Molecular hydrodynamics of the moving contact line

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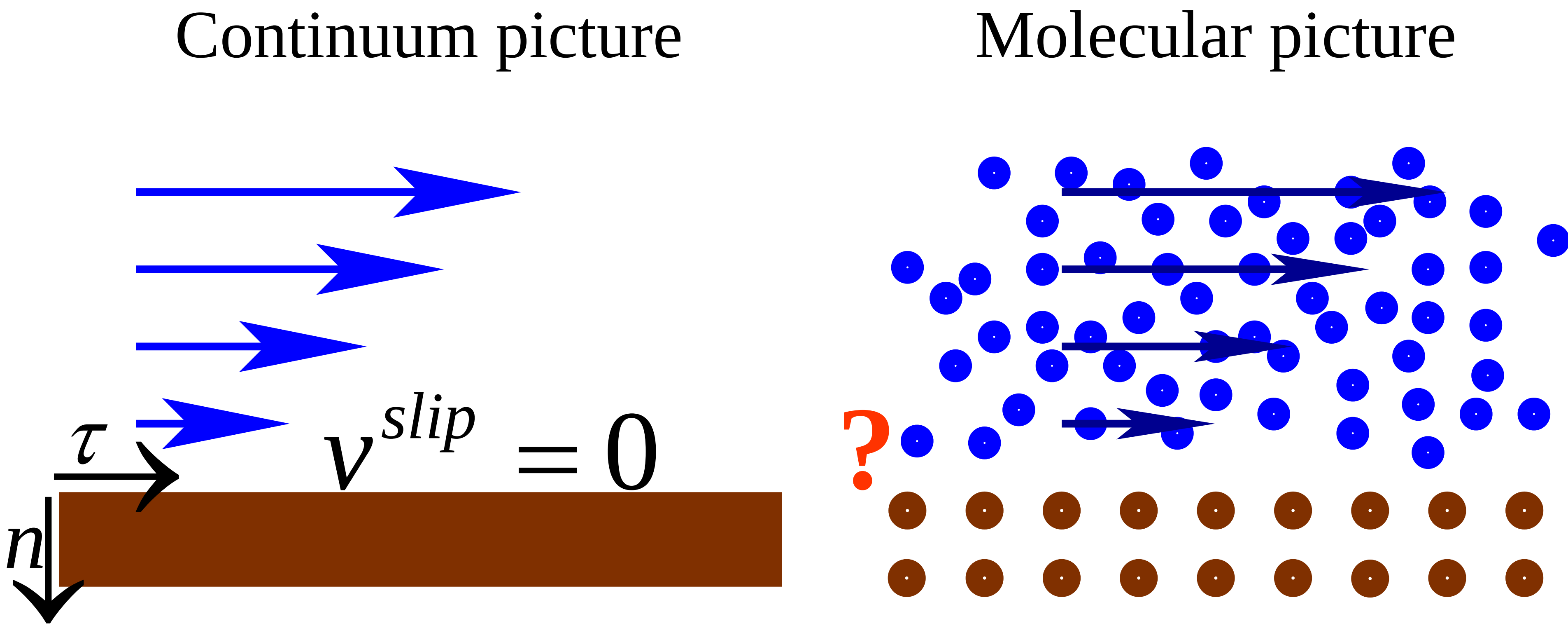
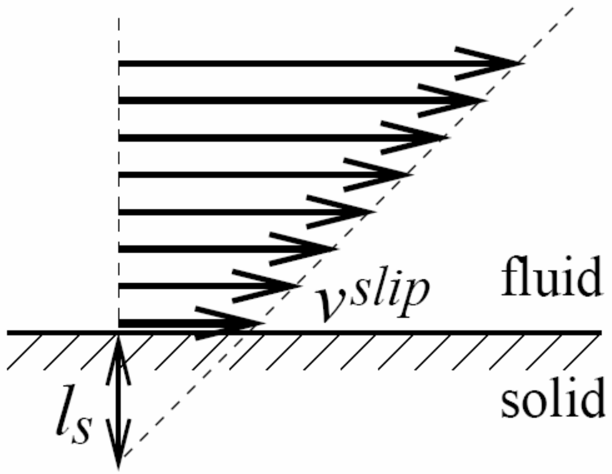


No-Slip Boundary Condition, **A Paradigm**

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

from **Navier** Boundary Condition **(1823)**

to **No-Slip** Boundary Condition



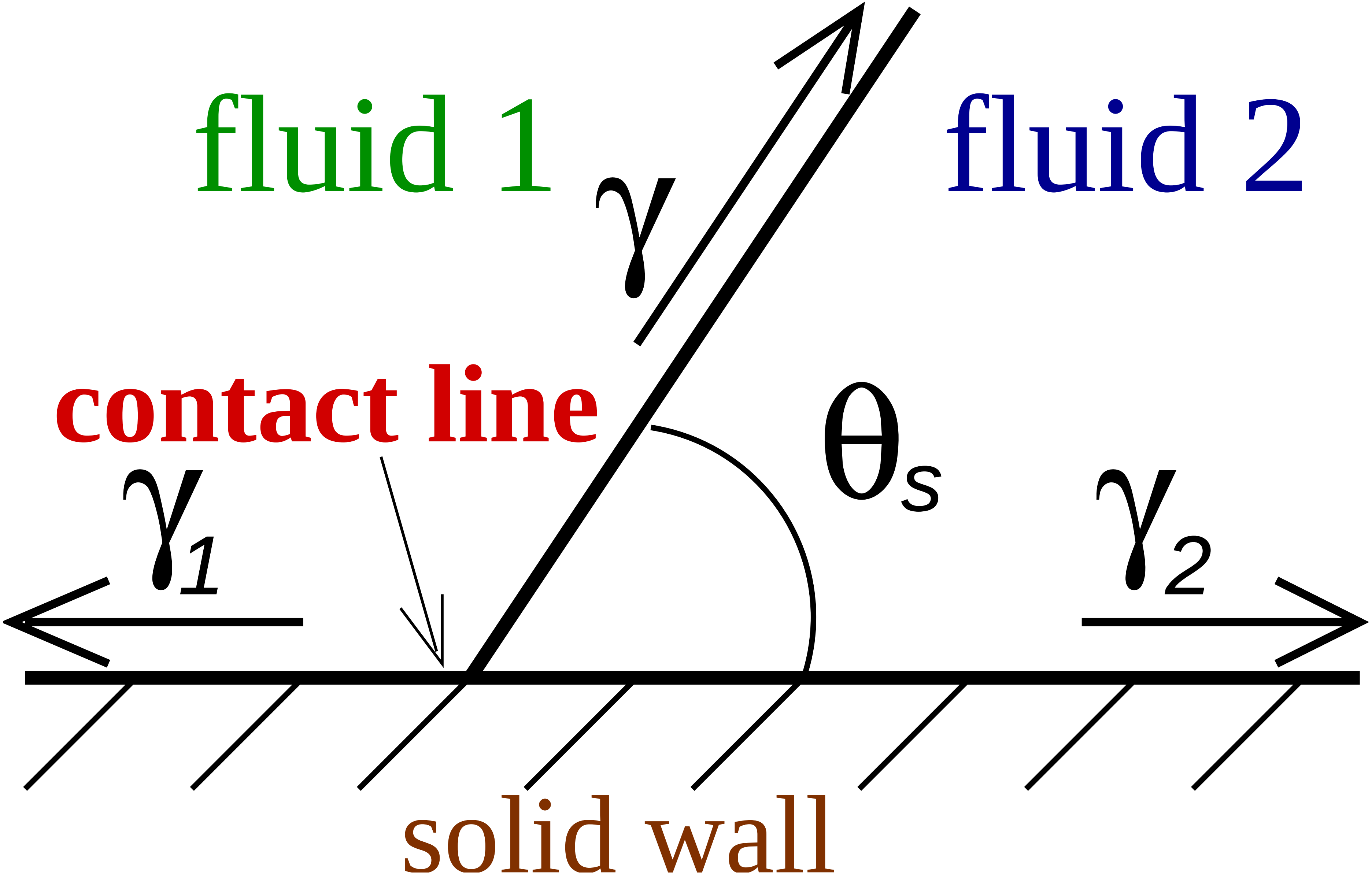
$$v_{\tau}^{slip} = l_s \cdot \dot{\gamma}$$

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

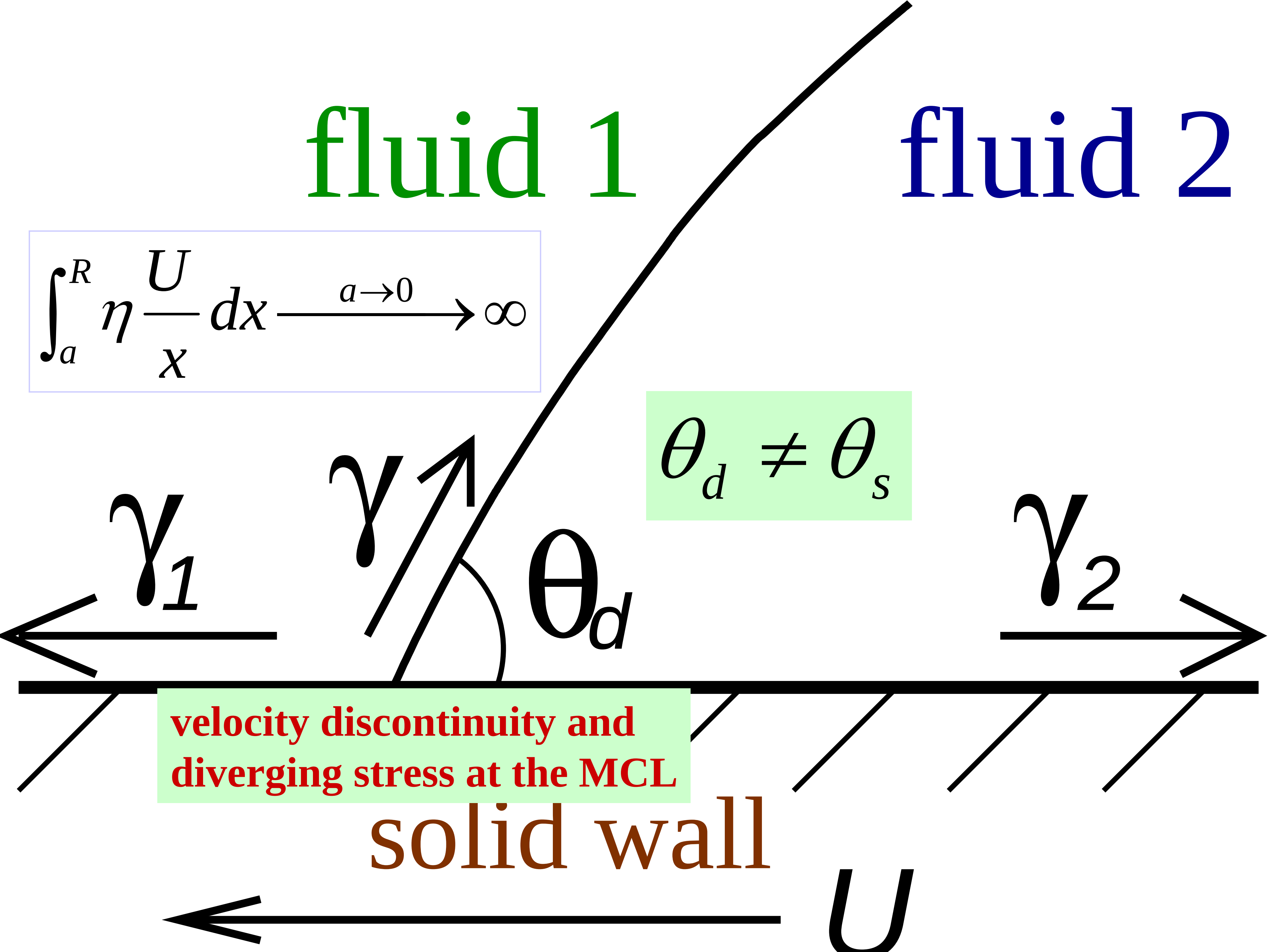
l_s: ***slip length***, from nano- to micrometer

Practically, **no slip** in macroscopic flows

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



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



fluid 1
fluid 2
$\int_a^R \eta \frac{U}{x} dx \xrightarrow{a \to 0} \infty$
$\theta_d \neq \theta_s$
γ_1
γ
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);

Ren & E, preprint

- 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, PRL **93**, 094501 (2004)

Dussan and Davis, J. Fluid Mech. **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).

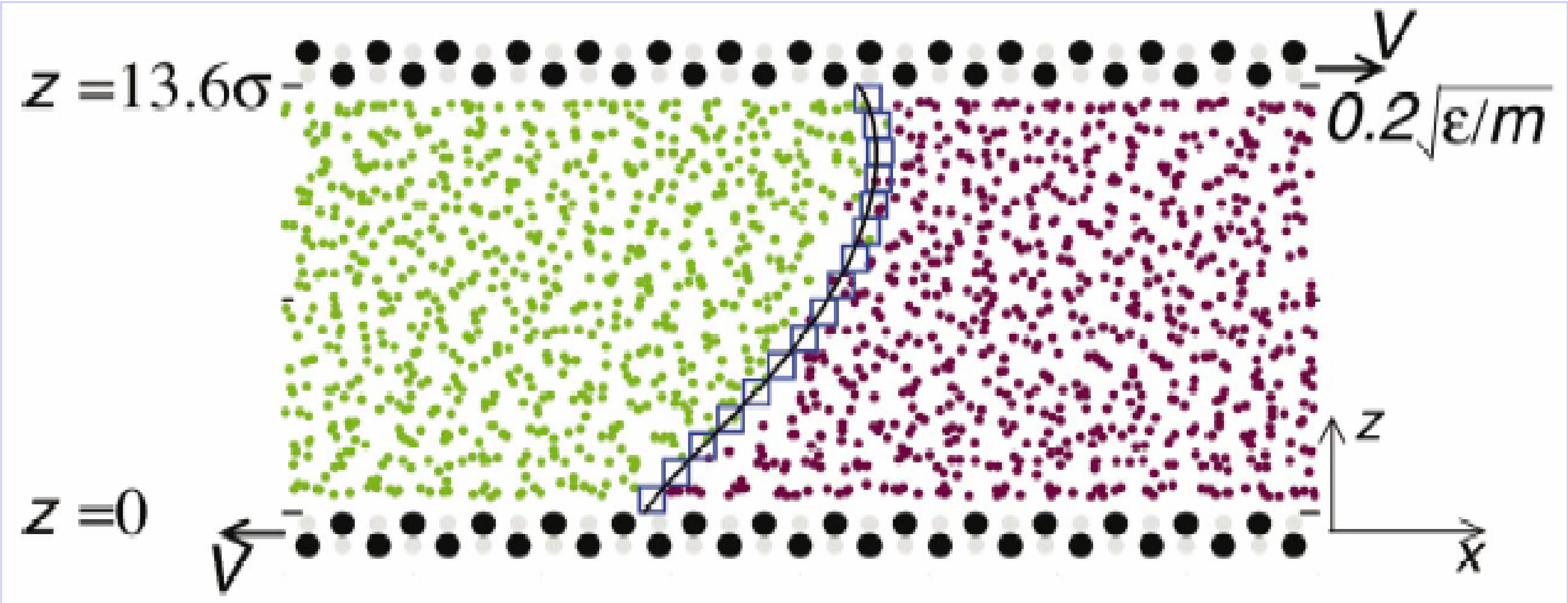
a) To construct **a continuum hydrodynamic model** by removing conditions (3) and (4).

b) To make comparison with molecular dynamics simulations

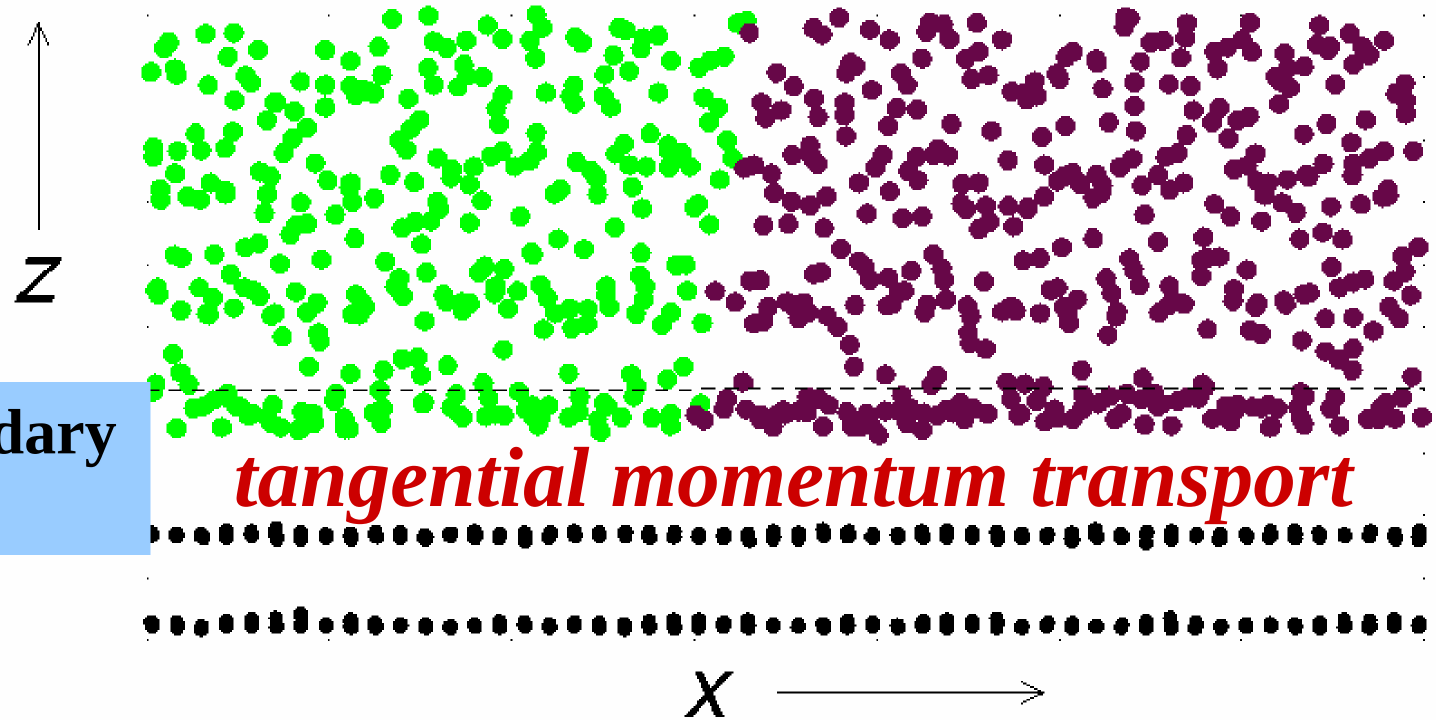
Molecular dynamics simulations
for two-phase Couette flow

- **Fluid-fluid molecular interactions**
- **Fluid-solid molecular interactions**
- **Densities (liquid)**
- **Solid wall structure (fcc)**
- **Temperature**

- ***System size***
- ***Speed of the moving walls***



Measurement at Solid–Fluid Boundary



boundary layer

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

as functions of x

Stress from the rate of tangential momentum transport per unit area

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

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

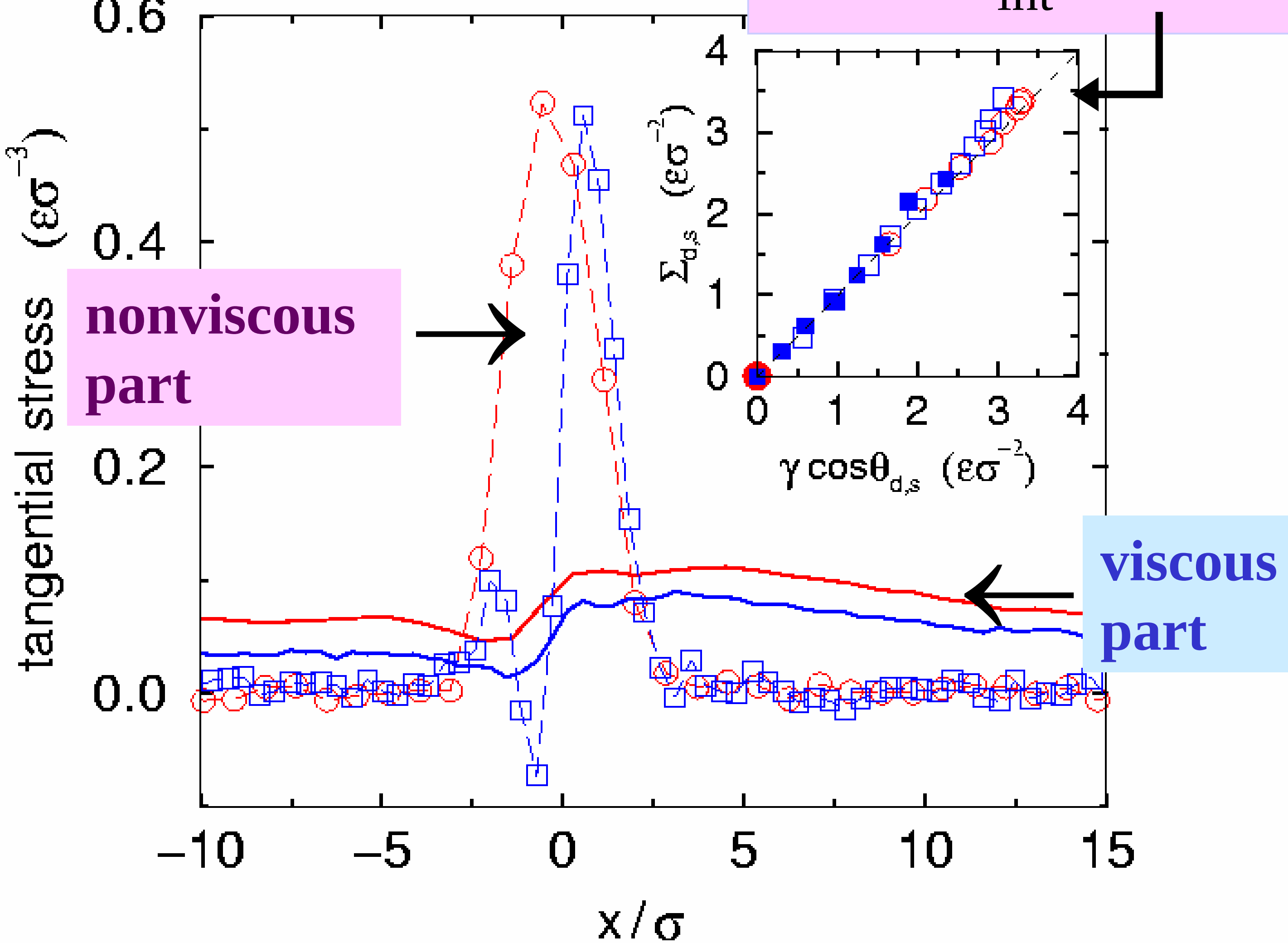
static Young component subtracted
>>> uncompensated Young stress

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

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

$$\int_{\text{int}} dx \tilde{\sigma}_{zx}^Y = \gamma \cos\theta_d + \gamma_2 - \gamma_1 \neq 0$$

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



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 ϕ (B.C.)**

supplemented with

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

$v_n = 0$ *impermeability B.C.*

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

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

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

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

1. Incompressible Newtonian fluid
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3. Impenetrable fluid-fluid interface
4. No-slip boundary condition

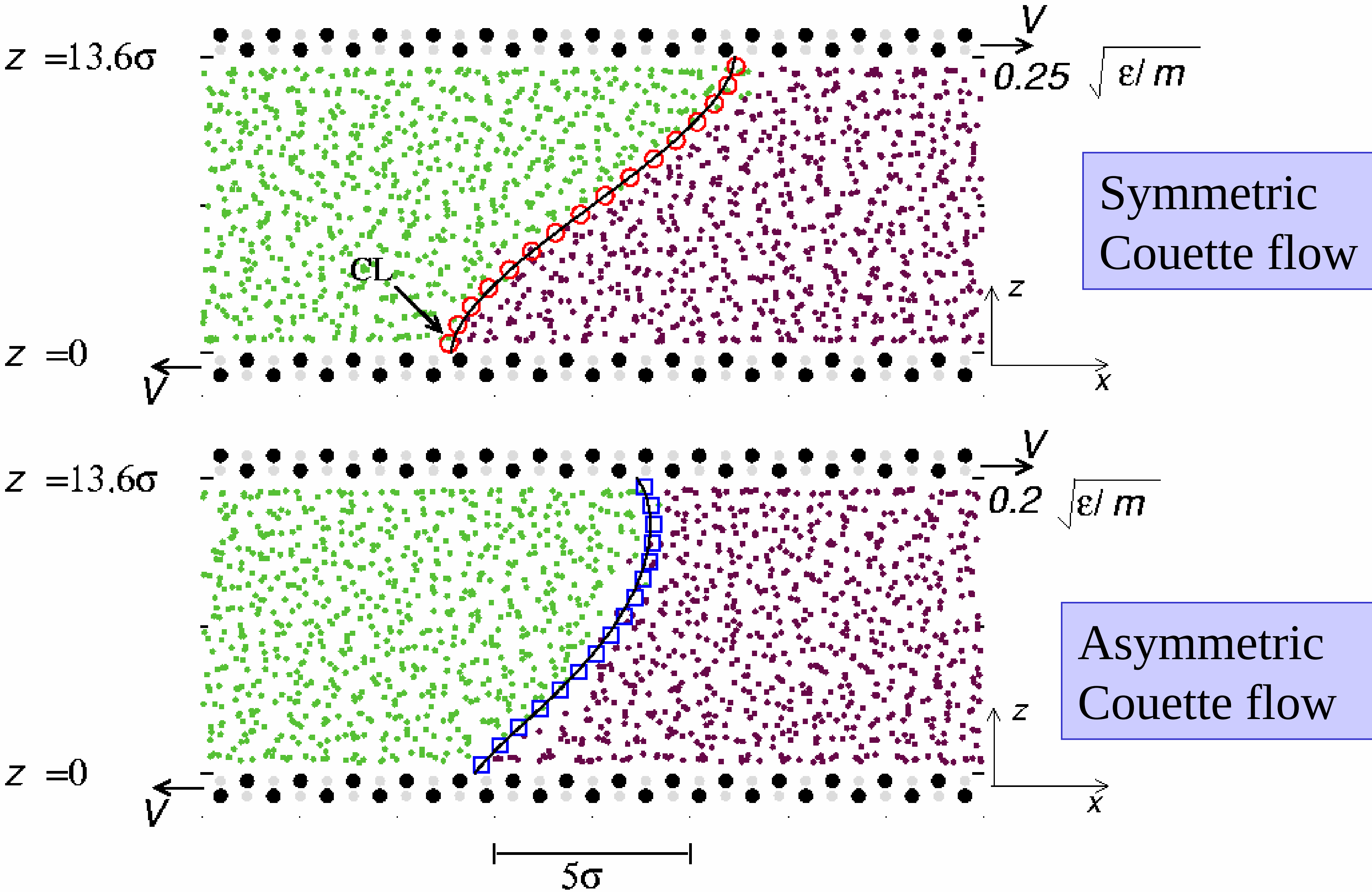
Condition (3) >>> Diffusion across the fluid-fluid interface

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

Condition (4) >>> GNBC

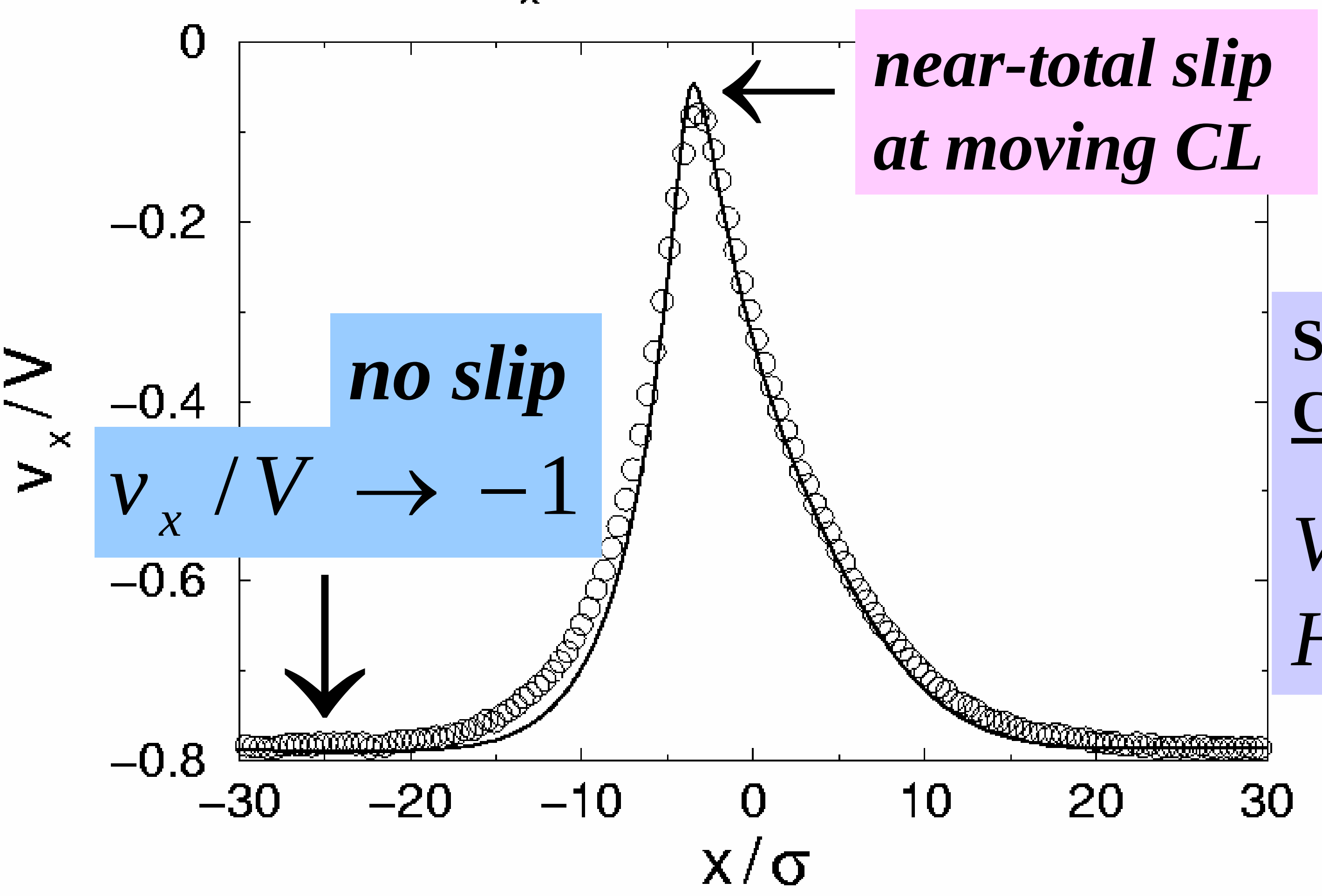
Stress singularity, i.e., infinite tangential force exerted by the fluid on the solid surface, is removed.

molecular positions projected onto the *xz* plane



Diffusion versus **Slip** in MD

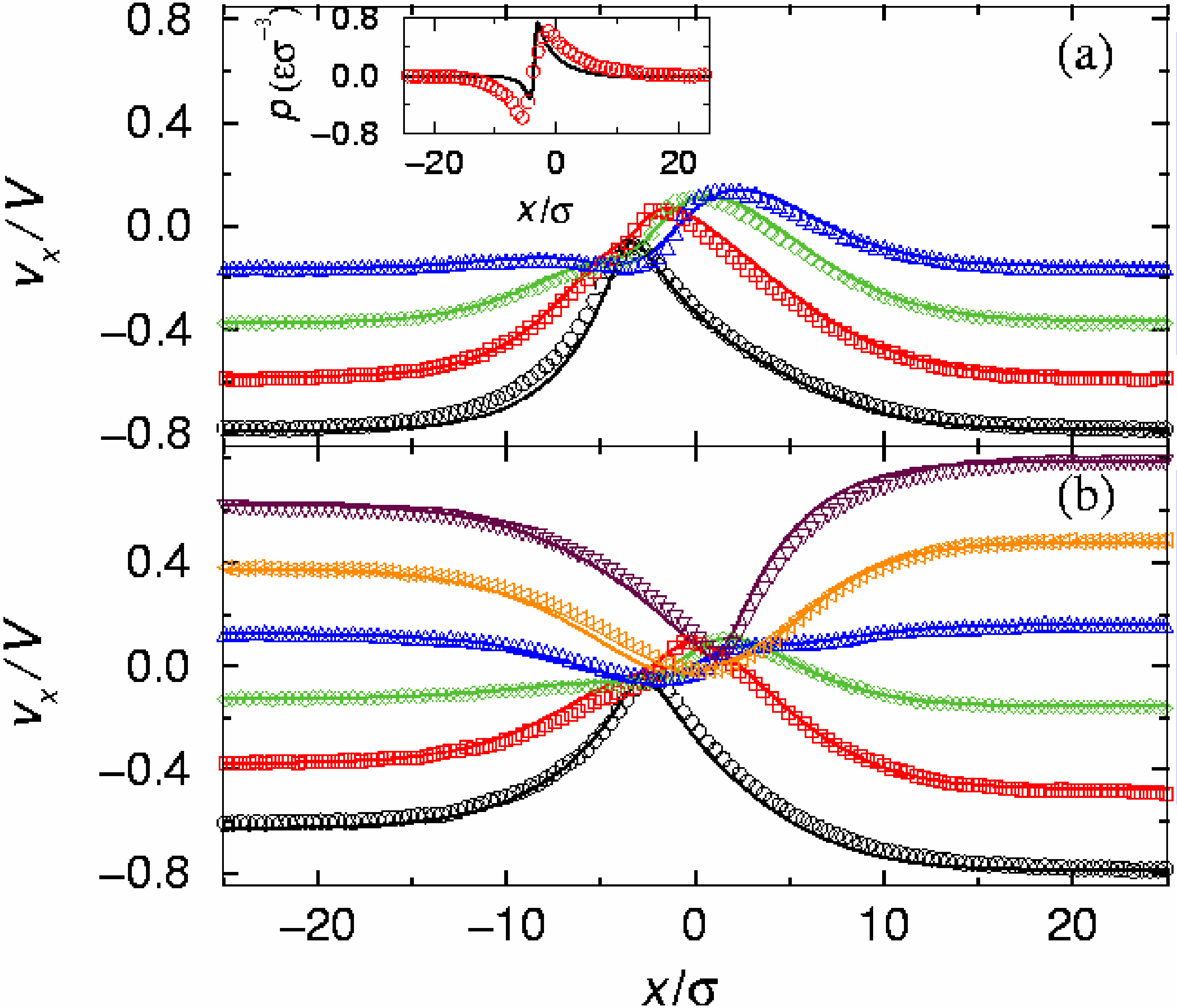
Boundary layer velocity profile
v_x=0 for total slip



<u>Symmetric Couette flow</u>

V=0.25
H=13.6

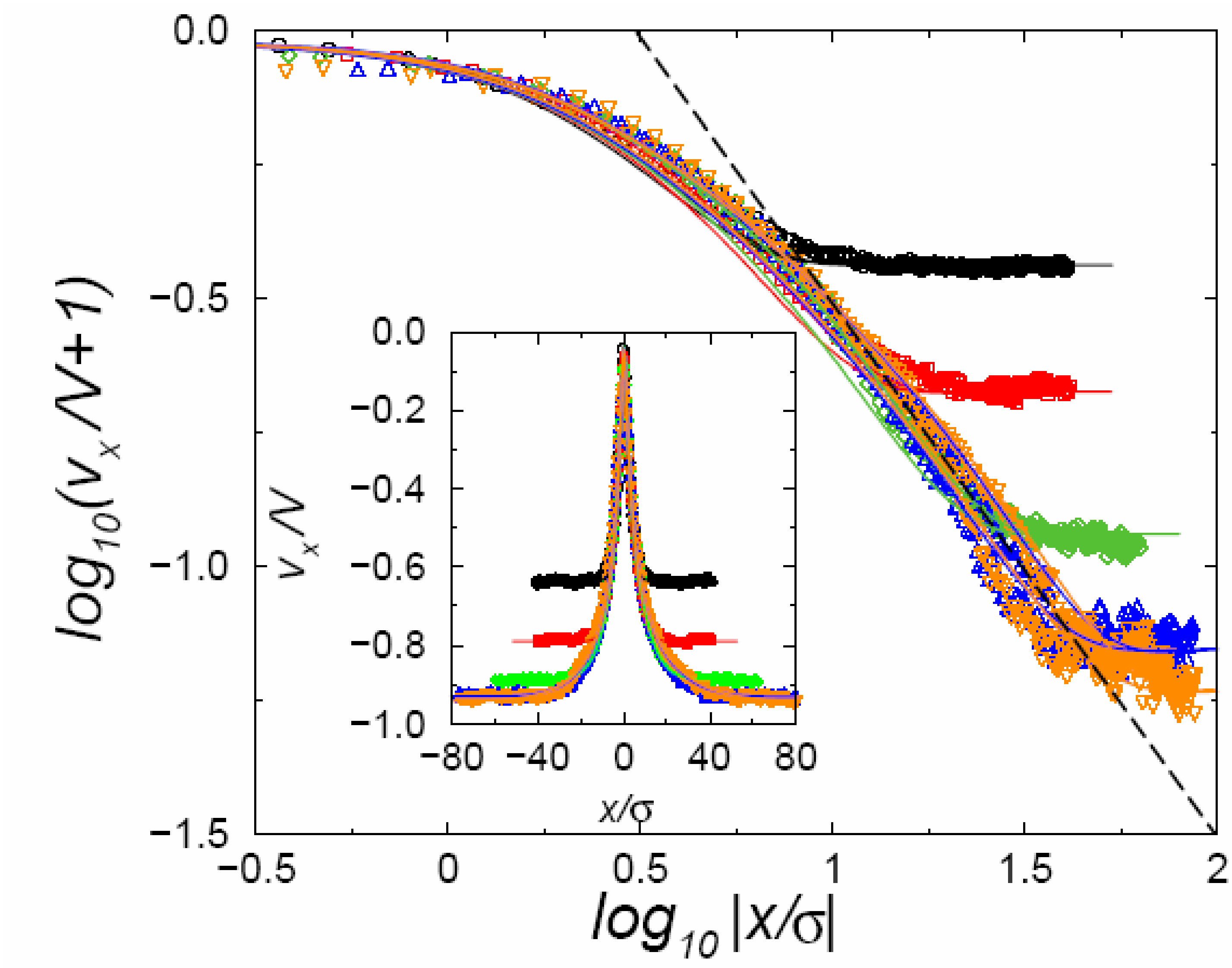
$v_x(x)$ *profiles at different z levels*



symmetric
Couette flow
V=0.25
H=13.6

asymmetricC
Couette flow
V=0.20
H=13.6

Power-law decay of partial slip away from the MCL, observed in driven cavity flows as well.



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

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

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

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

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

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

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