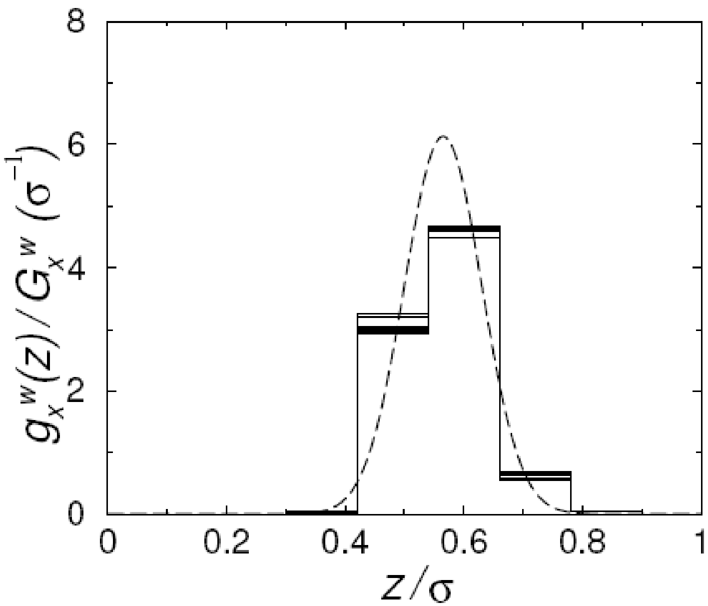
$$G_x^w, \quad G_x^f, \quad V_x^{slip}$$

as functions of x

Stress from the rate of tangential momentum transport per unit area



schematic illustration of the boundary layer



fluid force measured according to

$$G_x^f(x) = \int_0^{z_0} dz\,(\partial_x \sigma_{xx} + \partial_z \sigma_{zx})$$

$$= \partial_x \int_0^{z_0} dz\, \sigma_{xx}(x,z) + \sigma_{zx}(x,z_0)$$

normalized distribution of wall force

$\int_0^{z_0} dz[g_x^w(x,z)/G_x^w(x)] = 1$

The Generalized Navier boundary condition

$$\tilde{G}_x^w = -\beta v_x^{slip}$$

$$\tilde{G}_x^w + \tilde{G}_x^f = 0$$

The stress in the immiscible two-phase fluid:

viscous part **non-viscous part**

$$\sigma_{zx} = \eta[\partial_z v_x + \partial_x v_z] + \sigma_{zx}^Y$$

interfacial force

GNBC from continuum deduction

$$\beta v_x^{slip} = \tilde{G}_x^f = \tilde{\sigma}_{zx} = \sigma_{zx}^{visc} + \tilde{\sigma}_{zx}^Y$$

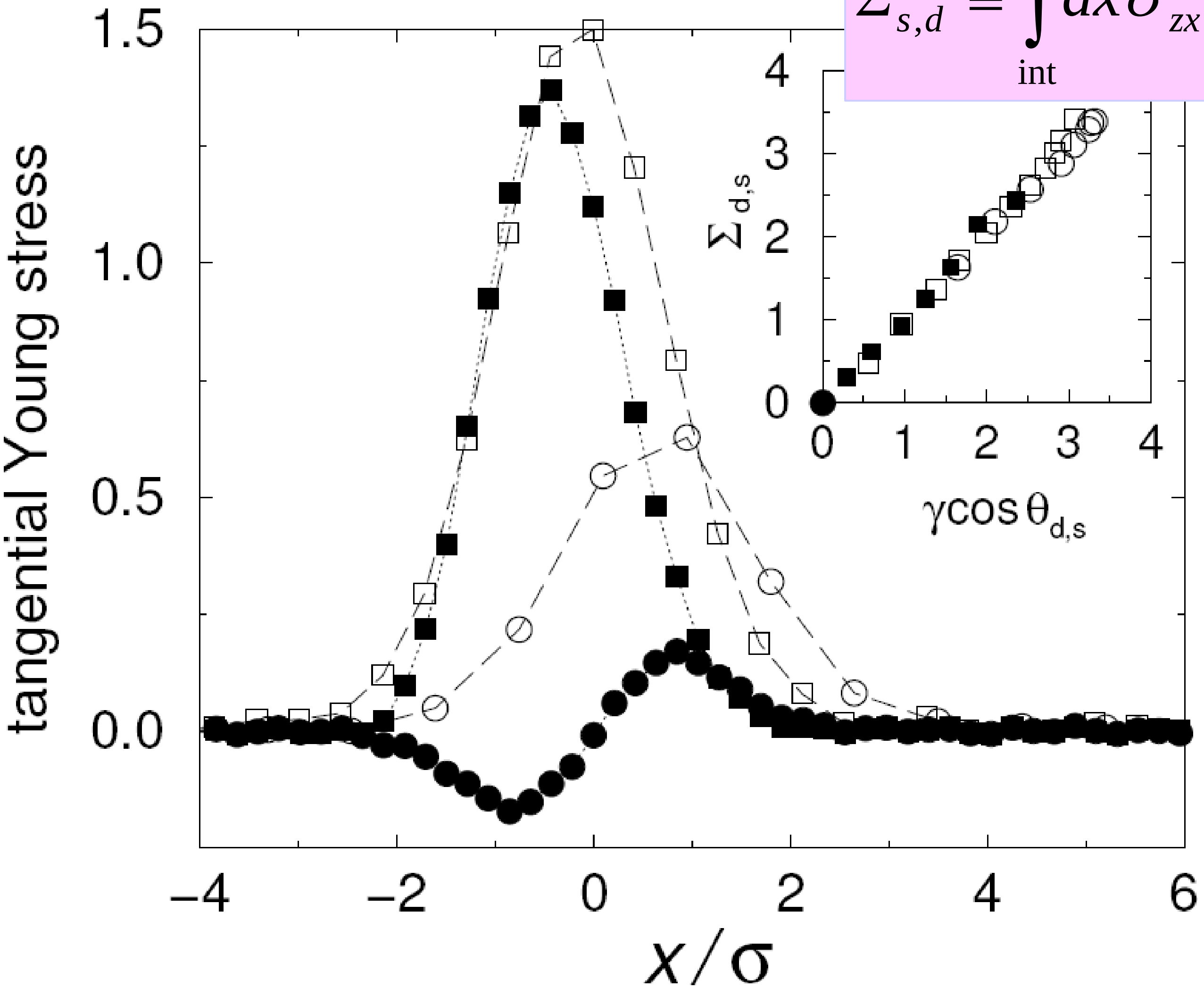
static Young component subtracted
\>>> uncompensated Young stress

$$\tilde{\sigma}_{zx}^Y = \sigma_{zx}^Y - \sigma_{zx}^0$$

A tangential force arising from the deviation from Young's equation

$$\int_{\text{int}} dx \tilde{\sigma}_{zx}^Y = \gamma \cos\theta_d - \gamma \cos\theta_s \neq 0$$

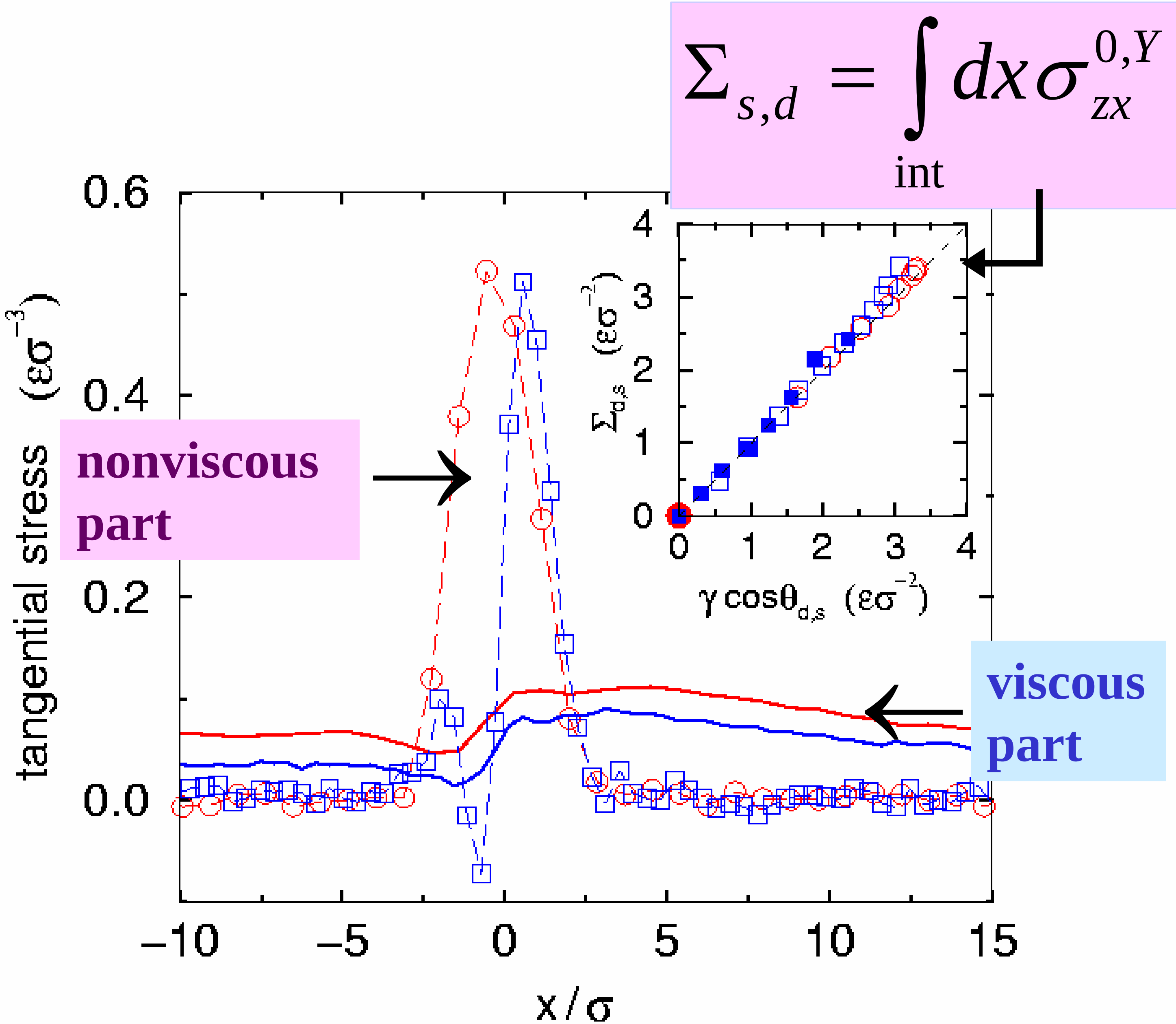
$$\Sigma_{s,d} \equiv \int_{\text{int}} dx\, \sigma_{zx}^{0,Y} = \gamma \cos\theta_{s,d}$$



σ_{zx}^{Y} **obtained by subtracting the Newtonian viscous component**

σ_{zx}^{0} : solid circle: **static** symmetric
solid square: **static** asymmetric

σ_{zx}^{Y} : empty circle: **dynamic** symmetric
empty square: **dynamic** asymmetric



$$\Sigma_{s,d} = \int_{\mathrm{int}} dx\, \sigma_{zx}^{0,Y}$$
nonviscous part
viscous part
tangential stress $(\varepsilon\sigma^{-3})$
x/σ
$\Sigma_{d,s}$ $(\varepsilon\sigma^{-2})$
$\gamma\cos\theta_{d,s}$ $(\varepsilon\sigma^{-2})$
0.6
0.4
0.2
0.0
−10
−5
0
5
10
15
0
1
2
3
4

Continuum Hydrodynamic Model:

- **Cahn-Hilliard (Landau) free energy functional**
- **Navier-Stokes equation**
- **Generalized Navier Boudary Condition (B.C.)**
- **Advection-diffusion equation**
- **First-order equation for relaxation of ϕ (B.C.)**

supplemented with

$\boxed{\nabla \cdot \mathbf{v} = 0}$ *incompressibility*

$\boxed{v_n = 0}$ *impermeability B.C.*

$\boxed{J_n \propto \partial_n \mu = 0}$ *impermeability B.C.*

$$\mathcal{F}_{CH}[\phi(\mathbf{r})] = \int d\mathbf{r} \left[\frac{K}{2} (\nabla\phi)^2 + \left(-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 \right) \right]$$

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\,\mathbf{v} \right] = -\nabla p + \nabla \cdot \boldsymbol{\sigma}^v + \mu \nabla \phi + \mathbf{f}_e$$

$$\boldsymbol{\sigma}^v = \eta \left[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T \right]$$

$$\beta(\phi) v_\tau^{slip} = -\eta(\partial_n v_\tau + \partial_\tau v_n) + L(\phi)\partial_\tau \phi$$

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = M \nabla^2 \mu \qquad \mu = \delta \mathcal{F}_{CH} / \delta \phi$$

$$\frac{\partial \phi}{\partial t} + v_\tau \partial_\tau \phi = -\Gamma L(\phi) \qquad L(\phi) = K \partial_n \phi + \partial \gamma_{fs}(\phi) / \partial \phi$$

supplemented with

$$\nabla \cdot \mathbf{v} = 0 \qquad v_n = 0 \qquad J_n \propto \partial_n \mu = 0$$

GNBC:

an equation of tangential force balance

$$-\beta v_x^{slip} + \eta \partial_z v_x - K \partial_z \phi \partial_x \phi + \partial_x \gamma_{fs} = 0$$

$$\tilde{G}_x^w + \sigma_{zx}^{visc} + \sigma_{zx}^Y + \partial_x \gamma_{fs} = 0$$

Uncompensated Young stress:

$$\int_{\mathrm{int}} dx \left(-K \partial_z \phi \partial_x \phi + \partial_x \gamma_{fs} \right)$$

$$= \gamma \cos\theta_d + \left(\gamma_2 - \gamma_1 \right) = \gamma \left(\cos\theta_d - \cos\theta_s \right)$$

Dussan and Davis, JFM 65, 71-95 (1974):

1. Incompressible Newtonian fluid
2. Smooth rigid solid walls
3. Impenetrable fluid-fluid interface
4. No-slip boundary condition

Stress singularity: the tangential force exerted by the fluid on the solid surface is infinite.

Not even Herakles could sink a solid ! by Huh and Scriven (1971).

Condition (3) >>> Diffusion across the fluid-fluid interface

[Seppecher, Jacqmin, Chen---Jasnow---Vinals, Pismen---Pomeau, Briant---Yeomans]

Condition (4) >>> GNBC

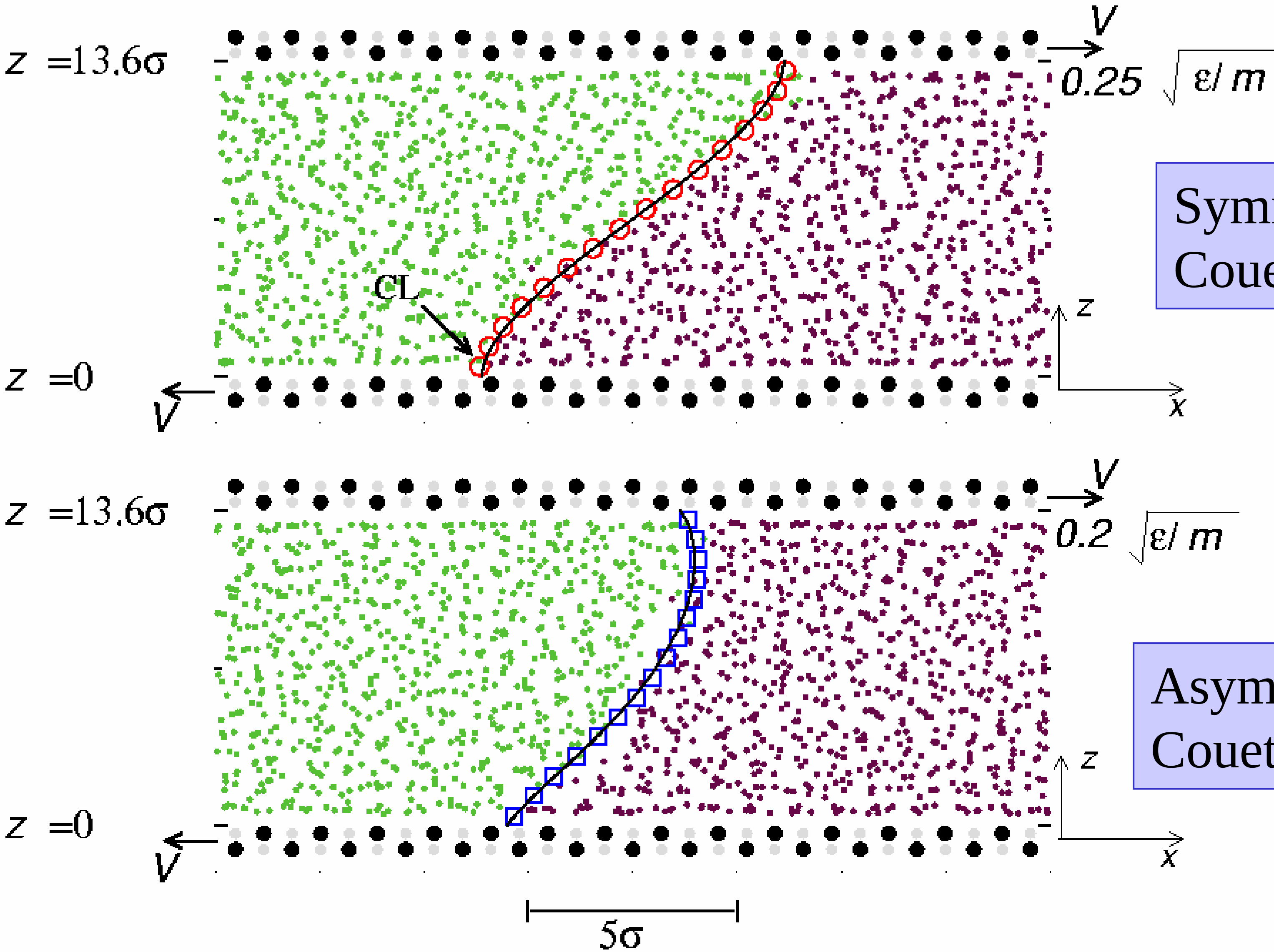
Stress singularity, i.e., infinite tangential force exerted by the fluid on the solid surface, is removed.

Comparison of MD and Continuum Results

- Most parameters determined from **MD** directly
- M and Γ optimized in fitting the **MD** results for ***one*** configuration
- All subsequent comparisons are ***without adjustable parameters*****.**

M and Γ should not be regarded as fitting parameters, Since they are used to realize the interface impenetrability condition, in accordance with the **MD** simulations.

molecular positions projected onto the *xz* plane

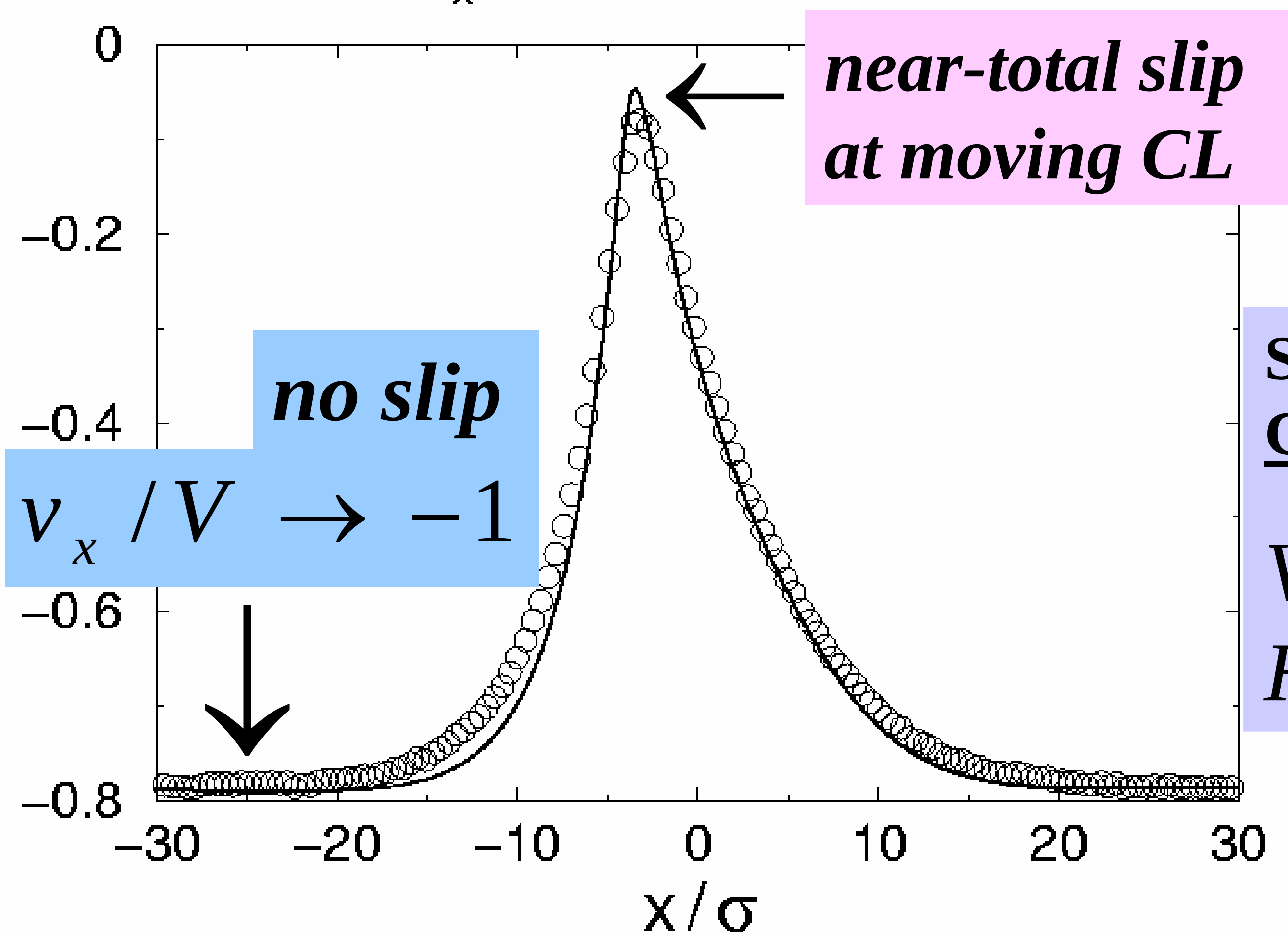


Symmetric Couette flow

Asymmetric Couette flow

Diffusion versus **Slip** in MD

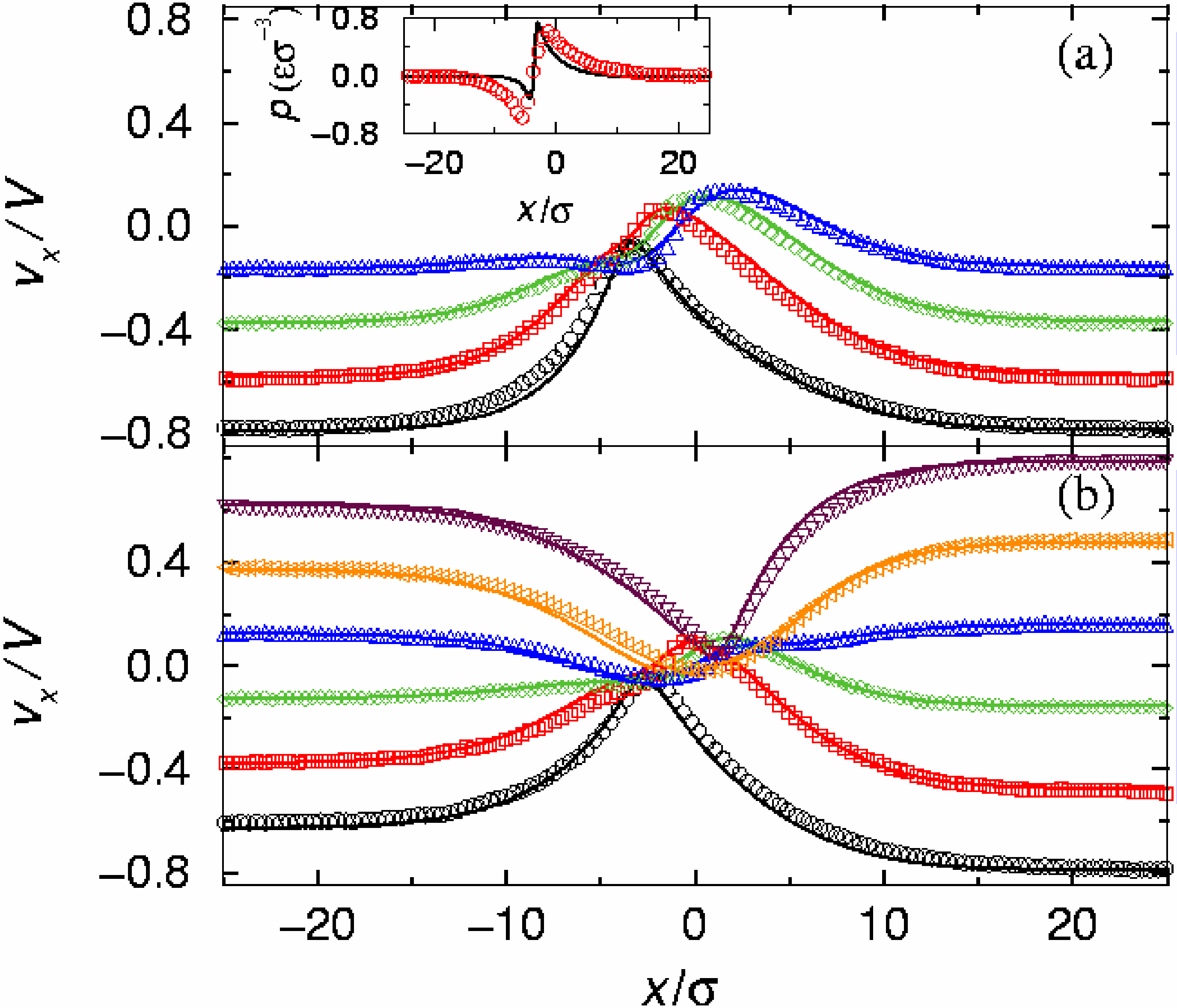
Boundary layer velocity profile
v_x=0 for total slip



Symmetric
Couette flow

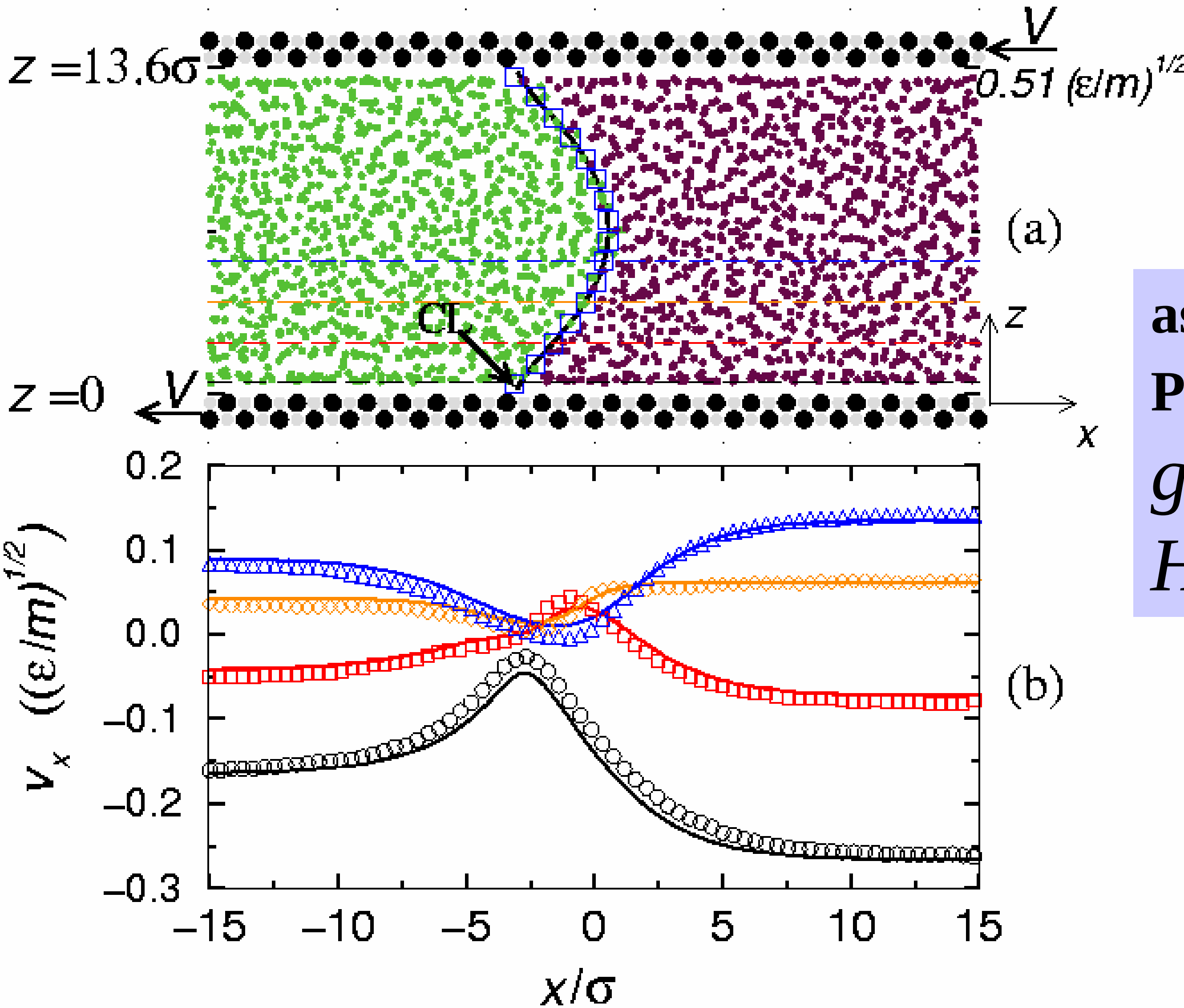
V=0.25
H=13.6

$v_x(x)$ *profiles at different z levels*



symmetric
Couette flow
V=0.25
H=13.6

asymmetricC
Couette flow
V=0.20
H=13.6



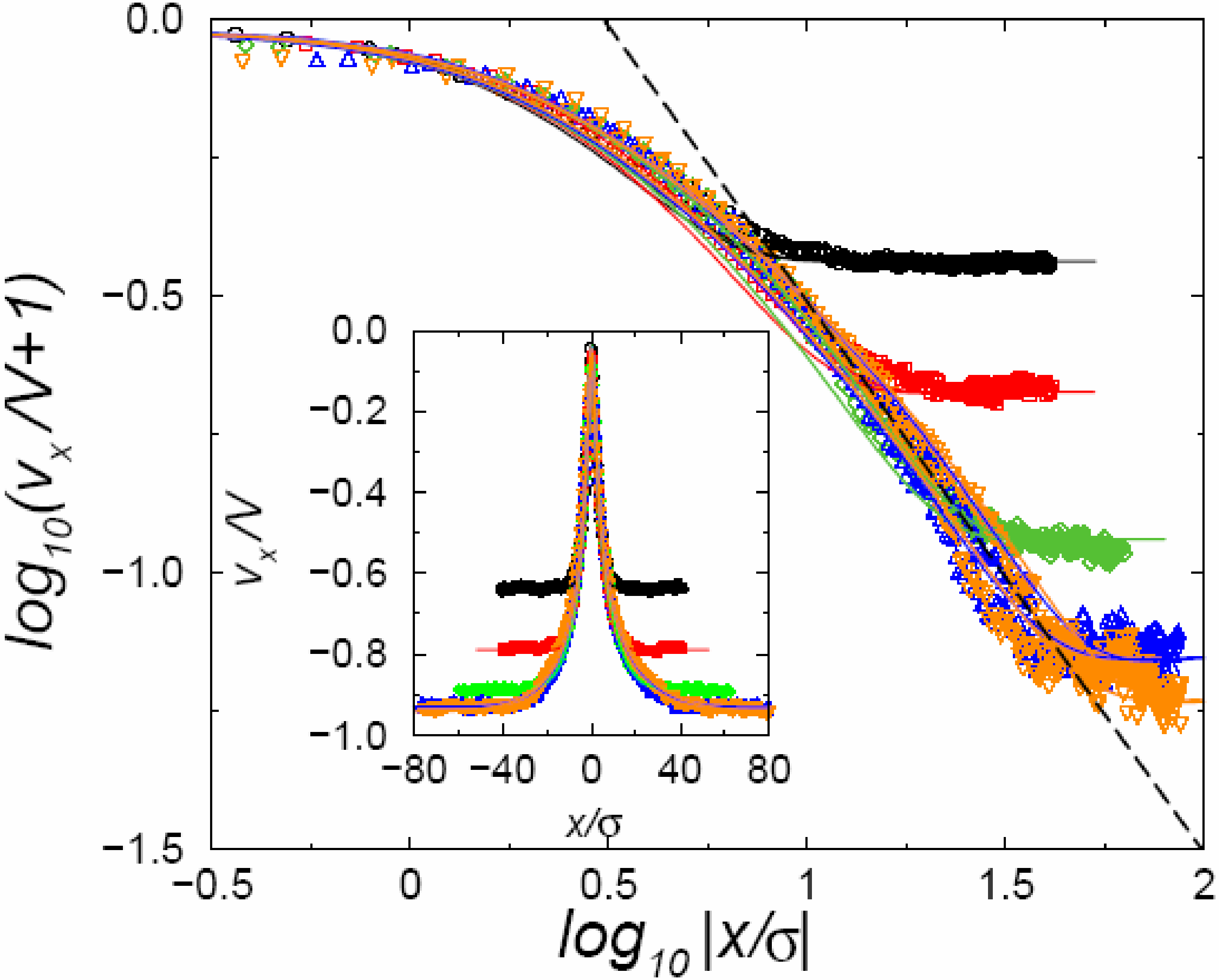
asymmetric Poiseuille flow

$g_{ext}=0.05$

$H=13.6$

Power-law decay of partial slip away from the MCL

from <u>complete slip</u> at the MCL to <u>no slip</u> far away,
governed by the NBC and the asymptotic *1/r* stress



The continuum hydrodynamic model for the moving contact line

A Cahn-Hilliard Navier-Stokes system supplemented with **the Generalized Navier boundary condition**, first uncovered from **molecular dynamics simulations**

Continuum predictions in agreement with **MD** results.

Now derived from
***the principle of minimum energy dissipation*,**
for ***irreversible*** thermodynamic processes
(linear response, Onsager 1931).

Qian, Wang, Sheng, J. Fluid Mech. 564, 333-360 (2006).

Onsager's principle for one-variable irreversible processes

Langevin equation: $$\gamma\dot{\alpha} = -\frac{\partial F(\alpha)}{\partial \alpha} + \zeta(t)$$

$$\langle \zeta(t)\zeta(t')\rangle = 2\gamma k_B T \delta(t-t')$$

Fokker-Plank equation for **probability density** $P(\alpha, t)$

$$\frac{\partial P}{\partial t} = D\left[\frac{\partial^2 P}{\partial \alpha^2} + \frac{1}{k_B T}\frac{\partial}{\partial \alpha}\left(\frac{\partial F}{\partial \alpha}P\right)\right]$$

Einstein relation $\gamma D = k_B T$

Transition probability $P_2(\alpha', t+\Delta t; \alpha, t)$

$$P_2(\alpha', t+\Delta t; \alpha, t) = \frac{1}{\sqrt{4\pi D\Delta t}}\exp\left[-\frac{(\alpha'-\alpha)^2}{4D\Delta t}\right]\exp\left[-\frac{F(\alpha')-F(\alpha)}{2k_B T}\right]$$

The most probable course derived from minimizing

$$A = \frac{\gamma(\alpha'-\alpha)^2}{2\Delta t} + [F(\alpha')-F(\alpha)] \approx \left[\frac{\gamma}{2}\dot{\alpha}^2 + \frac{\partial F(\alpha)}{\partial \alpha}\dot{\alpha}\right]\Delta t$$

Euler-Lagrange equation: $$\gamma\dot{\alpha} = \frac{\gamma(\alpha'-\alpha)}{\Delta t} = -\frac{\partial F(\alpha)}{\partial \alpha}$$

$$\text{Probability} \sim e^{-\textbf{Action}}$$

Onsager 1931
Onsager-Machlup 1953

$$\langle \zeta(t)\zeta(t') \rangle = 2\gamma k_B T \delta(t - t')$$

$$\text{Action} = \frac{1}{4\gamma k_{\mathrm{B}} T} \int dt \left[\zeta(t)\right]^2 = \frac{1}{4\gamma k_{\mathrm{B}} T} \int dt \left[\gamma\dot{\alpha} + \frac{\partial F(\alpha)}{\partial \alpha}\right]^2$$

for the statistical distribution of the noise (random force)

$$\frac{1}{4\gamma k_{\mathrm{B}} T} \left[\gamma\dot{\alpha} + \frac{\partial F(\alpha)}{\partial \alpha}\right]^2 \Delta t \rightarrow$$

$$\frac{\gamma\dot{\alpha}^2}{4k_{\mathrm{B}} T}\Delta t + \frac{1}{2k_B T}\frac{\partial F(\alpha)}{\partial \alpha}\dot{\alpha}\Delta t = \frac{\Delta\alpha^2}{4D\Delta t} + \frac{1}{2k_B T}\frac{\partial F(\alpha)}{\partial \alpha}\Delta\alpha$$

The principle of minimum energy dissipation (Onsager 1931)

$$\sum_{j=1}^{n} \rho_{ij}\dot{\alpha}_j = -\frac{\partial F(\alpha_1, \cdots, \alpha_n)}{\partial \alpha_i}, \quad (i = 1, \cdots, n)$$

Balance of the viscous force and the "elastic" force from

a variational principle

$$\delta\left[\Phi(\dot{\alpha}, \dot{\alpha}) + \dot{F}(\alpha, \dot{\alpha})\right] = \sum_{i=1}^{n}\left(\frac{\partial \Phi}{\partial \dot{\alpha}_i} + \frac{\partial F}{\partial \alpha_i}\right)\delta\dot{\alpha}_i = 0$$

$$\Phi(\dot{\alpha}, \dot{\alpha}) \equiv \frac{1}{2}\sum_{i,j}\rho_{ij}\dot{\alpha}_i\dot{\alpha}_j$$

dissipation-function, positive definite and quadratic in the rates, half the rate of energy dissipation

$$\dot{F}(\alpha, \dot{\alpha}) \equiv \sum_{i=1}^{n}\frac{\partial F(\alpha_1, \cdots, \alpha_n)}{\partial \alpha_i}\dot{\alpha}_i$$

rate of change of the free energy

Minimum dissipation theorem for incompressible single-phase flows (*Helmholtz* 1868)

Consider a flow confined by solid surfaces.

Stokes equation:

$$-\nabla p + \eta \nabla^2 \mathbf{v} = 0$$

derived as ***the Euler-Lagrange equation*** by minimizing the functional

$$R_v[\mathbf{v}] = \int d\mathbf{r} \left[\frac{\eta}{2} (\partial_i v_j + \partial_j v_i)^2 \right]$$

for the rate of **viscous dissipation** in the bulk.

The values of the velocity fixed at the solid surfaces!

Taking into account the dissipation due to
the fluid slipping at the fluid-solid interface

$$R_s[\mathbf{v}] = \int dS \left[\beta\left(v_\tau^{slip}\right)^2\right]$$

Total rate of **dissipation** due to **viscosity** in the bulk and **slipping** at the solid surface

$$R_1[\mathbf{v}] = \int d\mathbf{r}\left[\frac{\eta}{2}(\partial_i v_j + \partial_j v_i)^2\right] + \int dS\left[\beta\left(v_\tau^{slip}\right)^2\right]$$

One more ***Euler-Lagrange equation*** at the solid surface with boundary values of the velocity subject to variation

Navier boundary condition:

$$\beta v_\tau^{slip} = -\sigma_{n\tau}^{visc} = -\eta(\partial_n v_\tau + \partial_\tau v_n)$$

Generalization to immiscible two-phase flows

A Landau free energy functional to stabilize
the interface separating the two immiscible fluids

$$\mathcal{F}[\phi(\mathbf{r})] = \int d\mathbf{r} \left[\frac{K}{2} (\nabla\phi)^2 + f(\phi) \right]$$

double-well structure for $f(\phi)$

Interfacial free energy per unit area
at the fluid-solid interface

$$\gamma_{fs}(\phi)$$

Variation of the total free energy $F = \mathcal{F}[\phi] + \int dS\, [\gamma_{fs}(\phi)]$

$$\delta \left\{ \mathcal{F}[\phi] + \int dS\, [\gamma_{fs}(\phi)] \right\} = \int d\mathbf{r}\, [\mu\delta\phi] + \int dS\, [L\delta\phi]$$

for defining μ and L.

μ and L :

$\boxed{\mu = \delta\mathcal{F}/\delta\phi = -K\nabla^2\phi + \partial f(\phi)/\partial\phi}$ chemical potential in the bulk:

$\boxed{L(\phi) = K\partial_n\phi + \partial\gamma_{fs}(\phi)/\partial\phi}$ at the fluid-solid interface

Deviations from the equilibrium measured by $\nabla\mu$ in the bulk and L at the fluid-solid interface.

Minimizing the total free energy subject to the conservation of ϕ leads to the equilibrium conditions:

$\boxed{\mu = Const.}$ $\boxed{L = 0}$

For small perturbations away from the two-phase equilibrium, **the additional rate of dissipation** (due to the coexistence of the two phases) arises from system responses (rates) that are linearly proportional to the respective perturbations/deviations.

Dissipation function (half the total rate of energy dissipation)

$$\Phi = \int d\mathbf{r} \left[\frac{\eta}{4}(\partial_i v_j + \partial_j v_i)^2\right] + \int dS \left[\frac{\beta}{2}\left(v_\tau^{slip}\right)^2\right] + \int d\mathbf{r} \left[\frac{\mathbf{J}^2}{2M}\right] + \int dS \left[\frac{\dot{\phi}^2}{2\Gamma}\right]$$

$$\Phi = \frac{1}{2}R_2 = \frac{1}{2}(R_1 + R_\phi) = \frac{1}{2}(R_v + R_s + R_d + R_r)$$

Rate of change of the free energy

$$\dot{F} = \int d\mathbf{r} \left[\mu \frac{\partial \phi}{\partial t}\right] + \int dS \left[L \frac{\partial \phi}{\partial t}\right]$$

kinematic transport of ϕ

$$\partial\phi/\partial t = \dot{\phi} - \mathbf{v} \cdot \nabla \phi$$

$$\int d\mathbf{r} \left[\mu \dot{\phi}\right] = \int d\mathbf{r} \left[-\mu \nabla \cdot \mathbf{J}\right]$$

continuity equation for ϕ

$$\int d\mathbf{r} \left[\nabla \cdot (\mu \mathbf{J})\right] = \int dS \left[\mu J_n\right] = 0$$

impermeability B.C.

$$\dot{F} = \int d\mathbf{r} \left[\nabla \mu \cdot \mathbf{J} - \mu \mathbf{v} \cdot \nabla \phi\right] + \int dS \left[L(\dot{\phi} - v_\tau \partial_\tau \phi)\right]$$

Minimizing $\Phi + \dot{F}$

$$\int d\mathbf{r}\left[\frac{\eta}{4}(\partial_i v_j + \partial_j v_i)^2\right] + \int dS\left[\frac{\beta}{2}\left(v_\tau^{slip}\right)^2\right] + \int d\mathbf{r}\left[\frac{\mathbf{J}^2}{2M}\right] + \int dS\left[\frac{\dot{\phi}^2}{2\Gamma}\right] +$$
$$\int d\mathbf{r}\left[\nabla\mu\cdot\mathbf{J} - \mu\mathbf{v}\cdot\nabla\phi\right] + \int dS\left[L(\dot{\phi} - v_\tau\partial_\tau\phi)\right].$$

with respect to the rates $\{\mathbf{v},\ \mathbf{J},\ \dot{\phi}\}$ yields

$$-\nabla p + \eta\nabla^2\mathbf{v} + \mu\nabla\phi = 0,$$ Stokes equation

$$\beta(\phi)v_\tau^{slip} = -\eta(\partial_n v_\tau + \partial_\tau v_n) + \underbrace{L(\phi)\partial_\tau\phi}_{\tilde{\sigma}_{zx}^{Y}},$$ GNBC

$$\mathbf{J} = -M\nabla\mu,$$

$$\dot{\phi} = \frac{\partial\phi}{\partial t} + \mathbf{v}\cdot\nabla\phi = -\nabla\cdot\mathbf{J} = M\nabla^2\mu$$ advection-diffusion equation

$$\dot{\phi} = \frac{\partial\phi}{\partial t} + v_\tau\partial_\tau\phi = -\Gamma L(\phi).$$ 1st order relaxational equation

Summary:

- Moving contact line calls for ***a slip boundary condition***.
- The generalized Navier boundary condition (**GNBC**) is derived for the immiscible two-phase flows from the principle of minimum energy dissipation (entropy production) by taking into account the fluid-solid interfacial dissipation.
- Landau's free energy & Onsager's linear dissipative response.
- Predictions from the hydrodynamic model are in excellent agreement with the full **MD** simulation results.
- "Unreasonable effectiveness" of a continuum model.
  - Landau-Lifshitz-Gilbert theory for micromagnets
  - Ginzburg-Landau (or BdG) theory for superconductors
  - Landau-de Gennes theory for nematic liquid crystals