

# Molecular hydrodynamics of the moving contact line

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in collaboration with

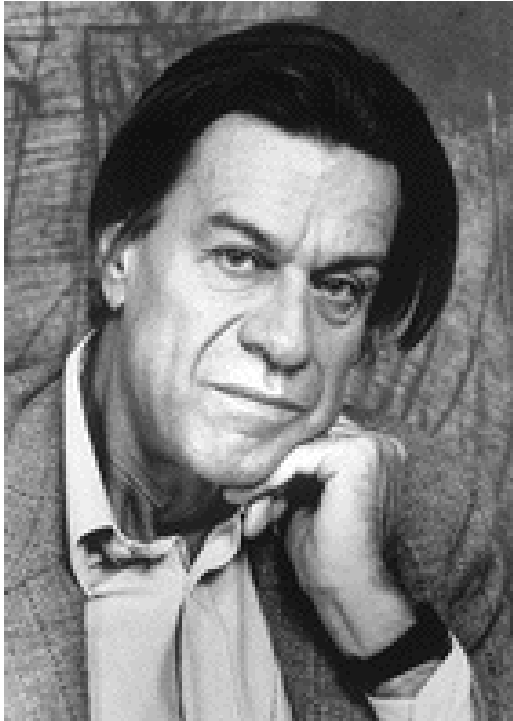
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Physics Department, Zhejiang University, Dec 18, 2007

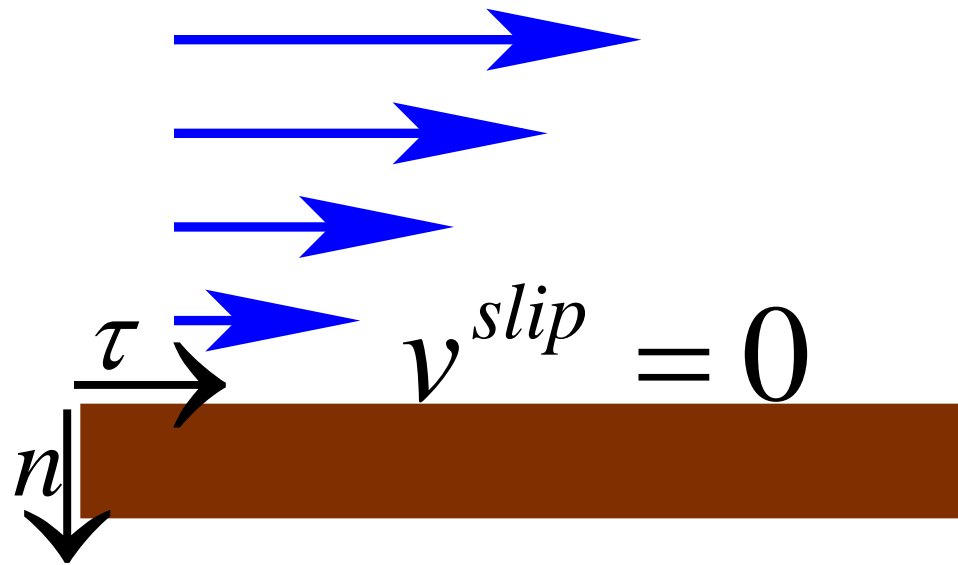
The **borders** between great empires are often populated by the most interesting ethnic groups. Similarly, **the interfaces between two forms of bulk matter** are responsible for some of the most unexpected actions.

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

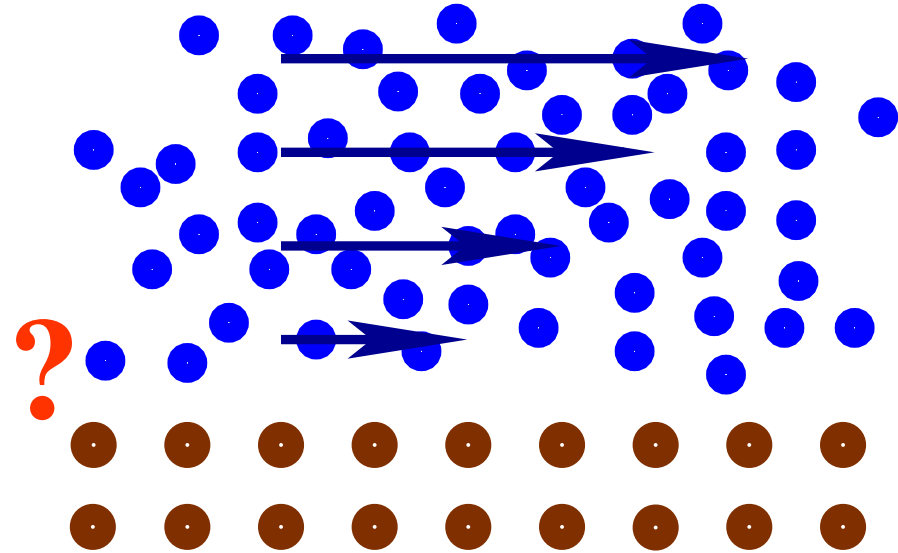


- The no-slip boundary condition and the moving contact line problem
- The generalized Navier boundary condition (GNBC) from **molecular dynamics (MD) simulations**
- Implementation of the new slip boundary condition in a **continuum hydrodynamic model** (phase-field formulation)
- Comparison of **continuum** 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

Continuum picture



Molecular picture

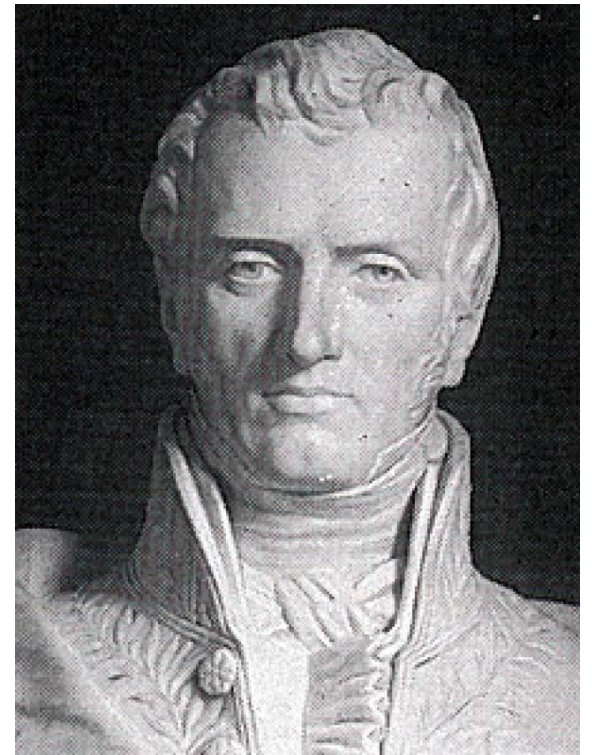


**No-Slip** Boundary Condition, **A Paradigm**

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



**James Clerk Maxwell**

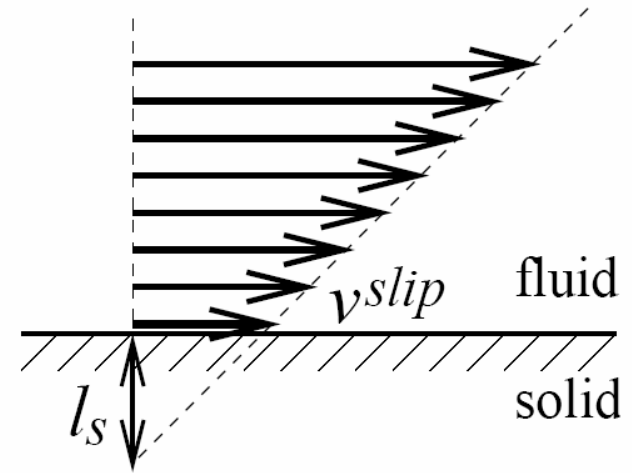


**Claude-Louis Navier**

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

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

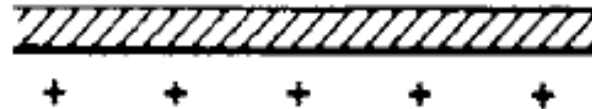
# Static wetting phenomena

Partial wetting



(a)

Complete wetting

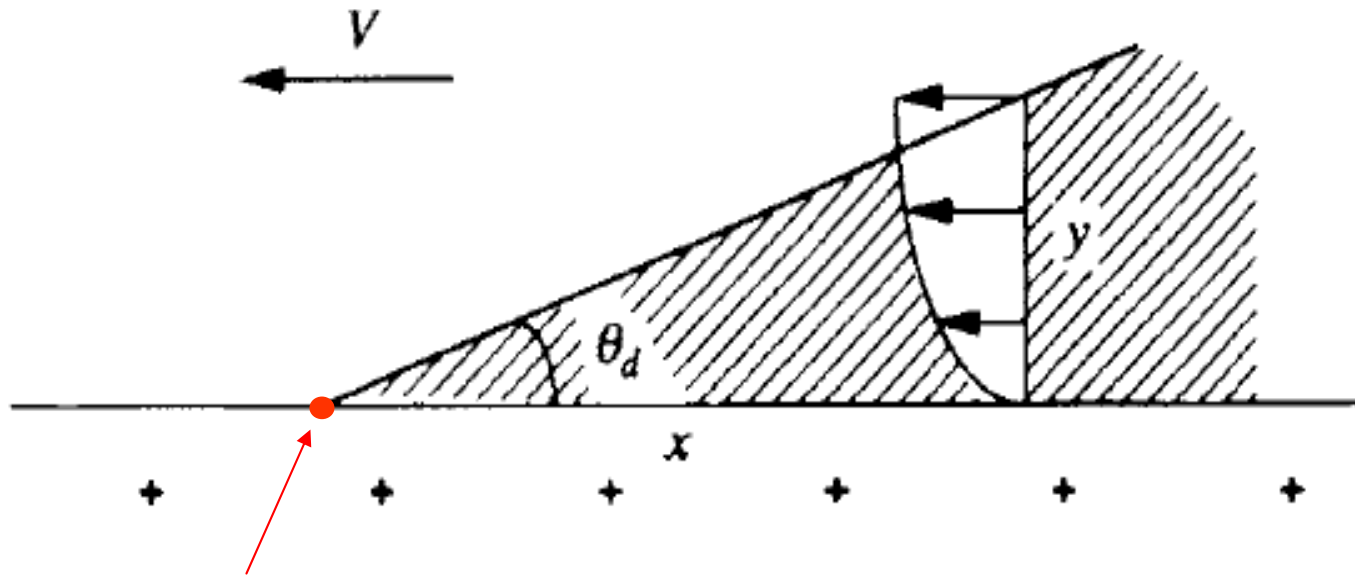


(b)



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.



fluid 1

fluid 2

contact line

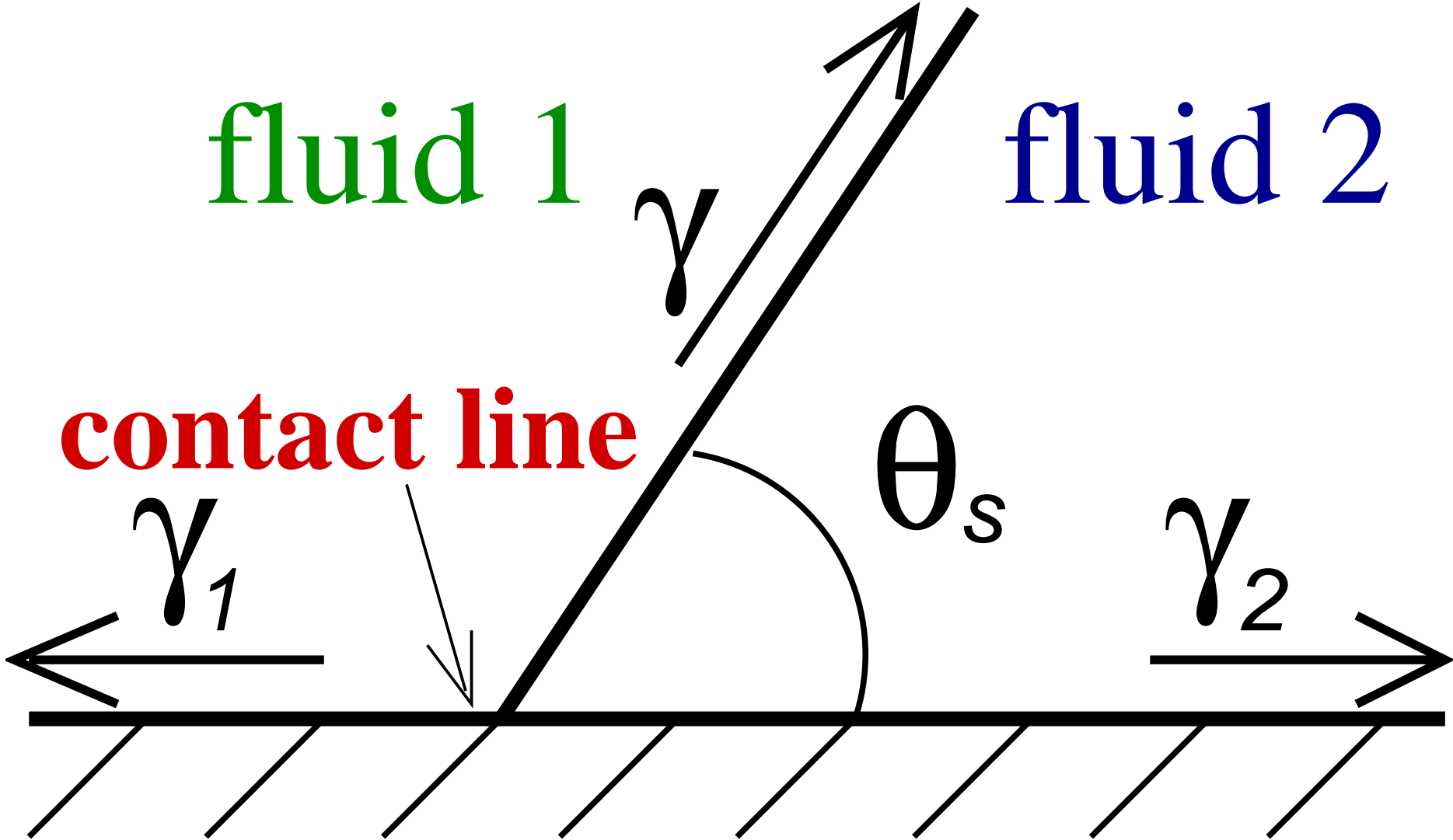
$\gamma_1$

$\theta_s$

$\gamma_2$

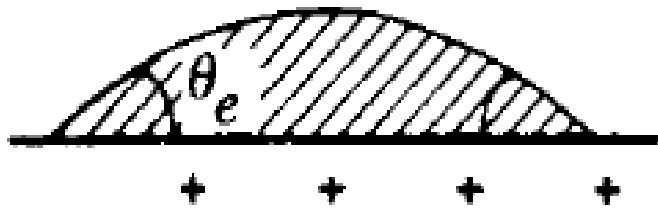
solid wall

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

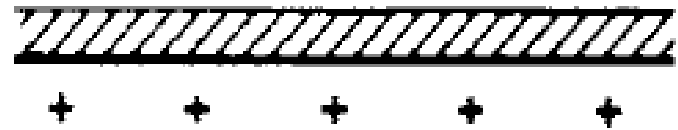


Manifestation of the contact angle:

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

$$\int_a^R \eta \frac{U}{x} dx \xrightarrow{a \rightarrow 0} \infty$$

$$\theta_d \neq \theta_s$$

$\gamma_1$

$\gamma$

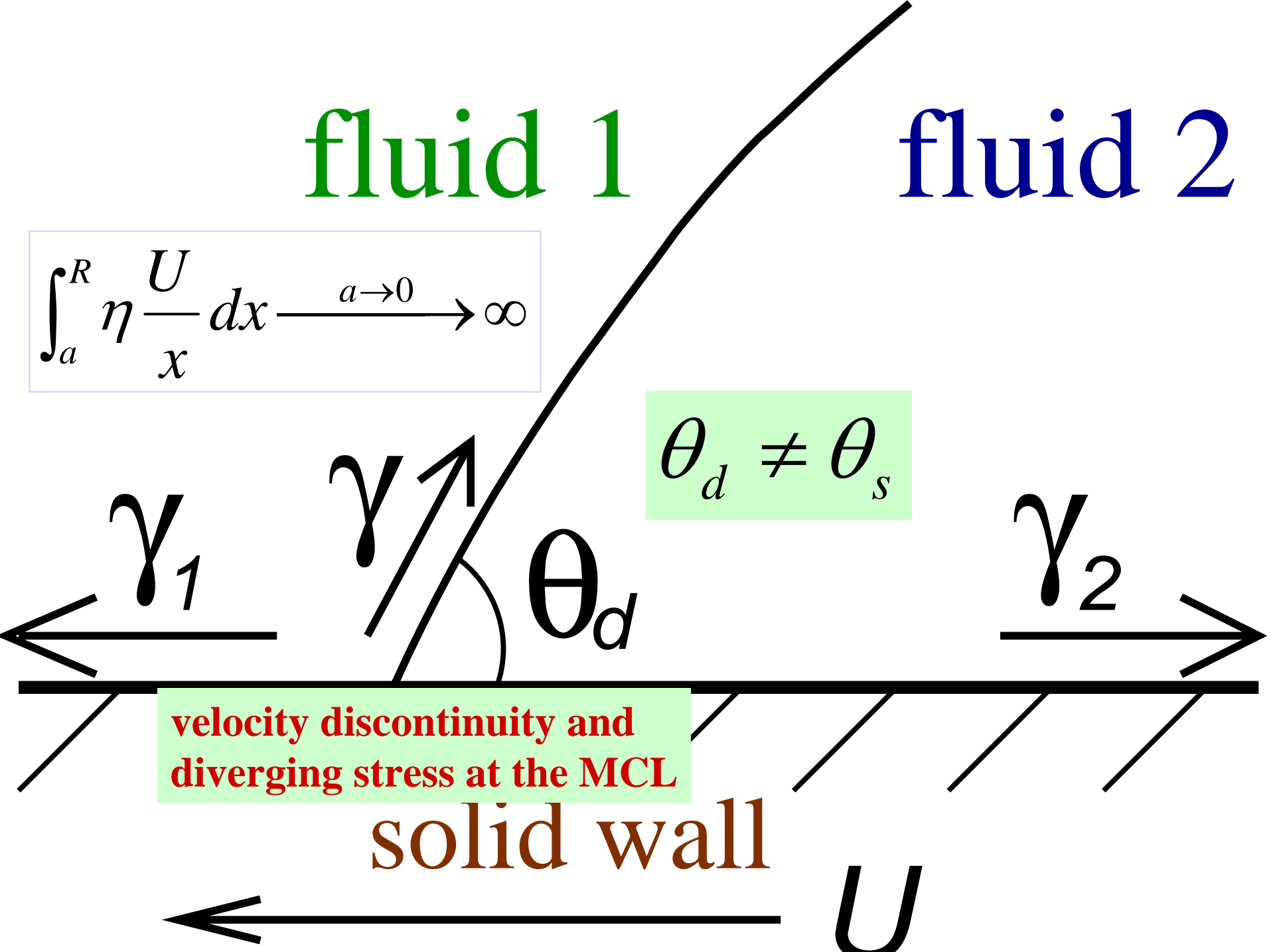
$\theta_d$

$\gamma_2$

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 !**

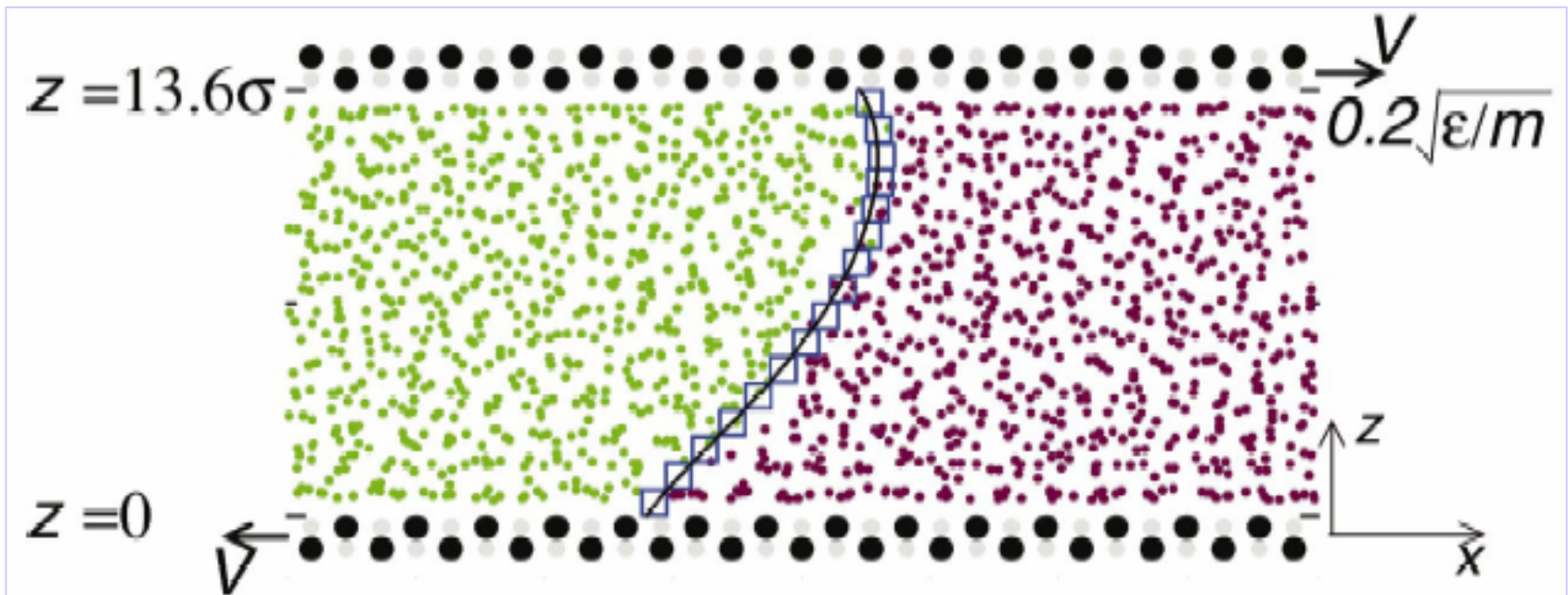
- Nature of the true B.C. ? (microscopic *slipping* mechanism)
- If *slip* occurs within a length scale  $S$  in the vicinity of the contact line, then what is the magnitude of  $S$  ?

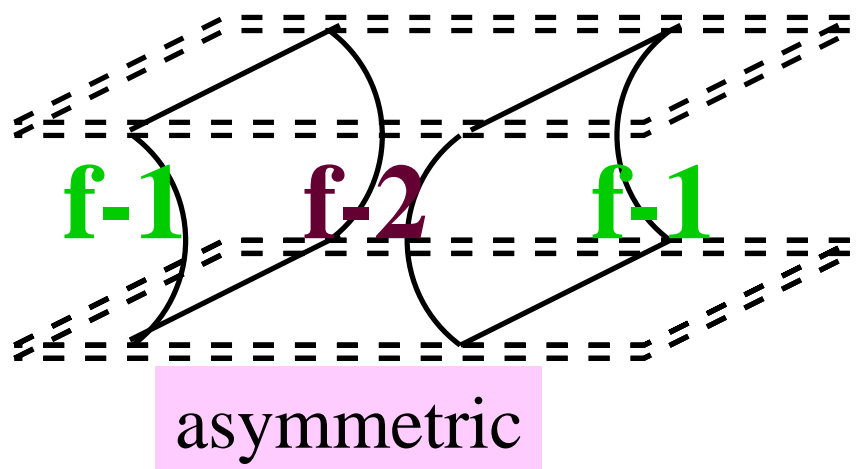
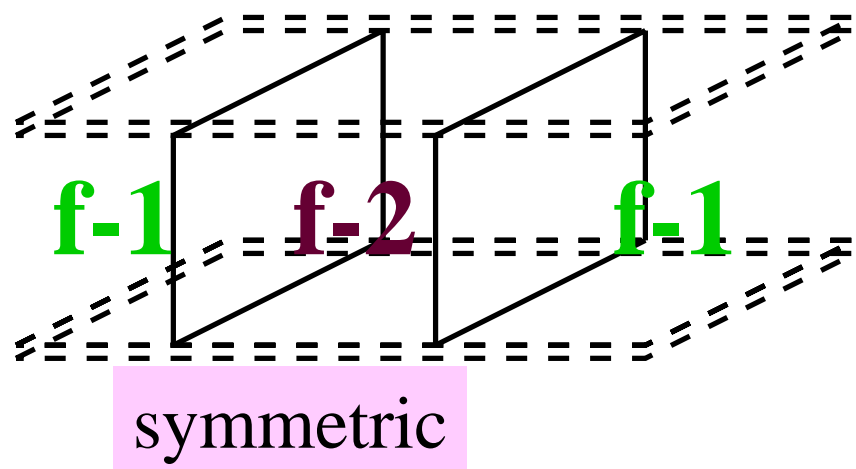
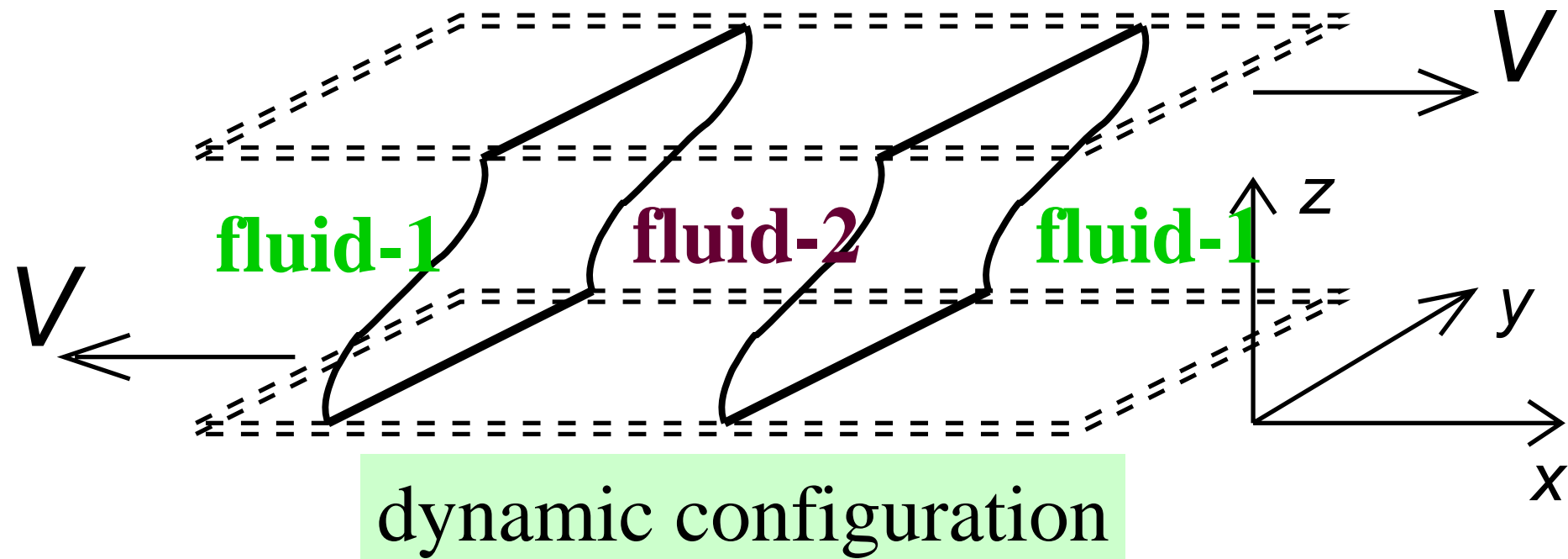
Qian, Wang & Sheng,  
PRE **68**, 016306 (2003)

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

# Molecular dynamics simulations for two-phase Couette flow

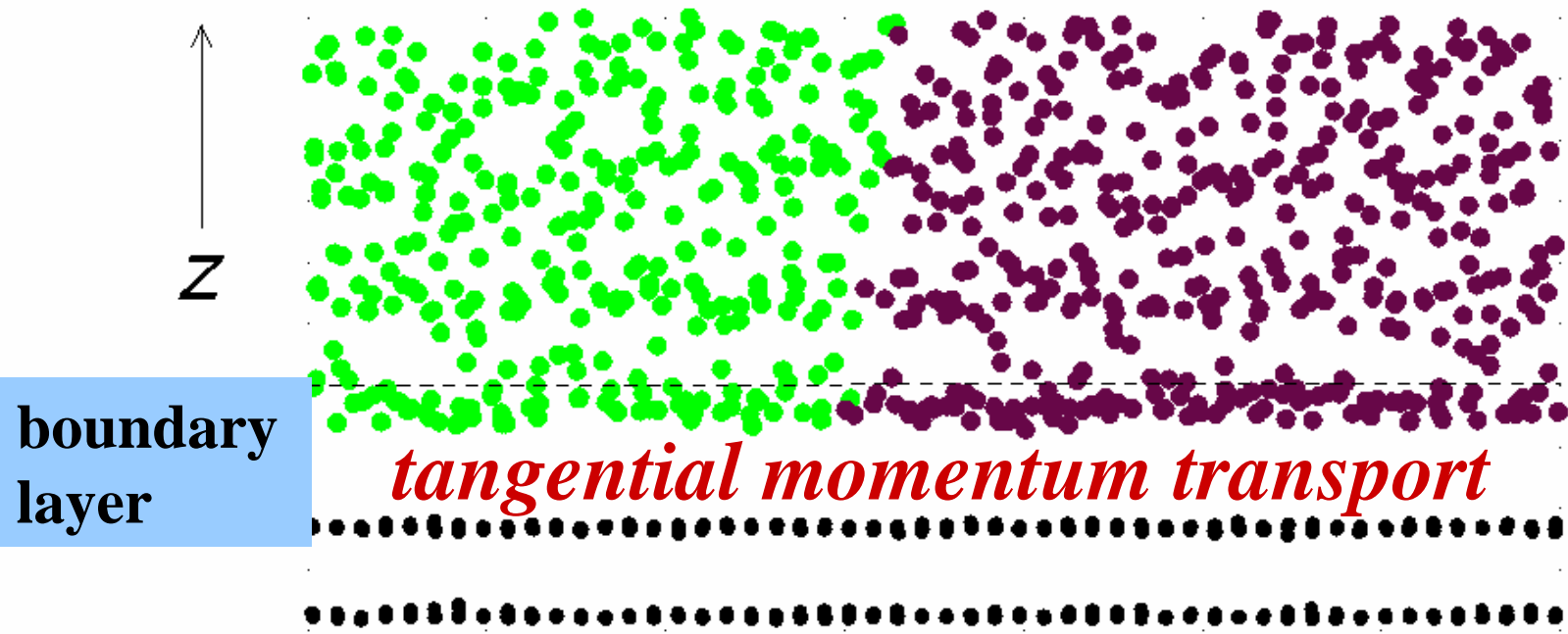
- **Fluid-fluid molecular interactions**
- **Fluid-solid molecular interactions**
- **Densities (liquid)**
- **Solid wall structure (fcc)**
- **Temperature**
- *System size*
- *Speed of the moving walls*





**static configurations**

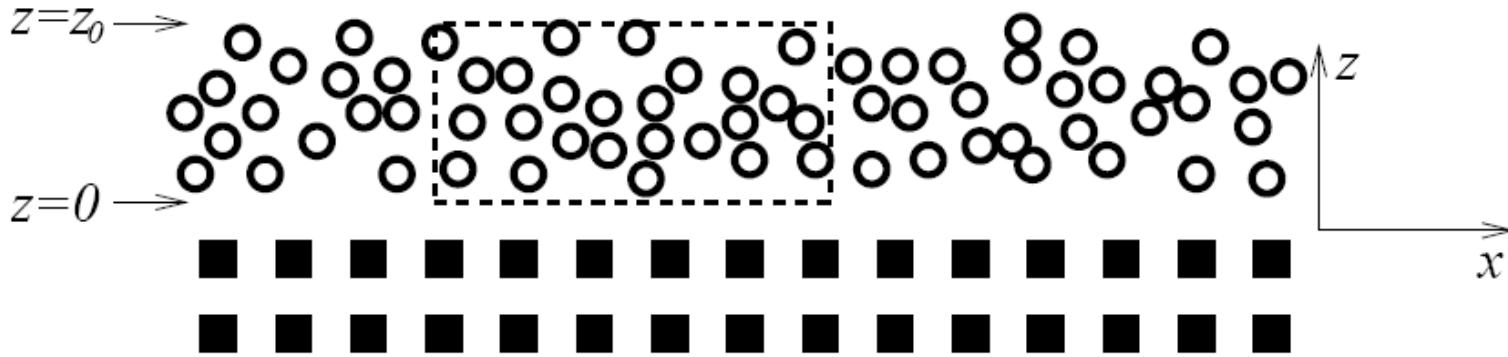
# Measurement at Solid–Fluid Boundary



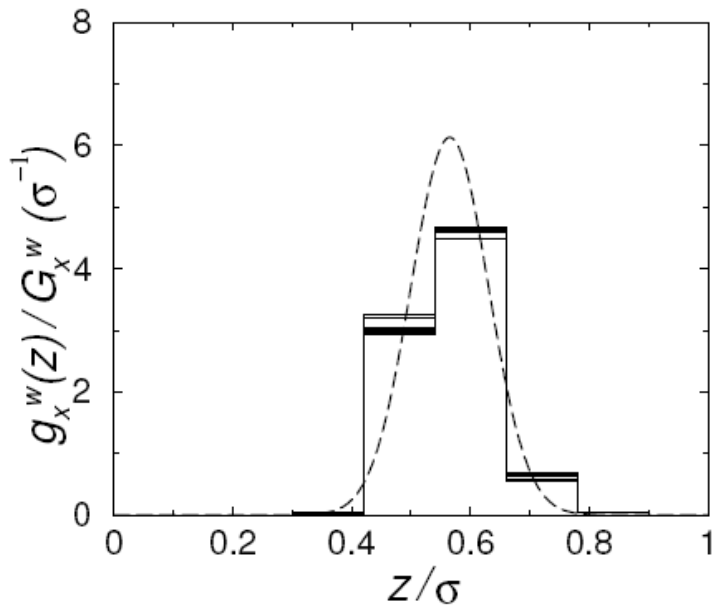
$$G_x^w, \quad G_x^f, \quad V_x^{slip}$$

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**

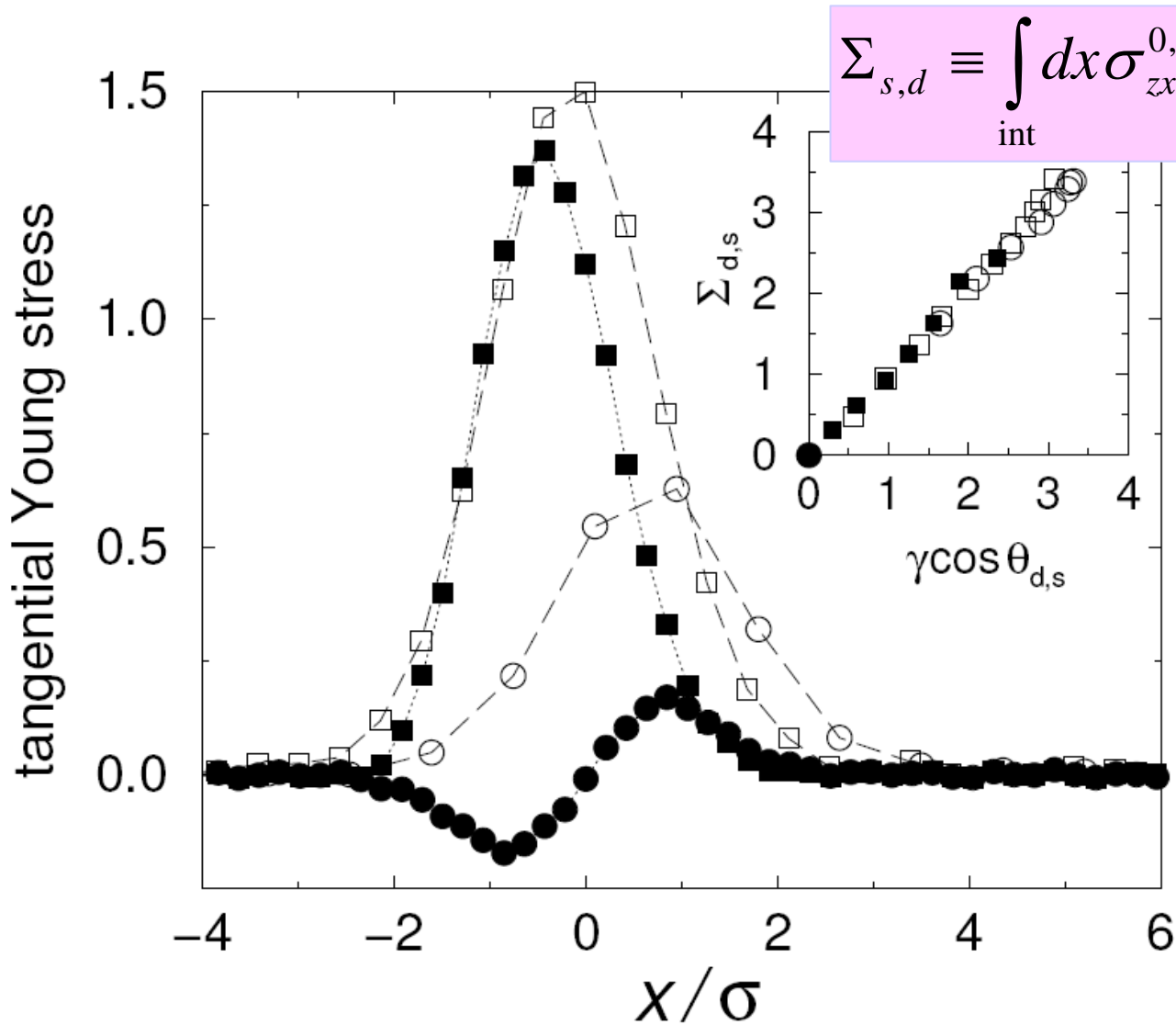
$$\beta v_x^{slip} = \tilde{G}_x^f = \tilde{\sigma}_{zx} = \sigma_{zx}^{visc} + \tilde{\sigma}_{zx}^Y$$

*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

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

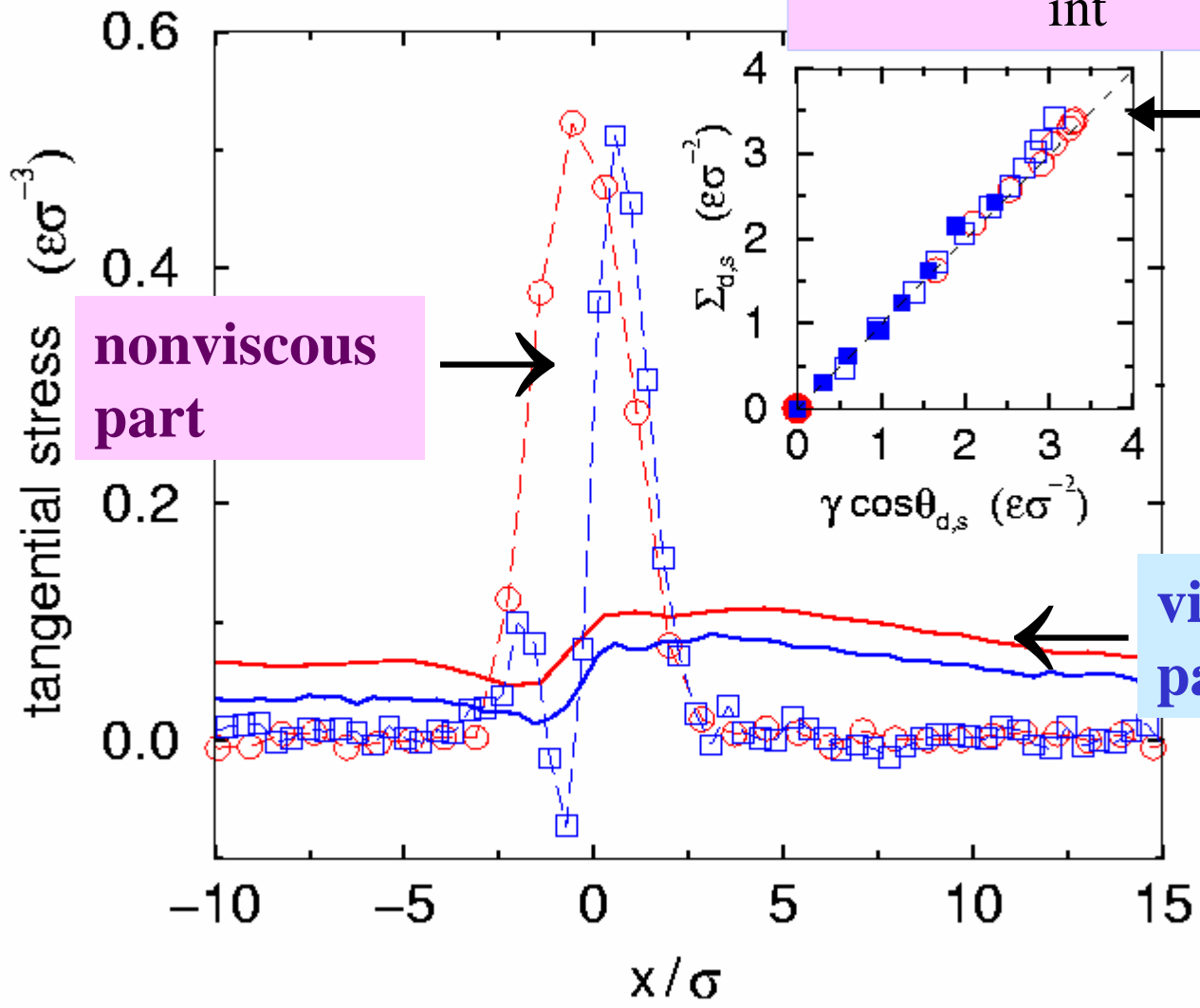


$\sigma_{zx}^Y$  obtained by subtracting the Newtonian viscous component

$\sigma_{zx}^0$  : solid circle: **static** symmetric  
 solid square: **static** asymmetric

$\sigma_{zx}^Y$  : empty circle: **dynamic** symmetric  
 empty square: **dynamic** asymmetric

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



# 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  $\phi$  (B.C.)

supplemented with

$$\nabla \cdot \mathbf{v} = 0 \quad \textit{incompressibility}$$

$$v_n = 0 \quad \textit{impermeability B.C.}$$

$$J_n \propto \partial_n \mu = 0 \quad \textit{impermeability B.C.}$$

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

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

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

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

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = M \nabla^2 \mu$$

$$\mu = \delta \mathcal{F}_{CH} / \delta \phi$$

$$\frac{\partial \phi}{\partial t} + v_\tau \partial_\tau \phi = -\Gamma L(\phi)$$

$$L(\phi) = K \partial_n \phi + \partial \gamma_{fs}(\phi) / \partial \phi$$

supplemented with

$$\nabla \cdot \mathbf{v} = 0$$

$$v_n = 0$$

$$J_n \propto \partial_n \mu = 0$$

# 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:

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

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

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.

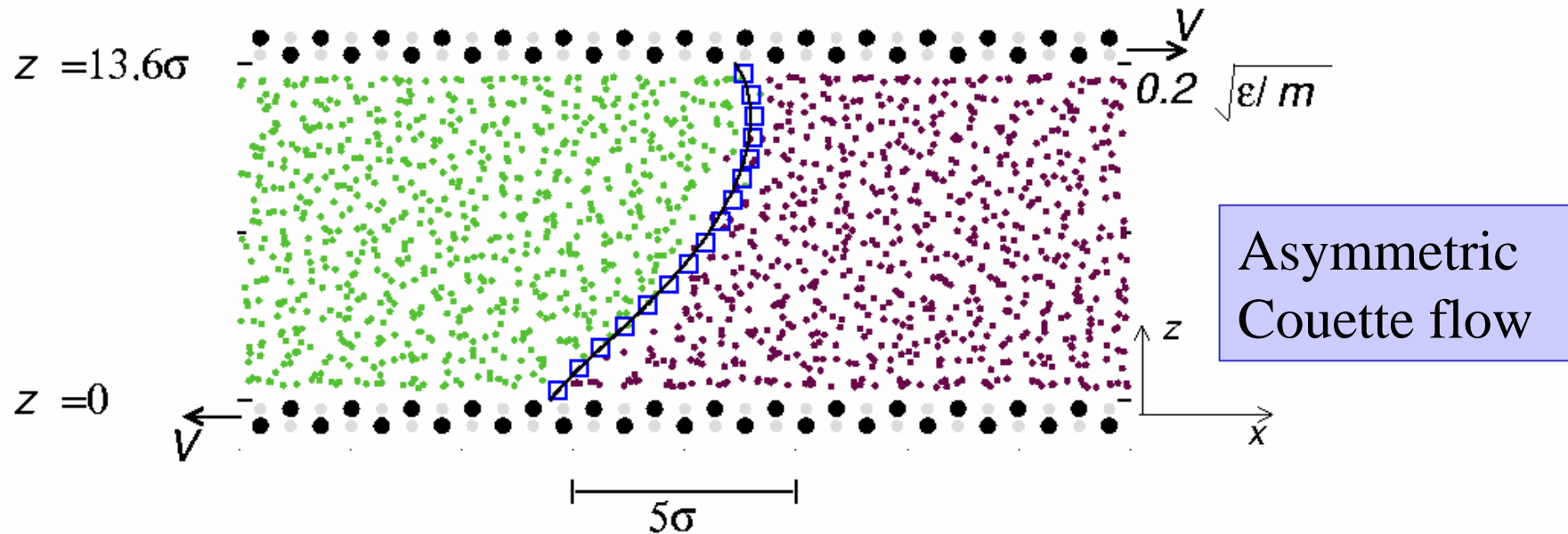
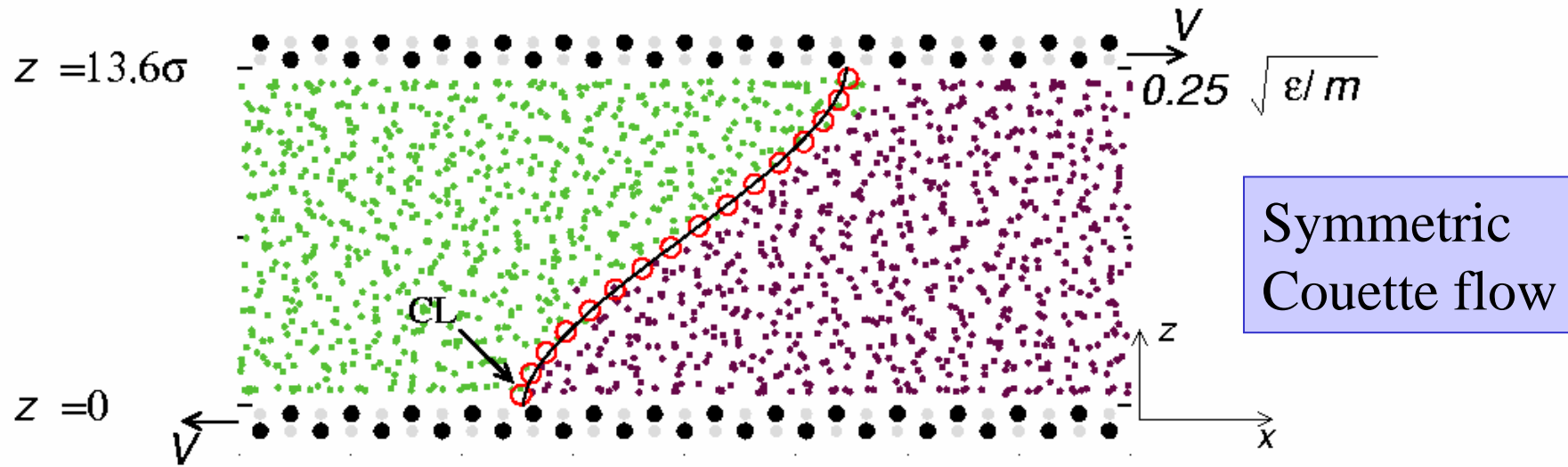
# Comparison of **MD** and **Continuum** Results

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

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



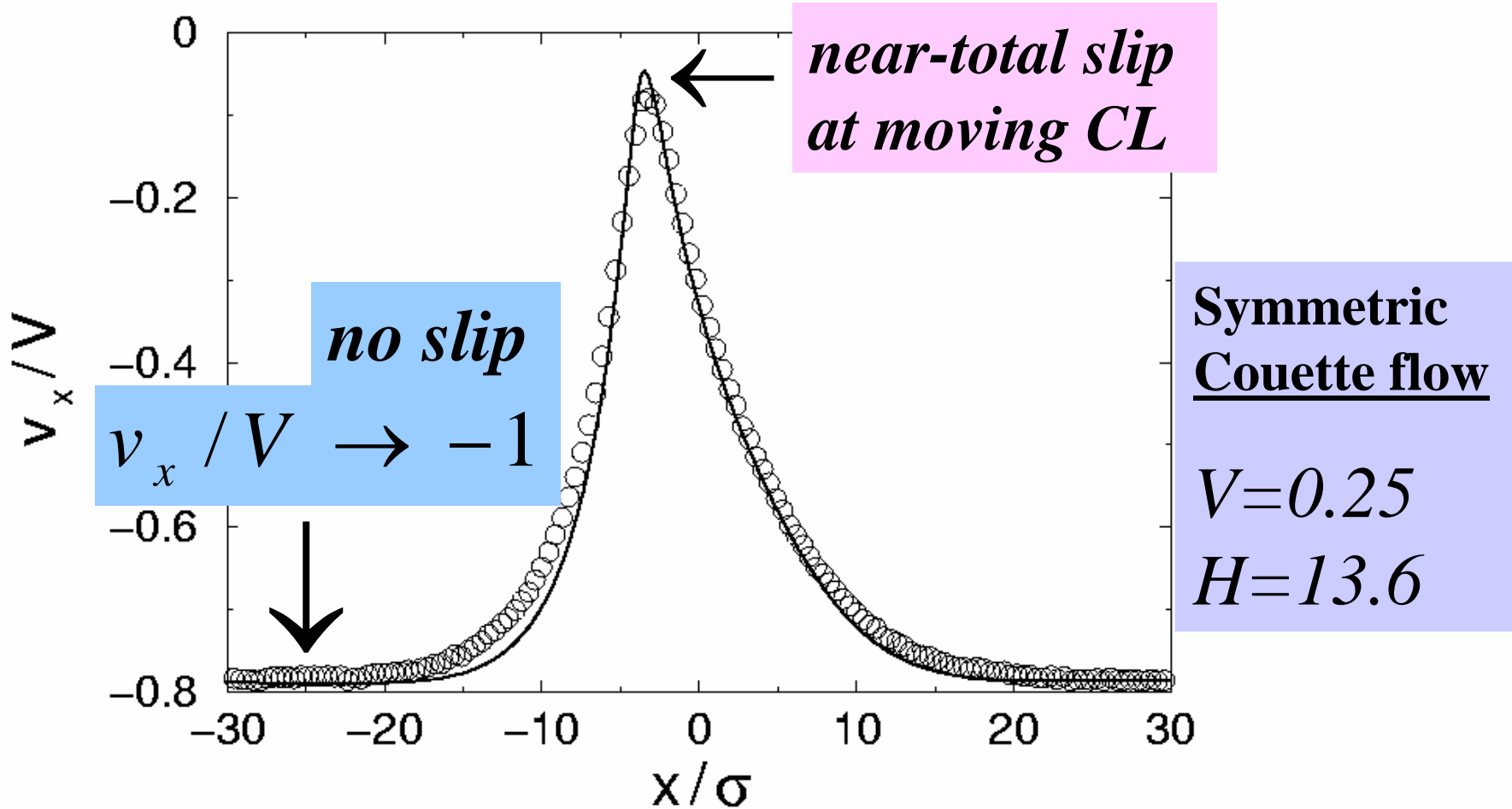
# molecular positions projected onto the $xz$ plane



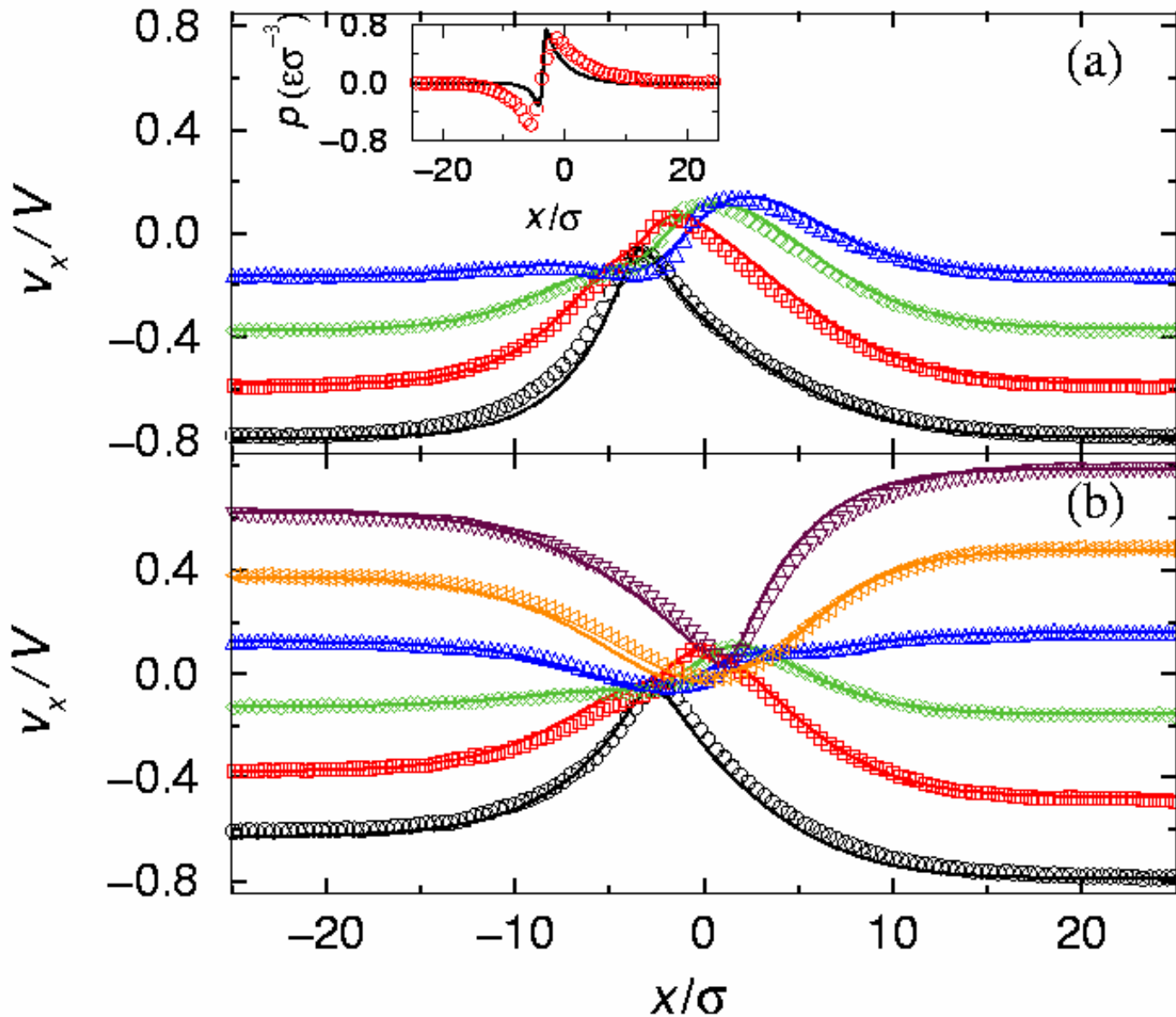
**Diffusion** versus **Slip** in MD

# Boundary layer velocity profile

$v_x = 0$  for total slip



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

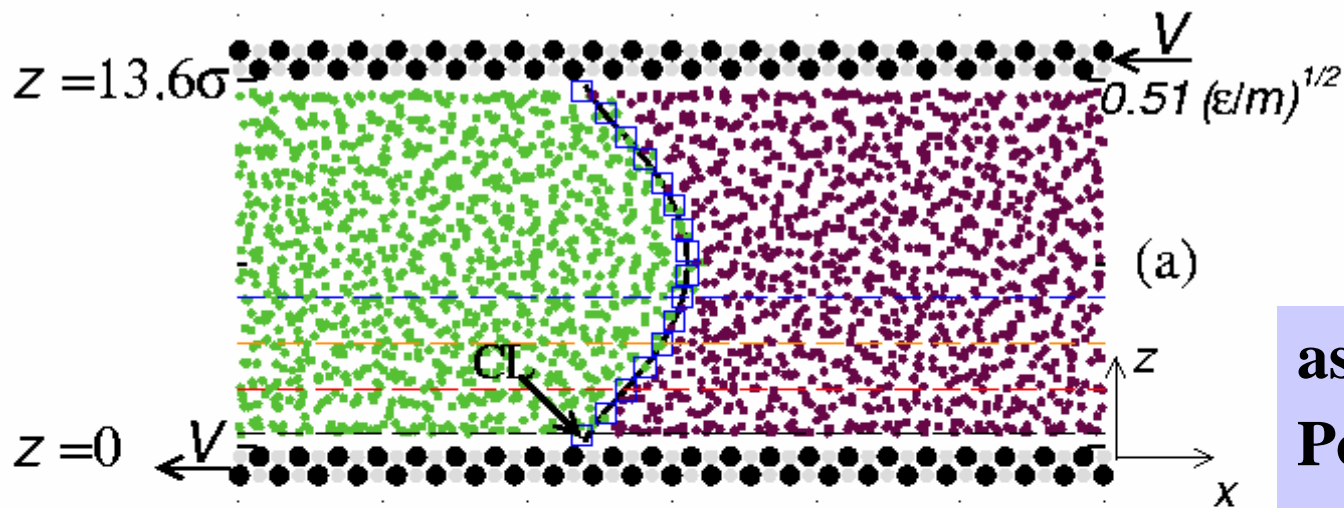


**symmetric**  
**Couette flow**

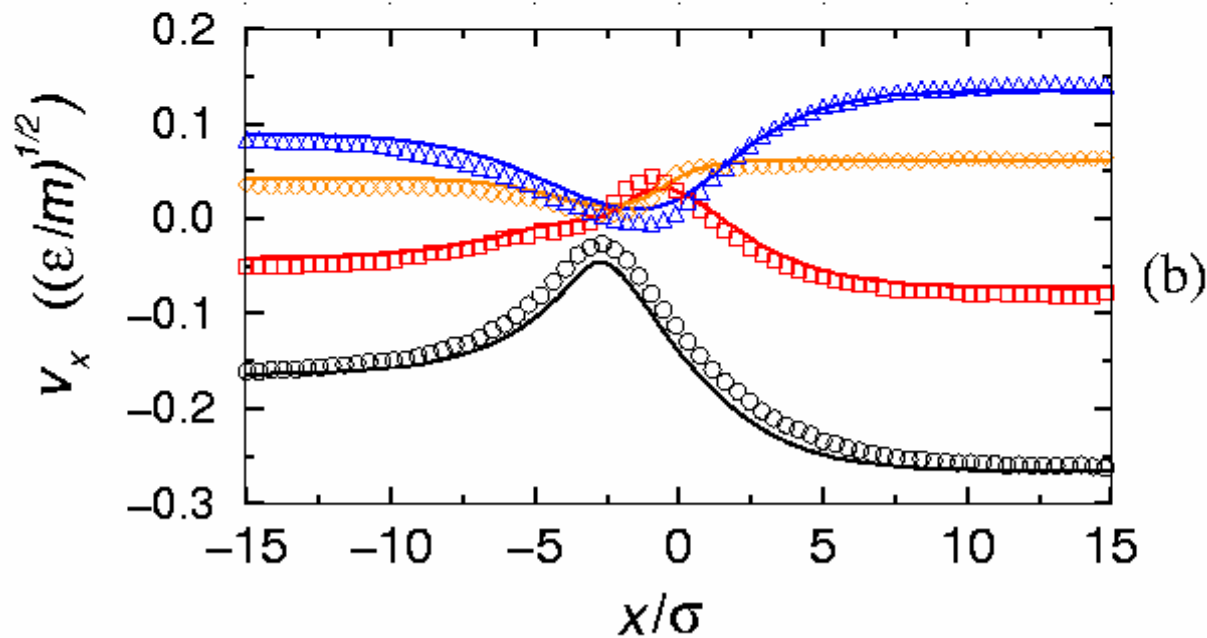
$V=0.25$   
 $H=13.6$

**asymmetric**  
**Couette flow**

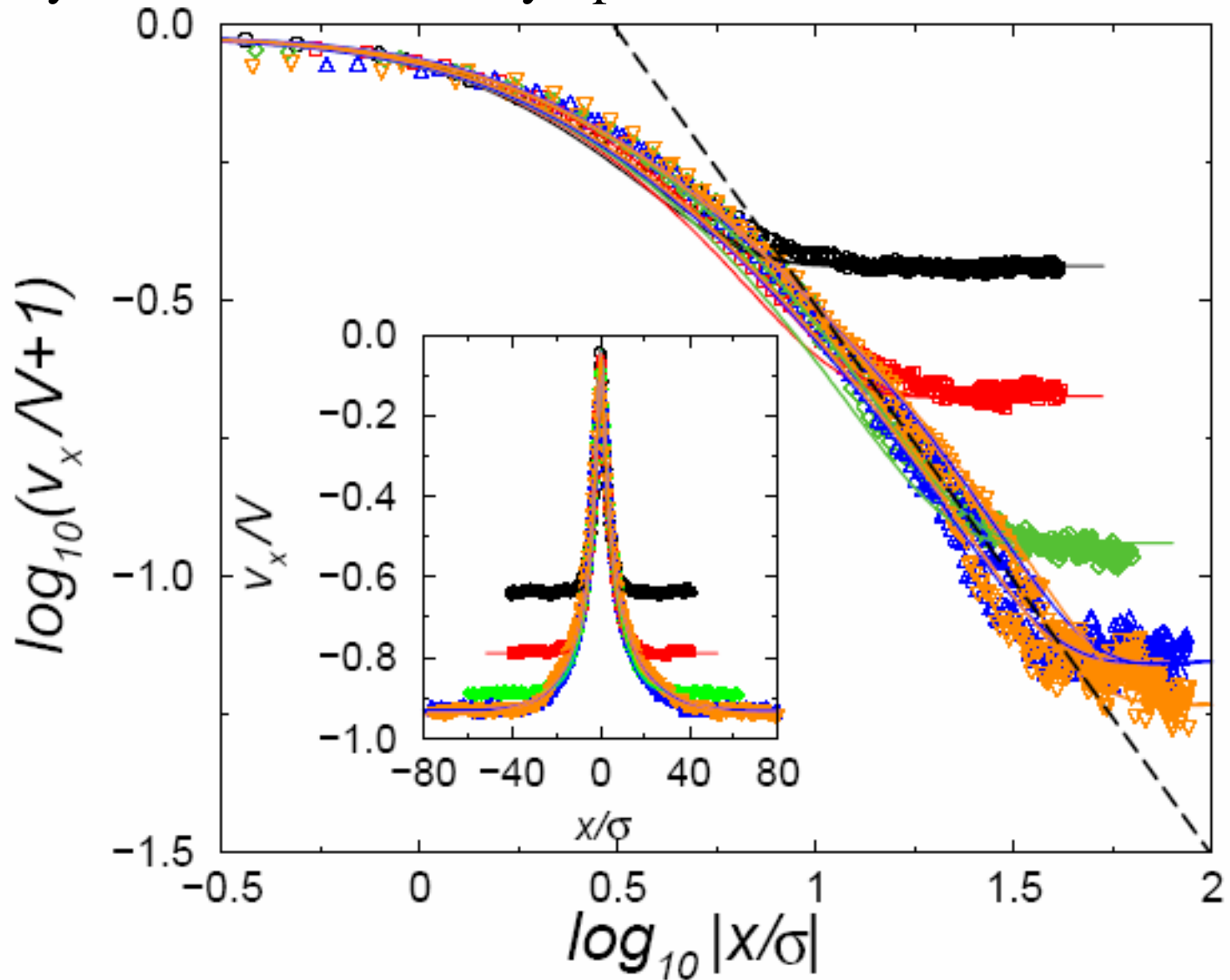
$V=0.20$   
 $H=13.6$



asymmetric  
 Poiseuille flow  
 $g_{ext} = 0.05$   
 $H = 13.6$



Power-law decay of partial slip away from the MCL  
from complete slip at the MCL to no slip 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**  $P(\alpha, t)$

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

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

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

Onsager 1931

Onsager-Machlup 1953

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

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

for the statistical distribution of the noise (random force)

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



# The principle of minimum energy dissipation (Onsager 1931)

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

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

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

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

$$\mathcal{F}[\phi(\mathbf{r})] = \int d\mathbf{r} \left[ \frac{K}{2} (\nabla\phi)^2 + f(\phi) \right] \quad \text{double-well structure for } f(\phi)$$

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  $\mu$  and  $L$ .

$\mu$  and  $L$  :

$$\mu = \delta\mathcal{F}/\delta\phi = -K\nabla^2\phi + \partial f(\phi)/\partial\phi$$

chemical potential  
in the **bulk**:

$$L(\phi) = K\partial_n\phi + \partial\gamma_{fs}(\phi)/\partial\phi$$
 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  $\phi$  leads to the equilibrium conditions:

$$\mu = \text{Const.}$$

$$L = 0$$

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)

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

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

## 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  $\phi$

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

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

$$\int d\mathbf{r} \left[ \nabla \cdot (\mu \mathbf{J}) \right] = \int dS \left[ \mu J_n \right] = 0 \quad \text{impermeability B.C.}$$

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

# Minimizing $\Phi + \dot{F}$

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

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

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

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

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

 $\tilde{\sigma}_{zx}^Y$ 

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

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

# 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