Molecular hydrodynamics of the moving contact line

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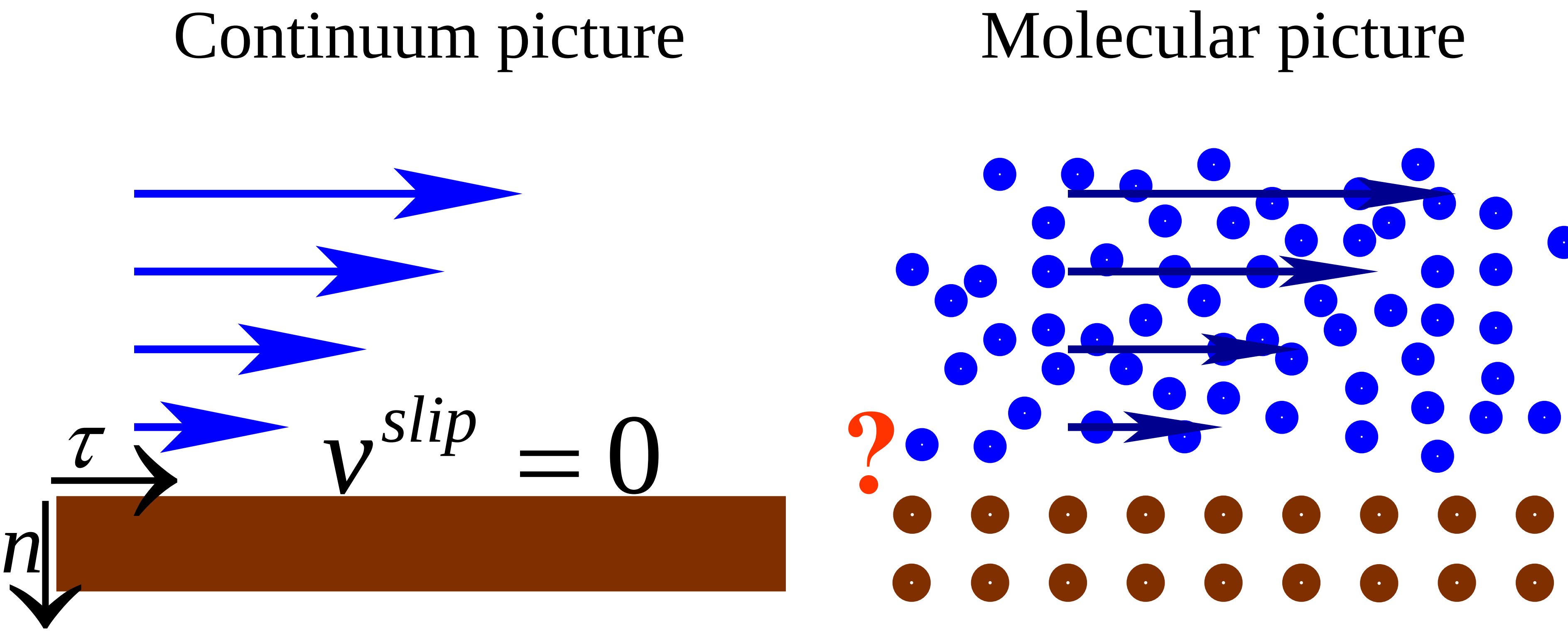
SISSA – Trieste – Italy, May 2007

- 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 (entropy production)

Wetting phenomena:
All the real world complexities we can have!

Moving contact line:
All the simplifications we can make and
all the simulations, *molecular and continuum*,
we can carry out! ***Numerical experiments***

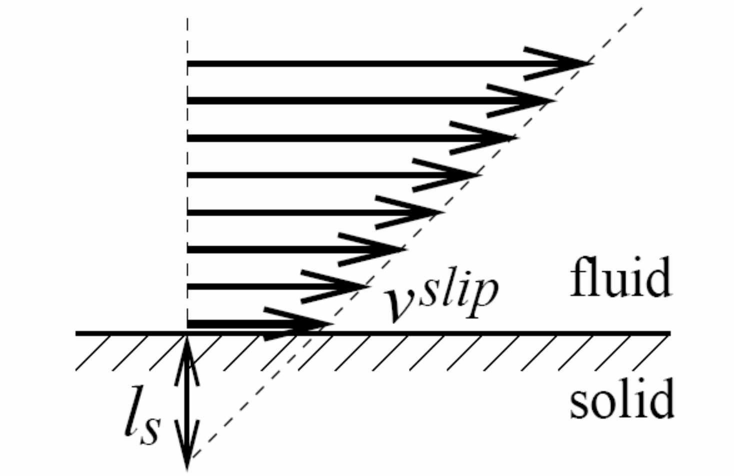
Offer a minimal model with solution to
this classical fluid mechanical problem,
under a general principle governing
thermodynamic irreversible processes



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

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

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



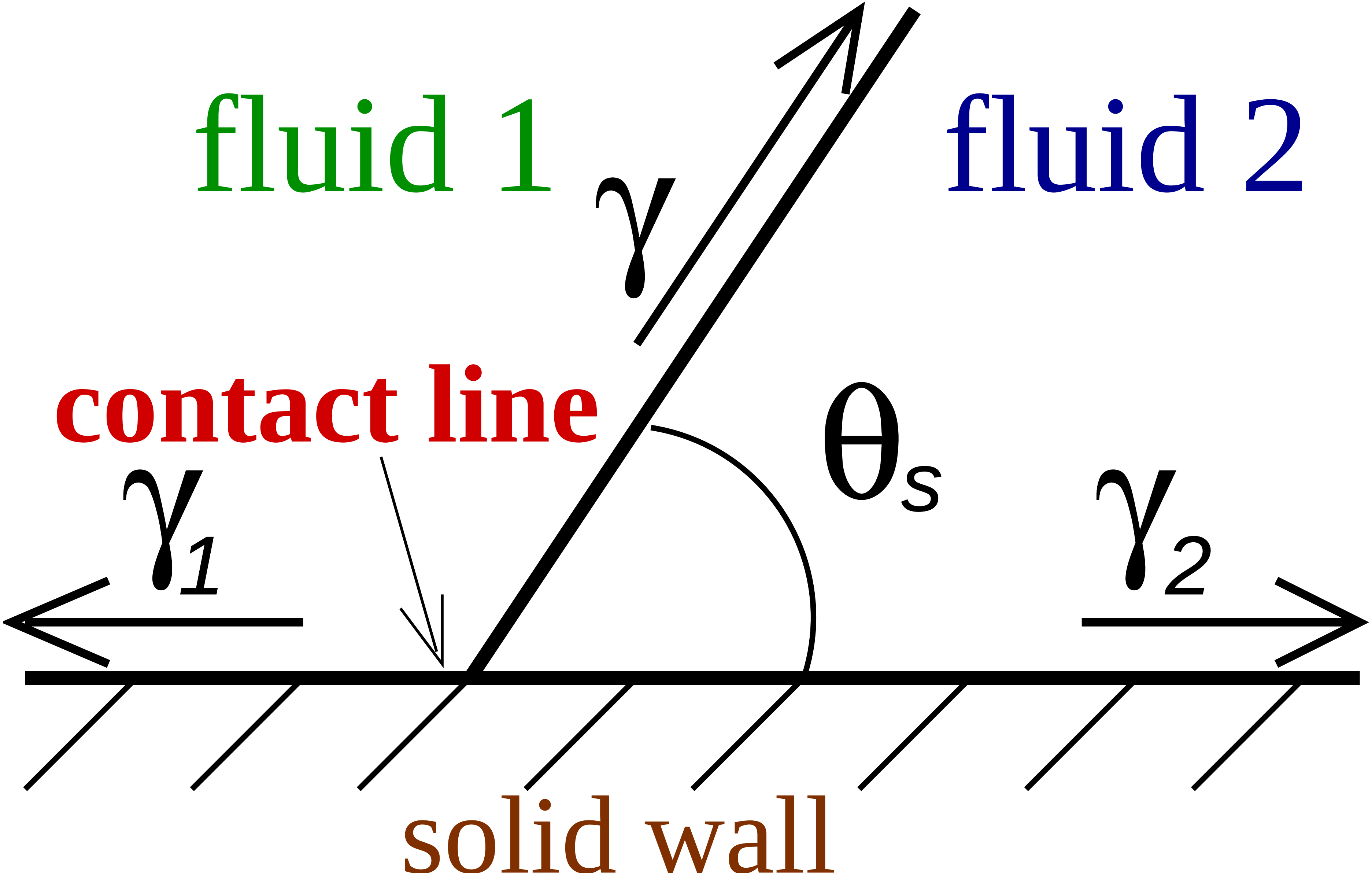
$$v_{\tau}^{slip} = l_s \cdot \dot{\gamma}$$

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

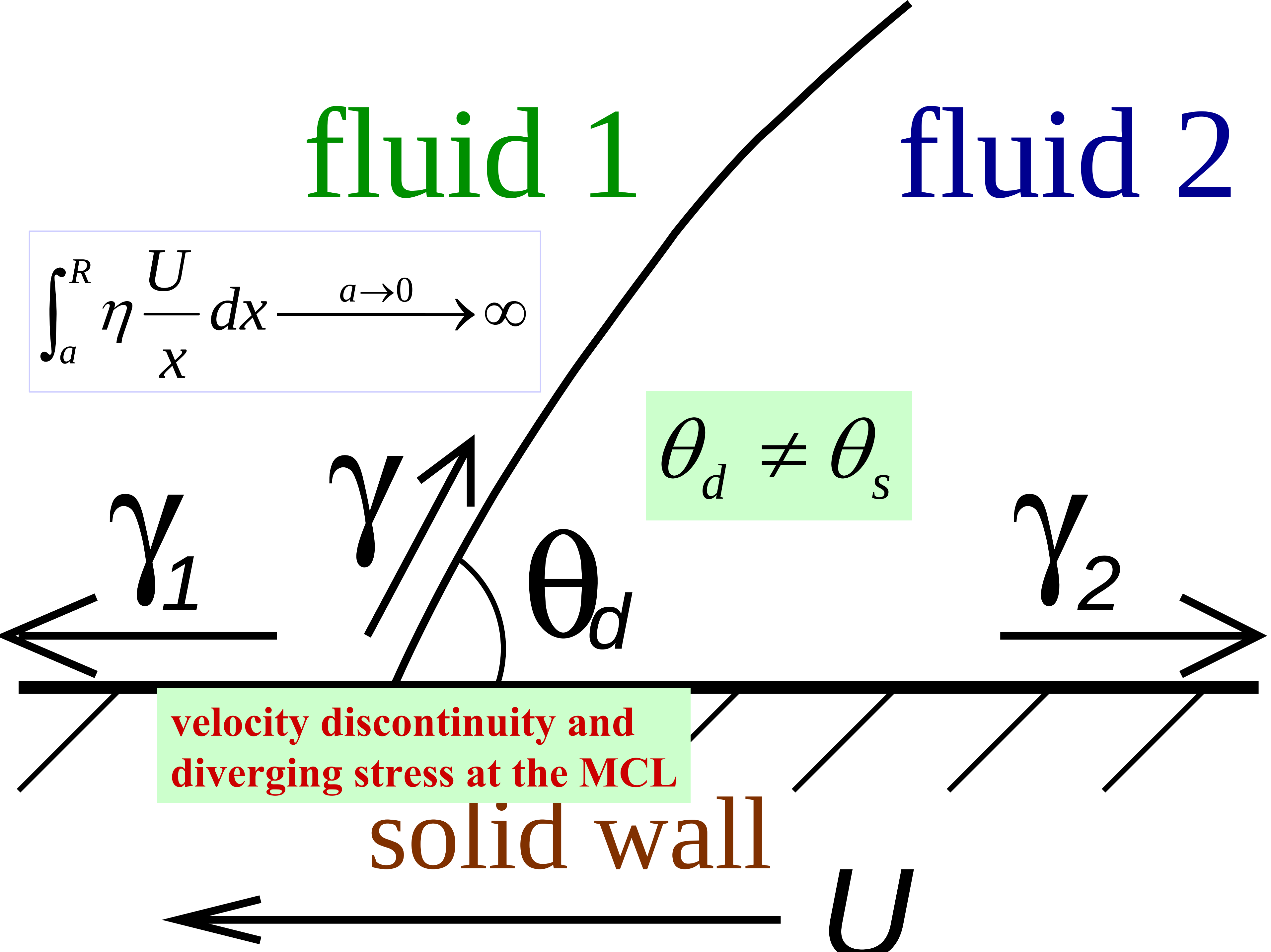
l_s: ***slip length***, from nano- to micrometer

Practically, **no slip** in macroscopic flows

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

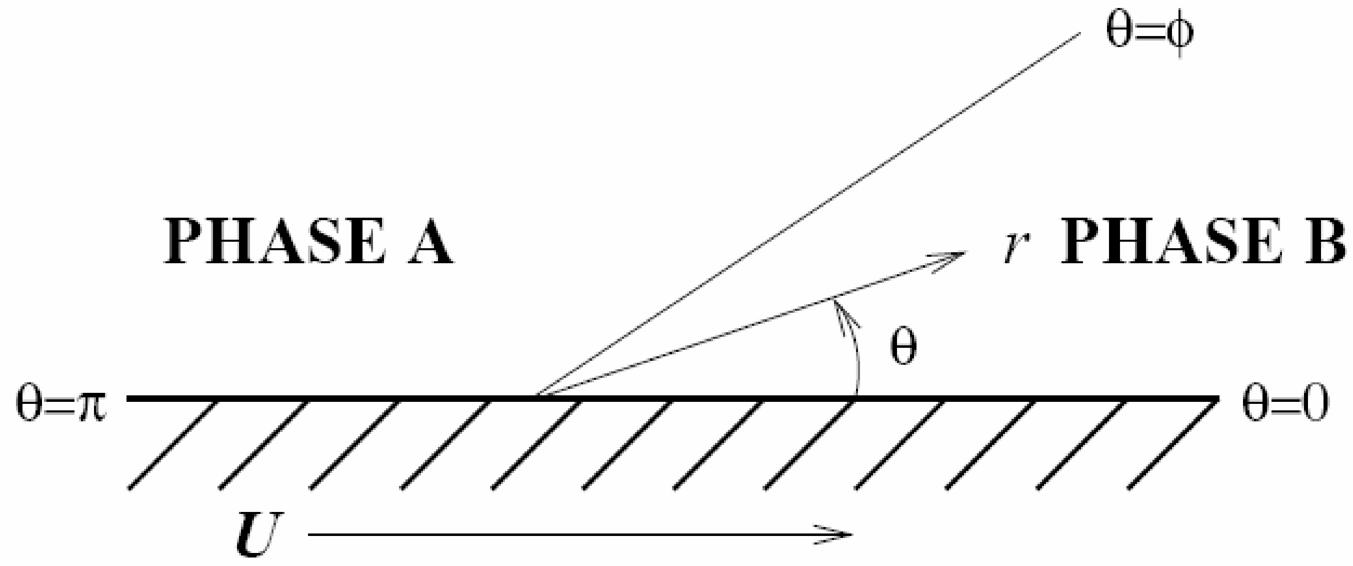


Young's equation (1805): $\gamma \cos\theta_s + \gamma_2 = \gamma_1$



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

The Huh-Scriven model



The similarity solution of the biharmonic equation **for 2D flow**

$\nabla^2(\nabla^2\psi) = 0$ (linearized Navier-Stokes equation)

$$\psi(r,\theta) = r(a\sin\theta + b\cos\theta + c\theta\sin\theta + d\theta\cos\theta)$$

8 coefficients in A and B, determined by 8 boundary conditions

Shear stress and pressure vary as $1/r$

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 condition (3) and/or (4).

b) To make comparison with molecular dynamics simulations

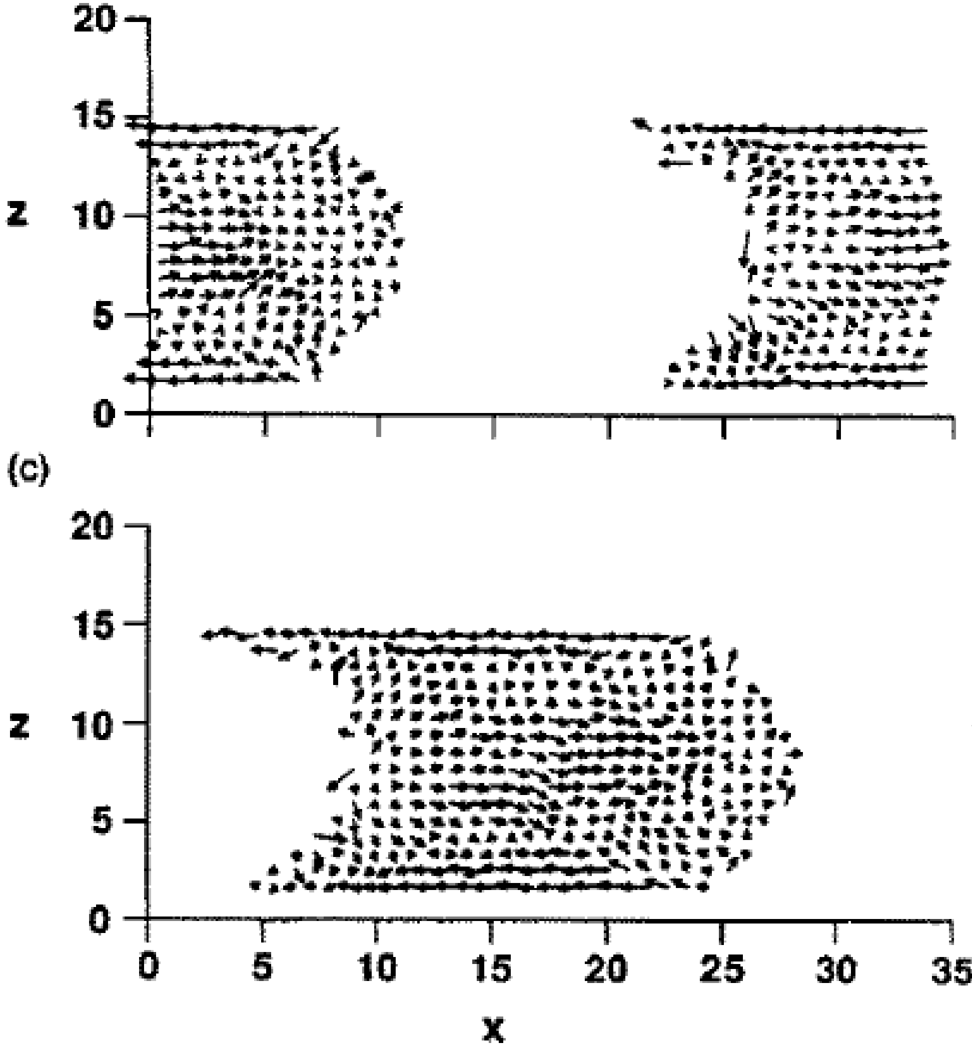
Numerical experiments done for
this classic fluid mechanical problem

- Koplik, Banavar and Willemsen, PRL (1988)
- Thompson and Robbins, PRL (1989)
- Slip observed in the vicinity of the MCL
- Boundary condition ???
- **Continuum deduction of molecular dynamics !**

Molecular dynamics of fluid flow at solid surfaces

Joel Koplik,[a] Jayanth R. Banavar,[b] and Jorge F. Willemsen
Schlumberger-Doll Research, Old Quarry Road, Ridgefield, Connecticut 06877-4108

(Received 6 September 1988; accepted 12 January 1989)

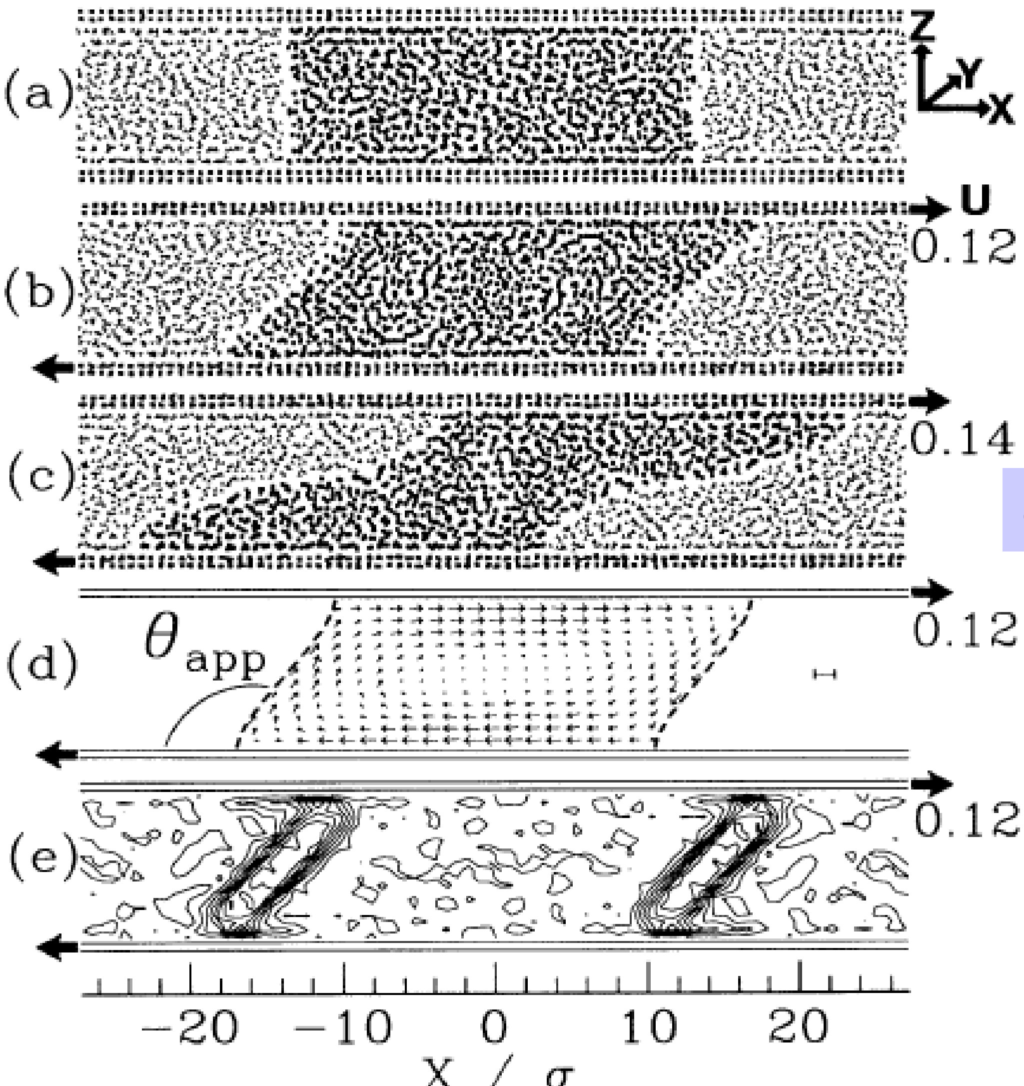


Immiscible two-phase Poiseuille flow

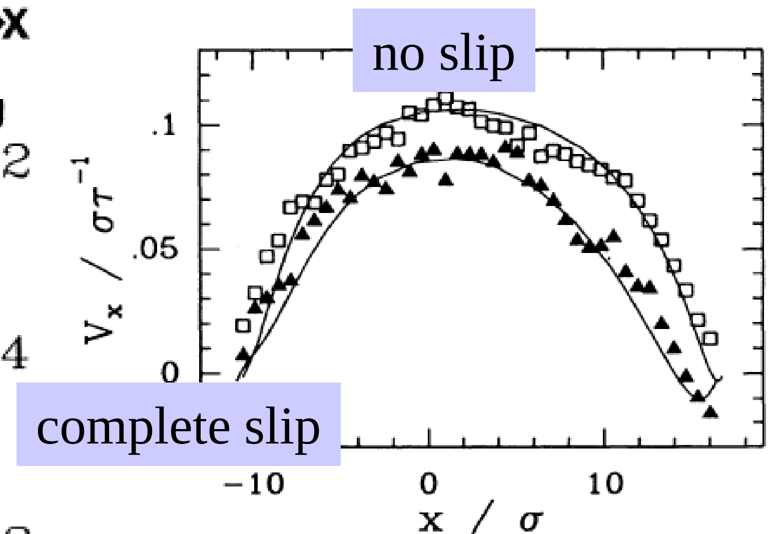
The walls are moving to the left in this reference frame, and away from the contact line the fluid velocity near the wall coincides with the wall velocity. **Near the contact lines the no-slip condition appears to fail**, however.

Simulations of Contact-Line Motion: Slip and the Dynamic Contact Angle

Peter A. Thompson and Mark O. Robbins
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 7 February 1989)



Slip profile



The discrepancy between the microscopic stress and $\partial V_x / \partial z$ suggests **a breakdown of local hydrodynamics**.

The kinetic model by Blake and Haynes: The role of interfacial tension

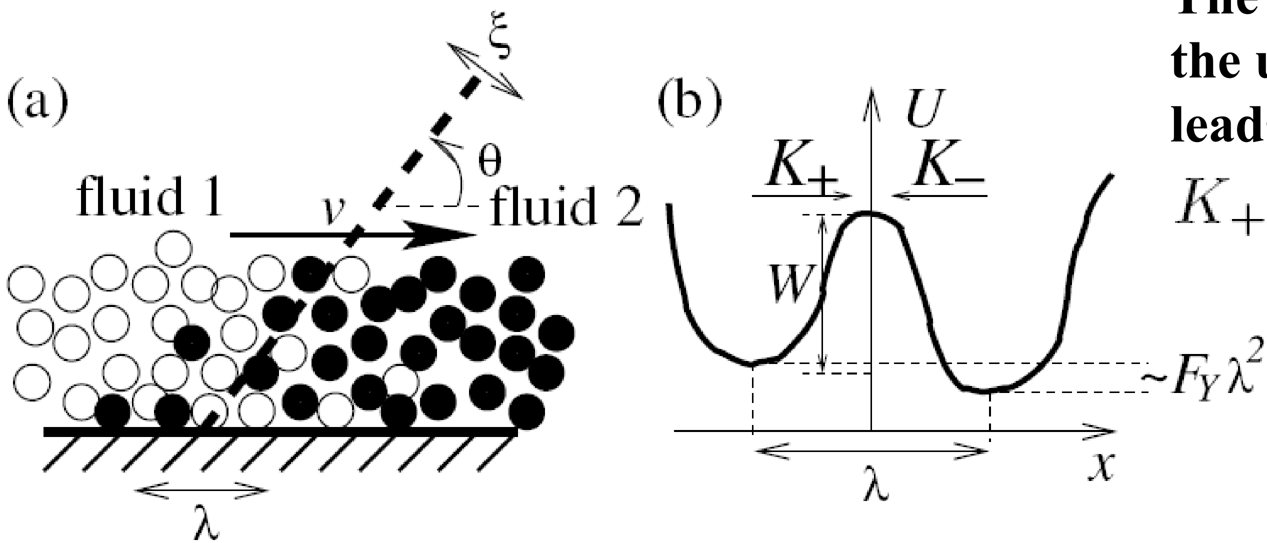
A fluctuating three phase **zone**.

Adsorbed molecules of one fluid interchange with those of the other fluid.

In equilibrium the net rate of exchange will be zero.

For a three-phase zone moving relative to the solid wall, the net displacement, is due to a nonzero net rate of exchange, driven by the unbalanced Young stress

$$\gamma \cos\theta_d + \gamma_2 - \gamma_1 \neq 0$$



The energy shift due to the unbalanced Young stress leads to two different rates K_+ and K_-:

$$K_{\pm} = k \exp\left[-\frac{1}{k_B T}\left(W \mp \frac{1}{2}F_Y\lambda^2\right)\right], \quad v = \lambda(K_+ - K_-) \propto \sinh\left(F_Y\lambda^2/2k_BT\right)$$

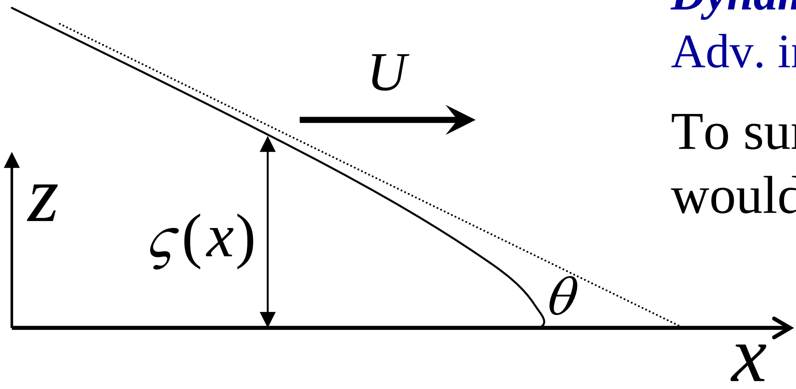
Two classes of models proposed to describe the contact line motion:

An Eyring approach:

Molecular adsorption/desorption processes at the contact line (three-phase zone);
Molecular dissipation at the tip is dominant.
T. D. Blake and J. M. Haynes, ***Kinetics of liquid/liquid displacement***, J. Colloid Interf. Sci. **30,** 421 (1969).

A hydrodynamic approach:

Dissipation dominated by **viscous shear flow** inside the wedge;
For wedges of small (apparent) contact angle, a lubrication approximation used to simplify the calculations;
A (molecular scale) cutoff introduced to remove the logarithmic singularity in viscous dissipation.
F. Brochard-Wyart and P. G. De Gennes, ***Dynamics of partial wetting***, Advances in Colloid and Interface Science **39**, 1 (1992).



F. Brochard-Wyart and P. G. De Gennes, *Dynamics of partial wetting*, Adv. in Colloid and Interface Sci. **39**, 1 (1992).

To summarize: a complete discussion of the dynamics would in principle require both terms in Eq. (21).

$$T\dot{S} = \frac{3\eta}{\theta} U^2 \ln \frac{x_{\max}}{x_{\min}} + CU^2 \qquad (21)$$

lubrication approximation: $v_x(z) = \dfrac{3U}{2\varsigma^2}(2\varsigma z - z^2)$

hydrodynamic term for the viscous dissipation in the wedge $\eta \int_{x_{\min}}^{x_{\max}} dx \int_{o}^{\varsigma(x)} dz (\partial_z v_x)^2$

molecular term due to the kinetic adsorption/desorption CU^2, $C = \exp\left(\dfrac{W}{k_B T}\right)\dfrac{k_B T}{\kappa \lambda^3}$

Wedge: Molecular cutoff $x_{\min}$ introduced to the viscous dissipation

DISSIPATION

Tip: Molecular dissipative coefficient C from kinetic mechanism of <u>contact-line **slip**</u>

No-slip boundary condition ?

Apparent Violation seen from the ***moving/slipping*** contact line

Infinite Energy Dissipation (unphysical singularity)

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

No-slip boundary condition breaks down !

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

  Qian, Wang & Sheng, Phys. Rev. E **68**, 016306 (2003)

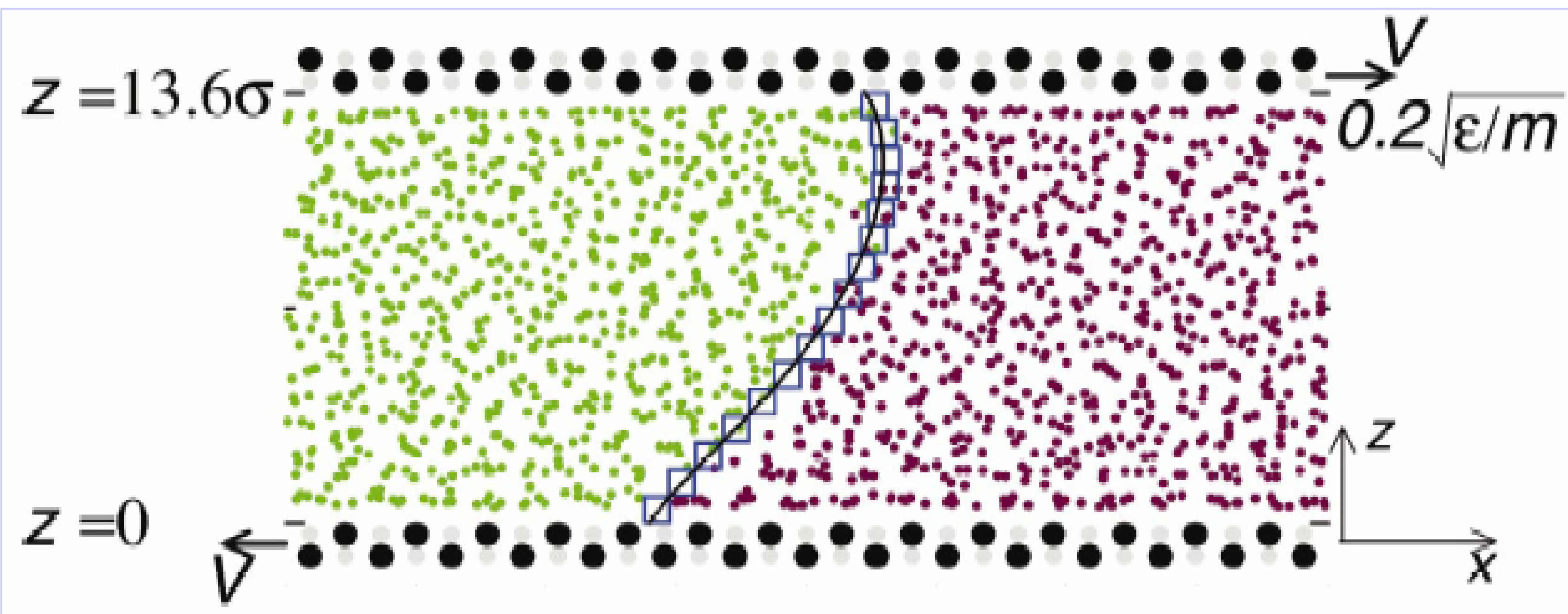
- If ***slip*** occurs within a length scale S in the vicinity of the contact line, then what is the magnitude of S ?

  Qian, Wang & Sheng, Phys. Rev. Lett. **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***



Two identical fluids: same density and viscosity,
but in general different fluid-solid interactions

Smooth solid wall:
solid atoms put on a crystalline structure

No contact angle hysteresis!

Modified Lennard-Jones Potentials

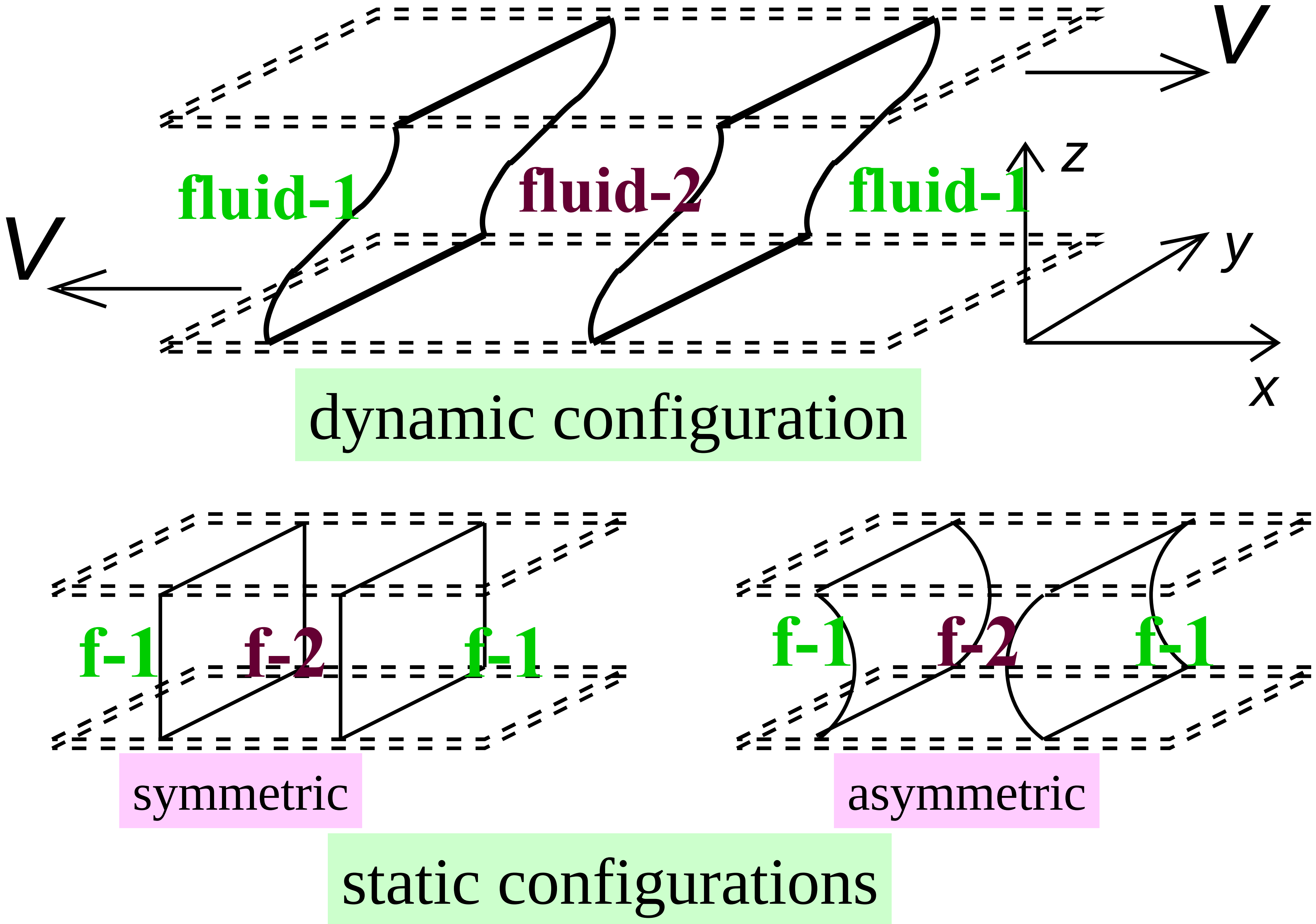
$$U_{ff} = 4\varepsilon[(\sigma / r)^{12} - \delta_{ff}(\sigma / r)^{6}]$$

$$U_{wf} = 4\varepsilon_{wf}[(\sigma_{wf} / r)^{12} - \delta_{wf}(\sigma_{wf} / r)^{6}]$$

$\delta_{ff} = 1$ **for like molecules**

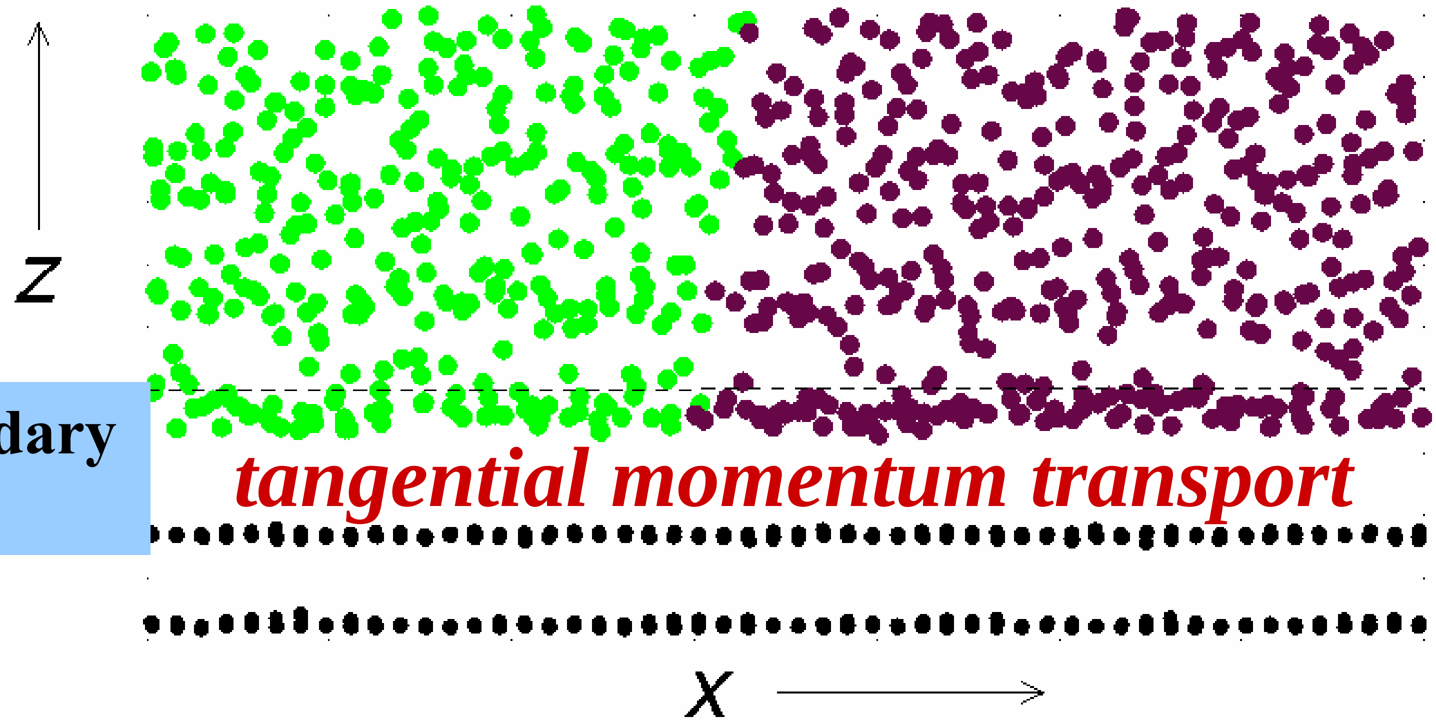
$\delta_{ff} = -1$ **for molecules of different species**

δ_{wf} **for *wetting* property of the fluid**



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

Measurement at Solid–Fluid Boundary

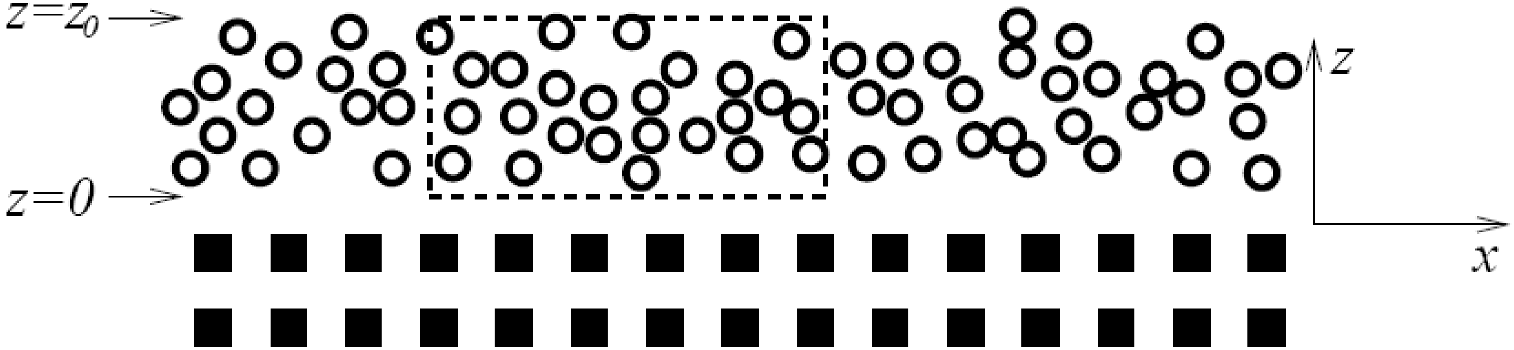


boundary layer

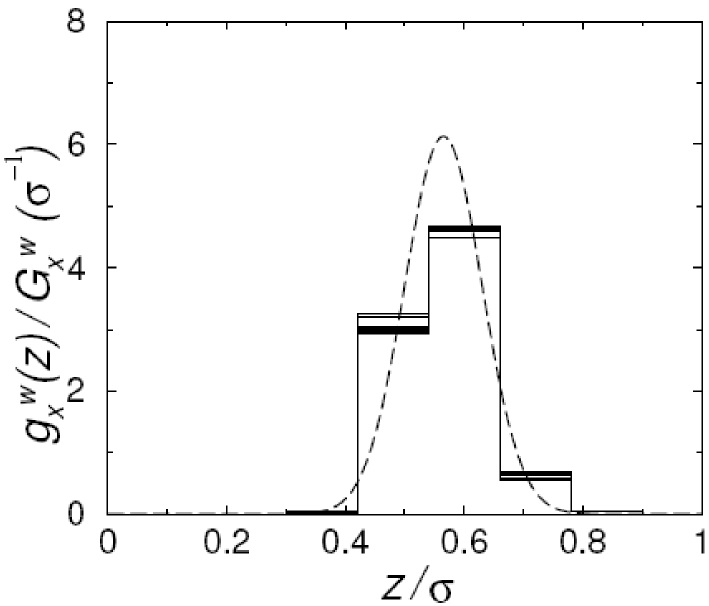
$$G_x^{w}, \quad G_x^{f}, \quad V_x^{slip}$$

as functions of x

Stress from the rate of tangential momentum transport per unit area



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

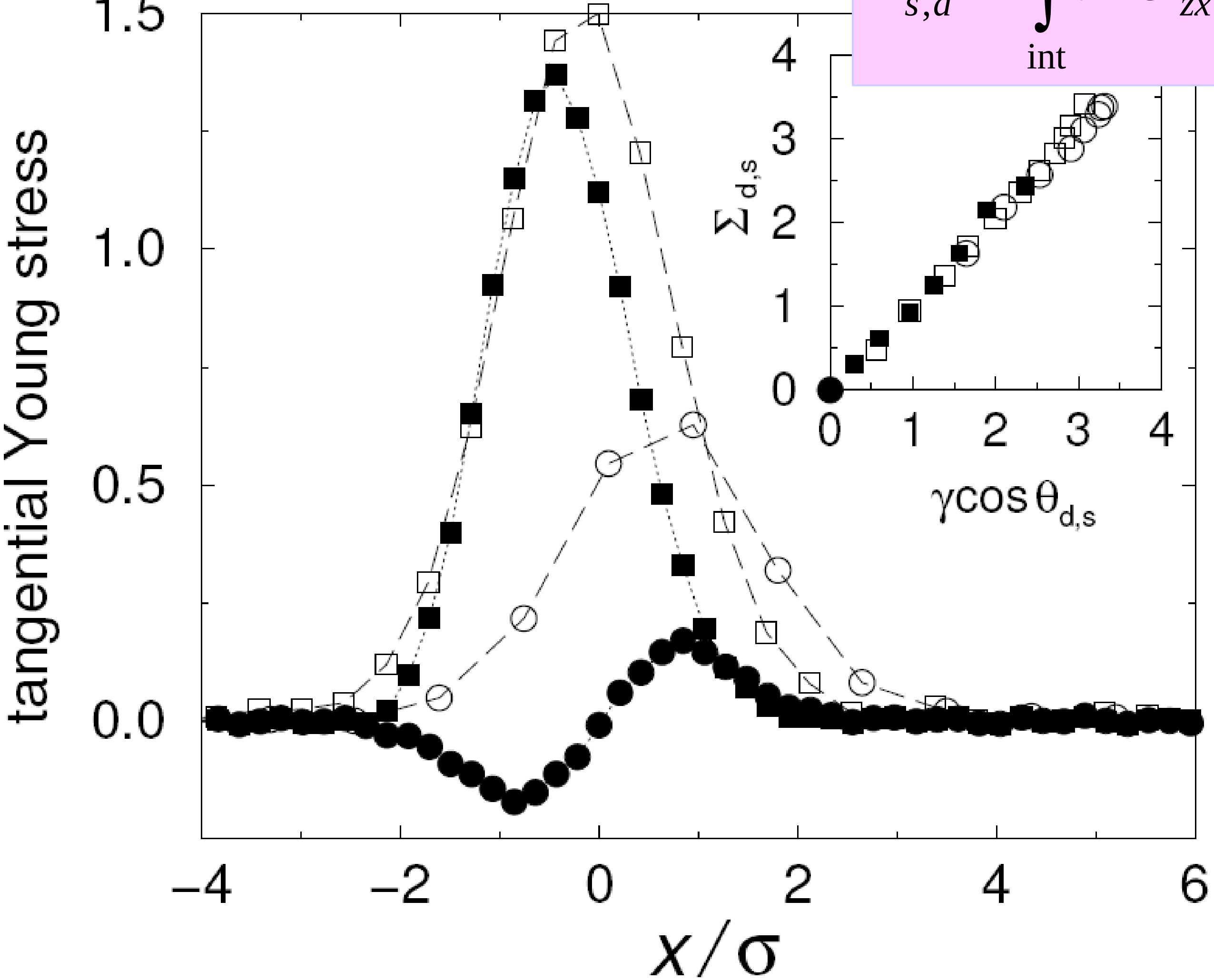
>>> uncompensated Young stress

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

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

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

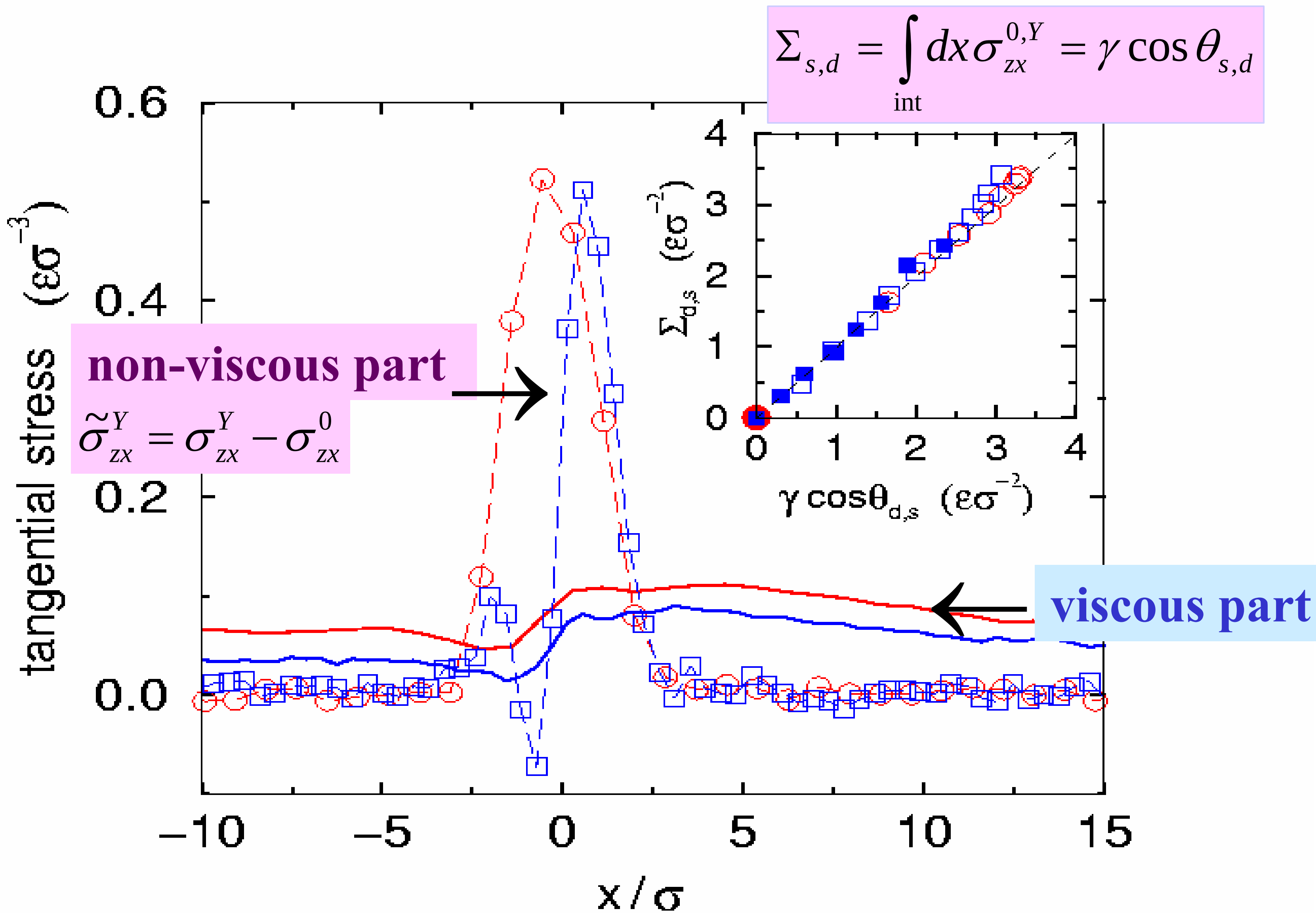
$$\Sigma_{s,d} \equiv \int_{\text{int}} dx\, \sigma_{zx}^{0,Y} = \gamma \cos\theta_{s,d}$$



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



Slip driven by **uncompensated Young stress** + **shear viscous stress**

Uncompensated Young Stress

missed in **Navier B. C.**

- **Net force due to hydrodynamic deviation** from static force balance (Young's equation)

$$\int_{\text{int}} \mathrm{d}x\,\tilde{\sigma}_{zx}^{Y} = \gamma\cos\theta_d - \gamma\cos\theta_s = \gamma\cos\theta_d + \gamma_2 - \gamma_1 \neq 0$$

- **NBC** NOT capable of describing the motion of contact line

- Away from the **CL**, the **GNBC** implies **NBC** for **single phase flows**.

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.*

Phase field modeling for a two-component system

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

interfacial thickness $\xi = \sqrt{K/r}$,

interfacial tension $\gamma = 2\sqrt{2}r^2\xi/3u$,

two homogeneous equilibrium phases

$\phi_{\pm} = \pm\sqrt{r/u} = \pm 1$

total free energy $F = \mathscr{F}[\phi] + \int \mathrm{d}S[\gamma_{fs}(\phi)]$

$$\delta\left\{\mathscr{F}[\phi] + \int \mathrm{d}S[\gamma_{fs}(\phi)]\right\} = \int \mathrm{d}\boldsymbol{r}[\mu\delta\phi] + \int \mathrm{d}S[L\delta\phi],$$

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

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

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

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

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

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

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

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

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
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.

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

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

Condition (4) >>> GNBC

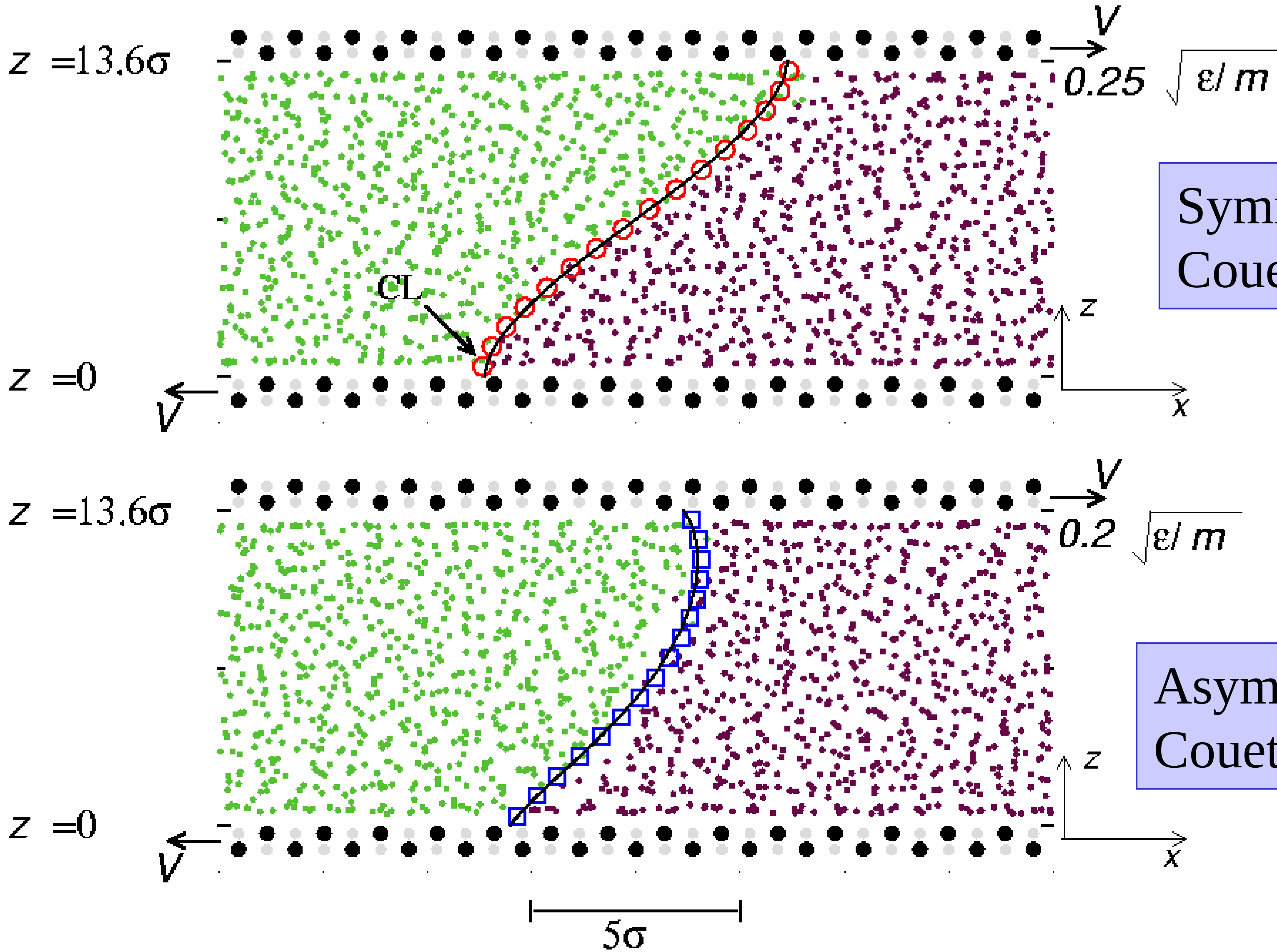
Stress singularity, i.e., infinite tangential force exerted by the fluid on the solid surface, is removed.

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

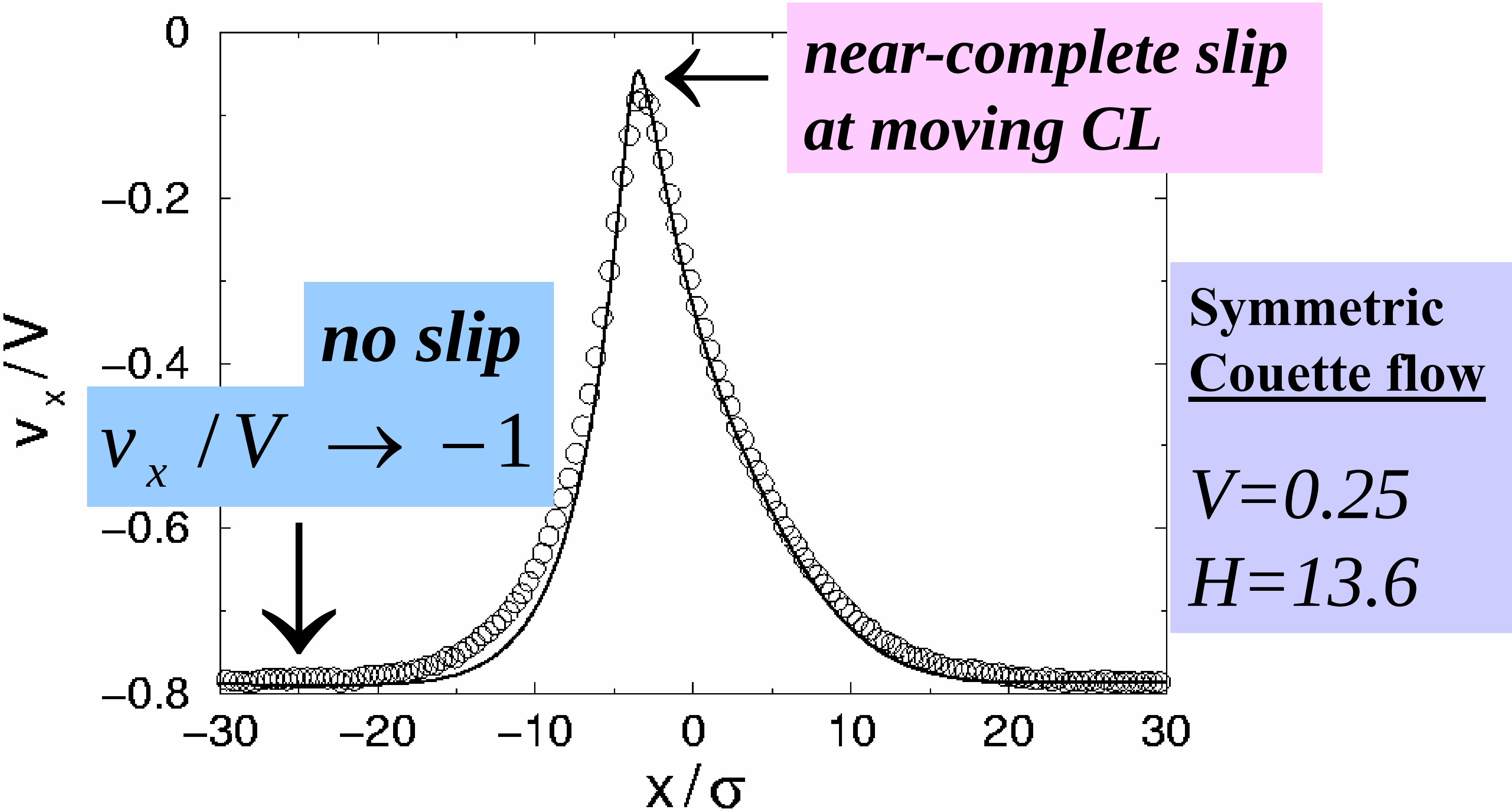


Symmetric Couette flow

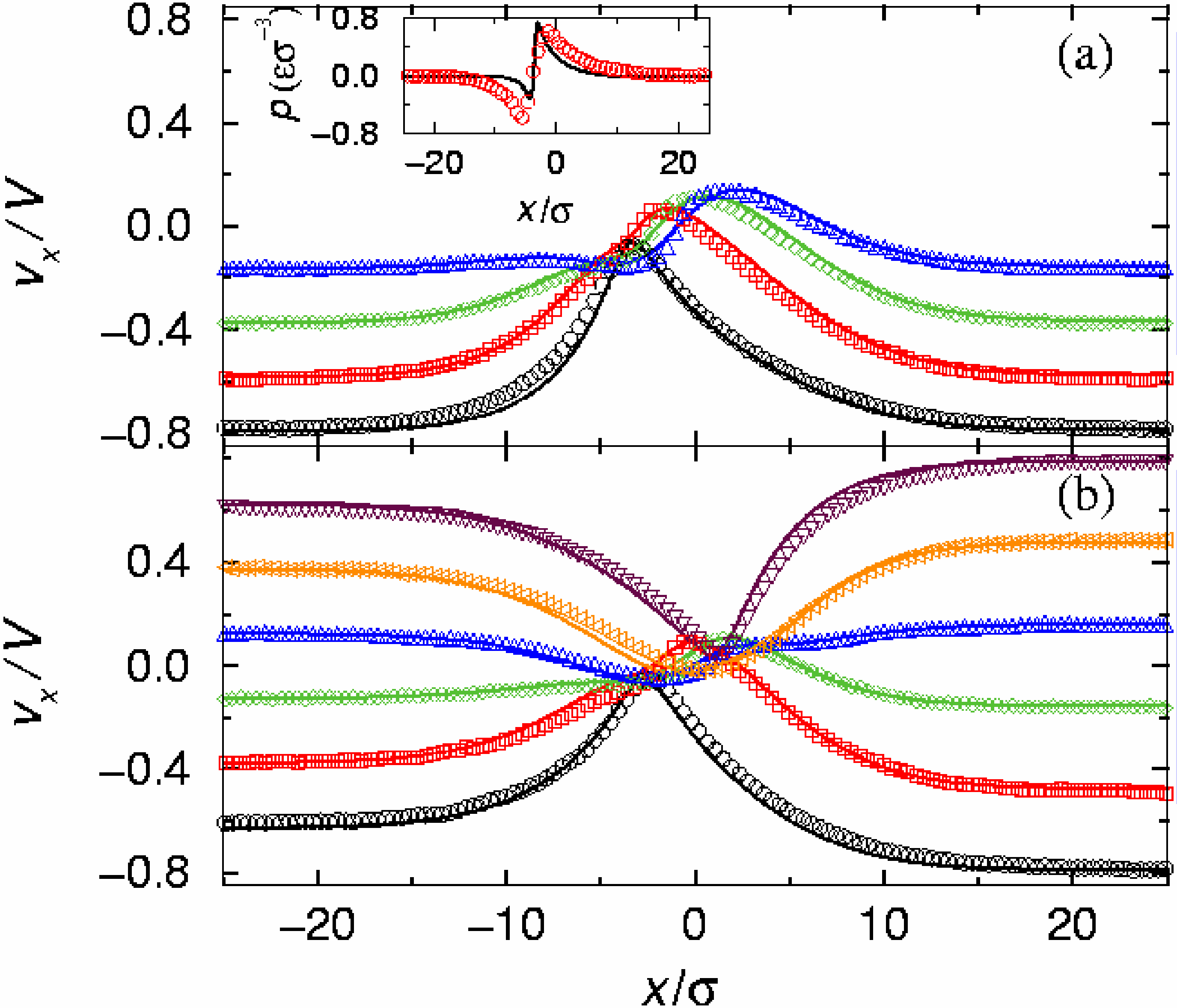
Asymmetric Couette flow

Diffusion versus **Slip** in MD

Boundary layer velocity profile
v_x=0 for total slip



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



symmetric
<u>Couette flow</u>

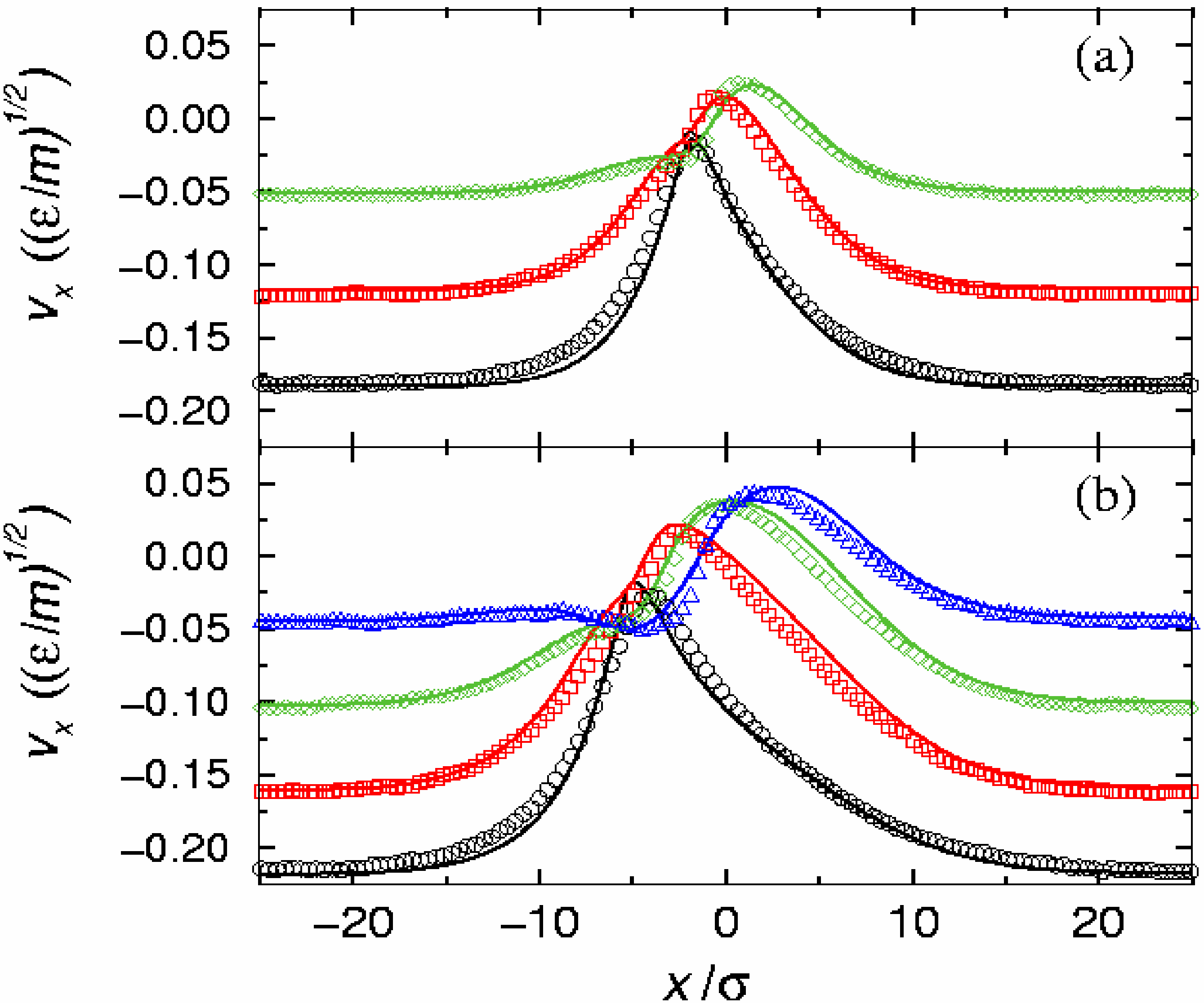
V=0.25

H=13.6

asymmetric<u>C</u>
<u>Couette flow</u>

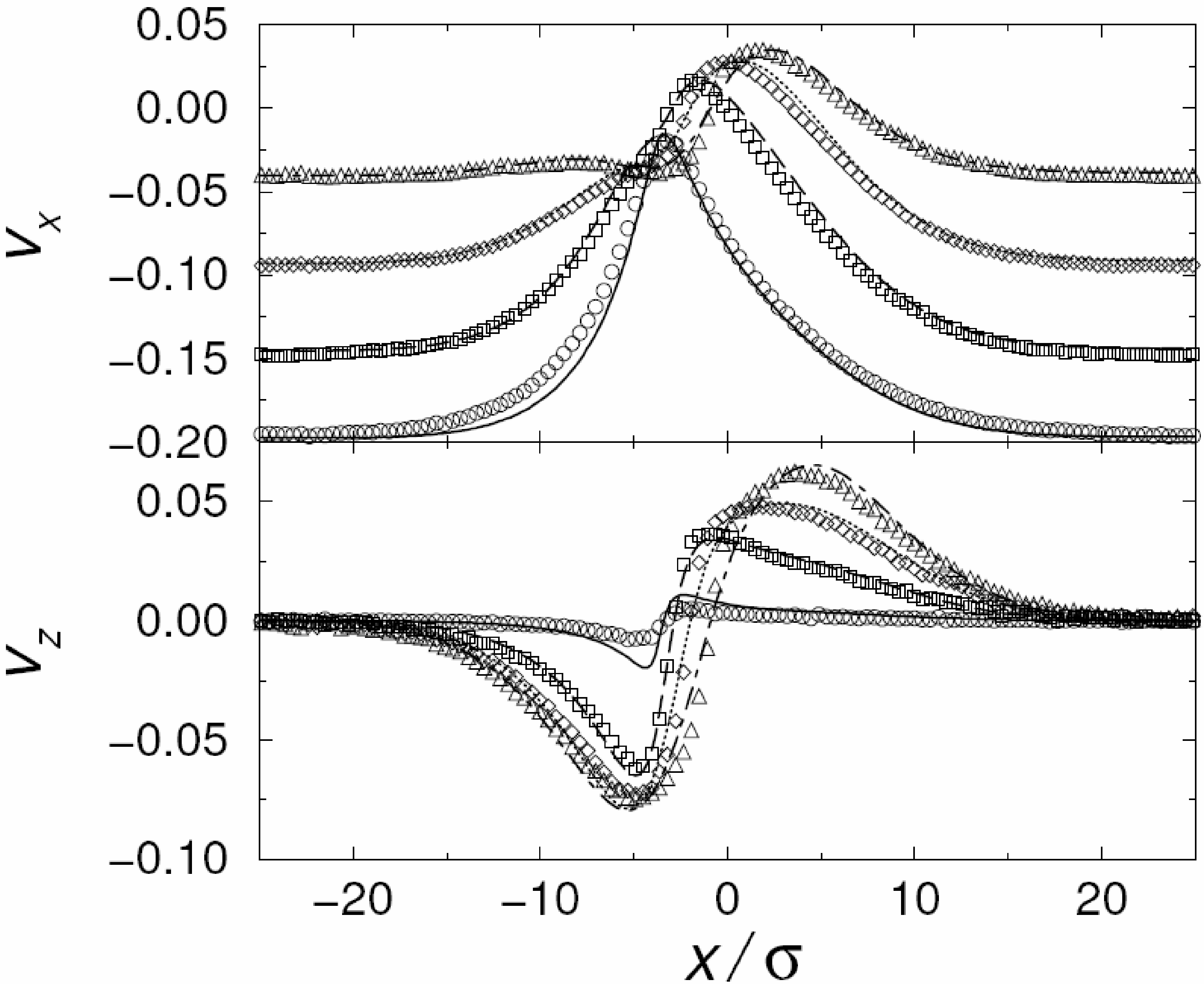
V=0.20

H=13.6

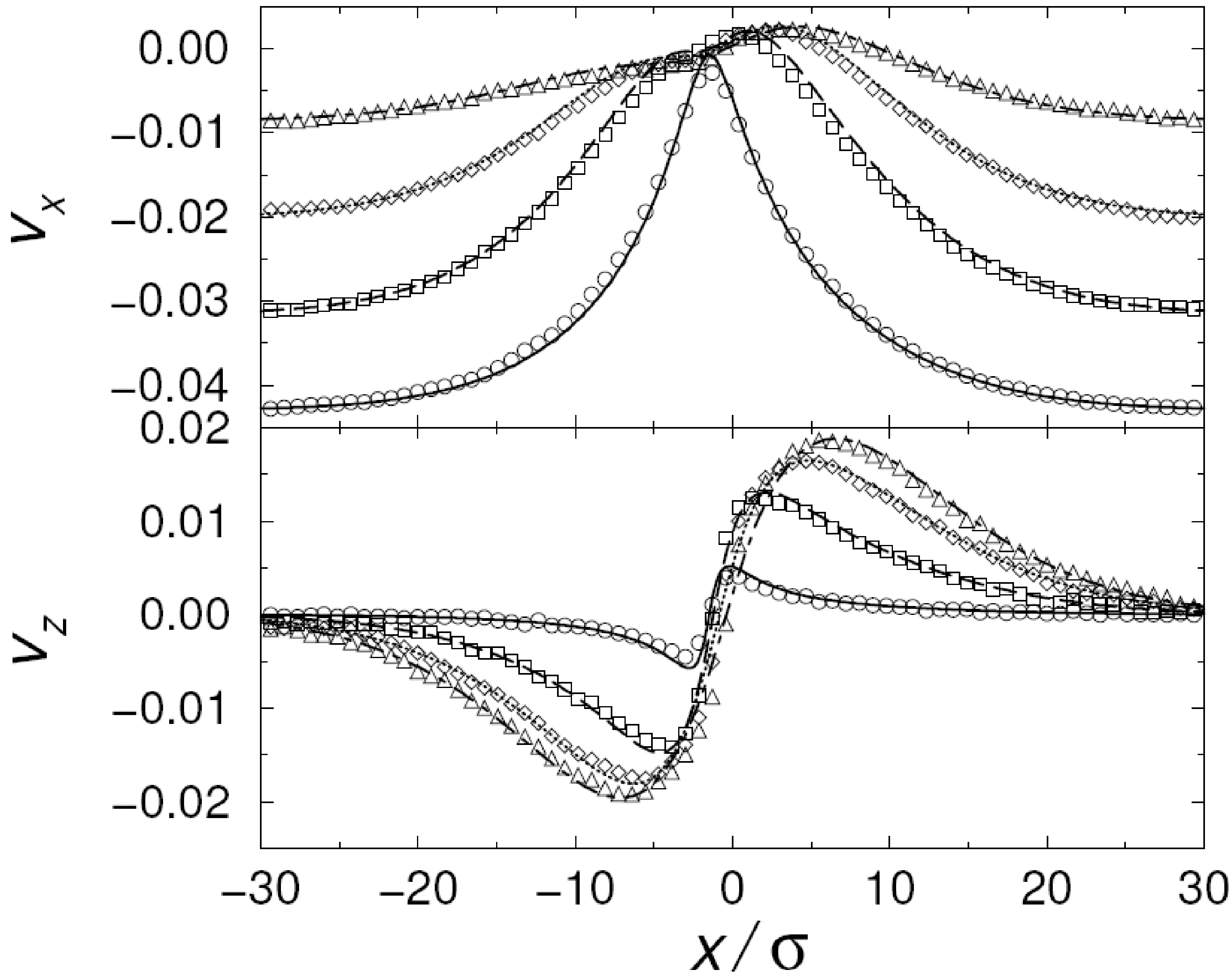


symmetric
<u>Couette</u>
V=0.25
H=10.2

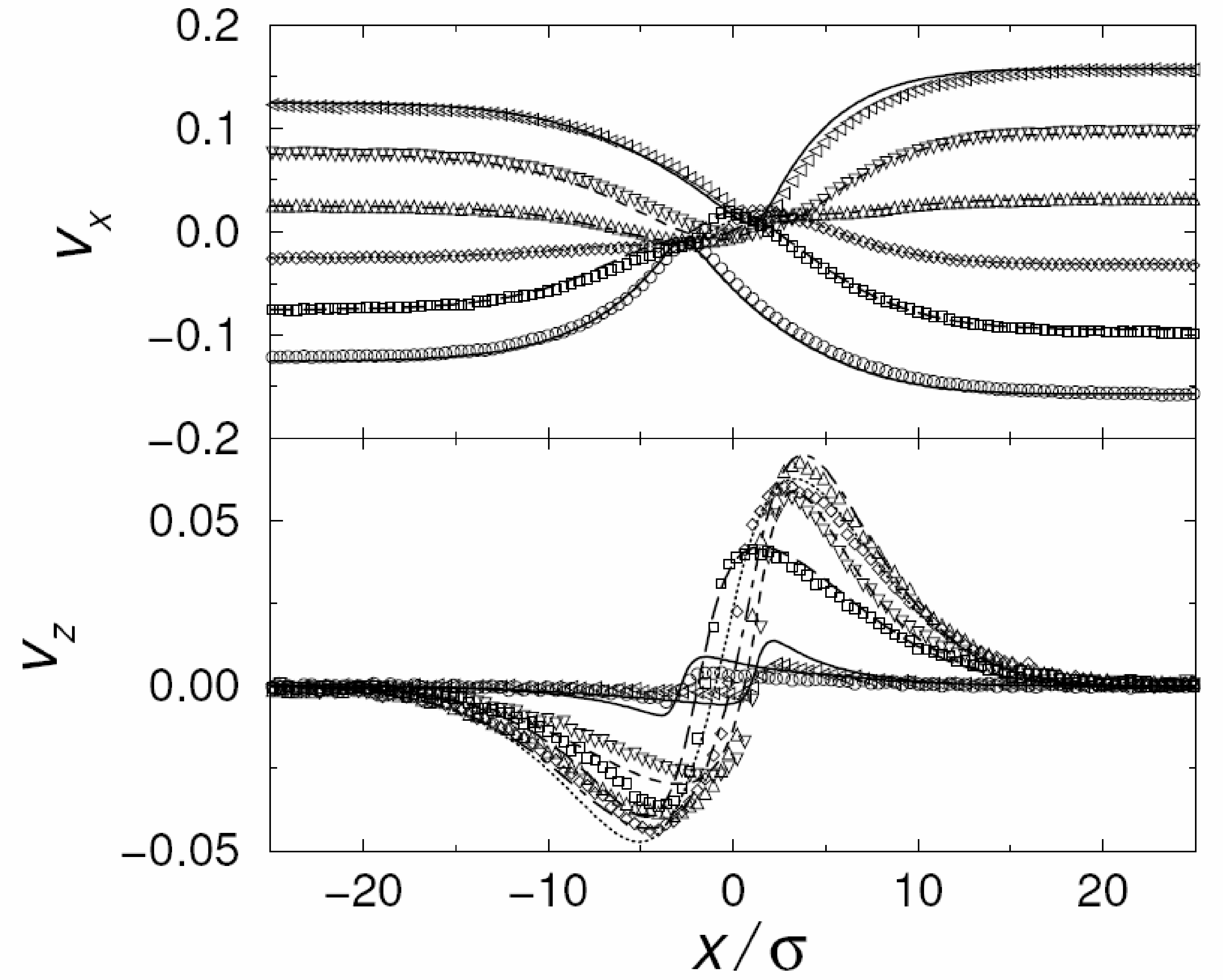
symmetric
<u>Couette</u>
V=0.275
H=13.6



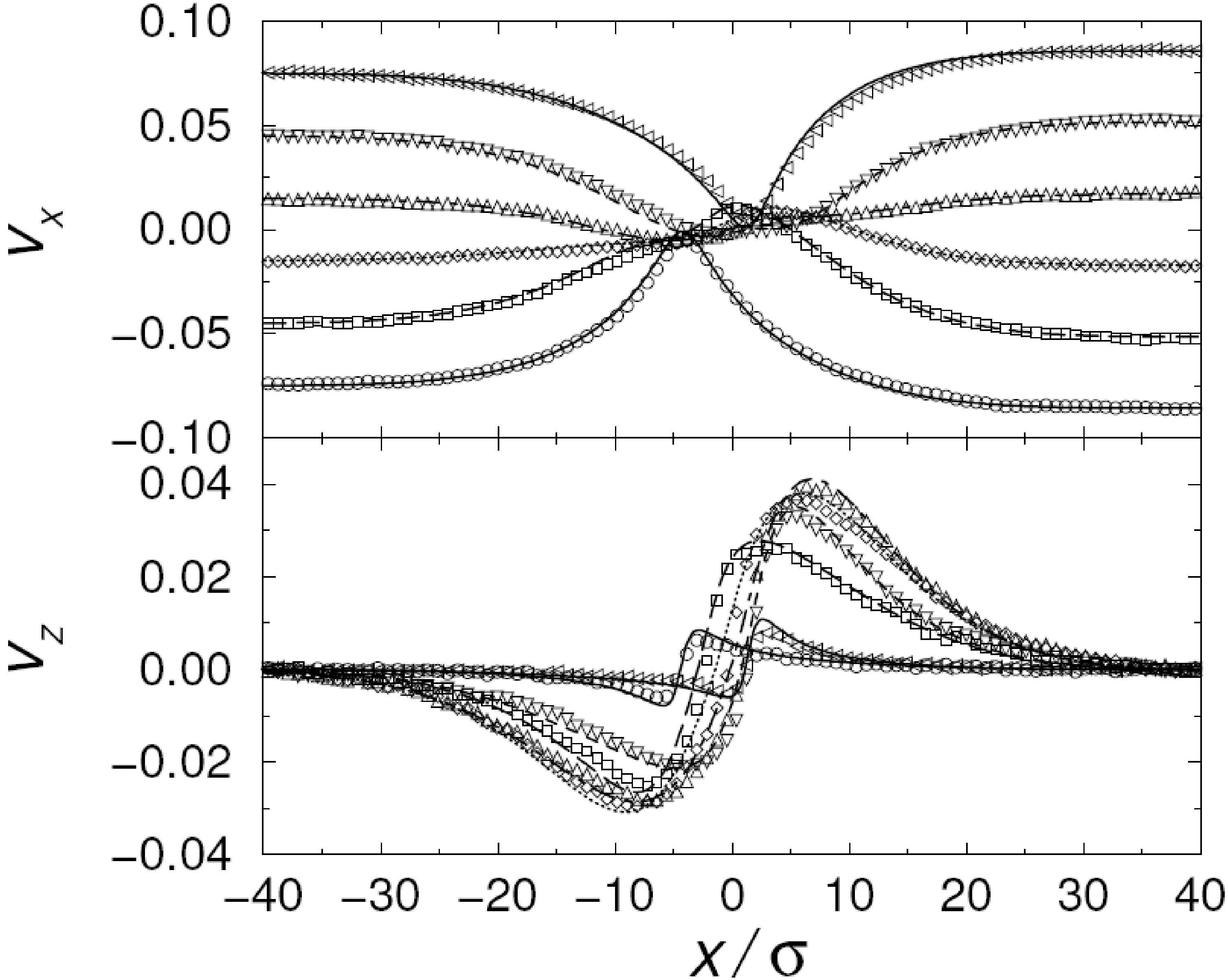
a symmetric case of immiscible Couette flow ($V = 0.25(\epsilon/m)^{1/2}$ and $H = 13.6\sigma$)



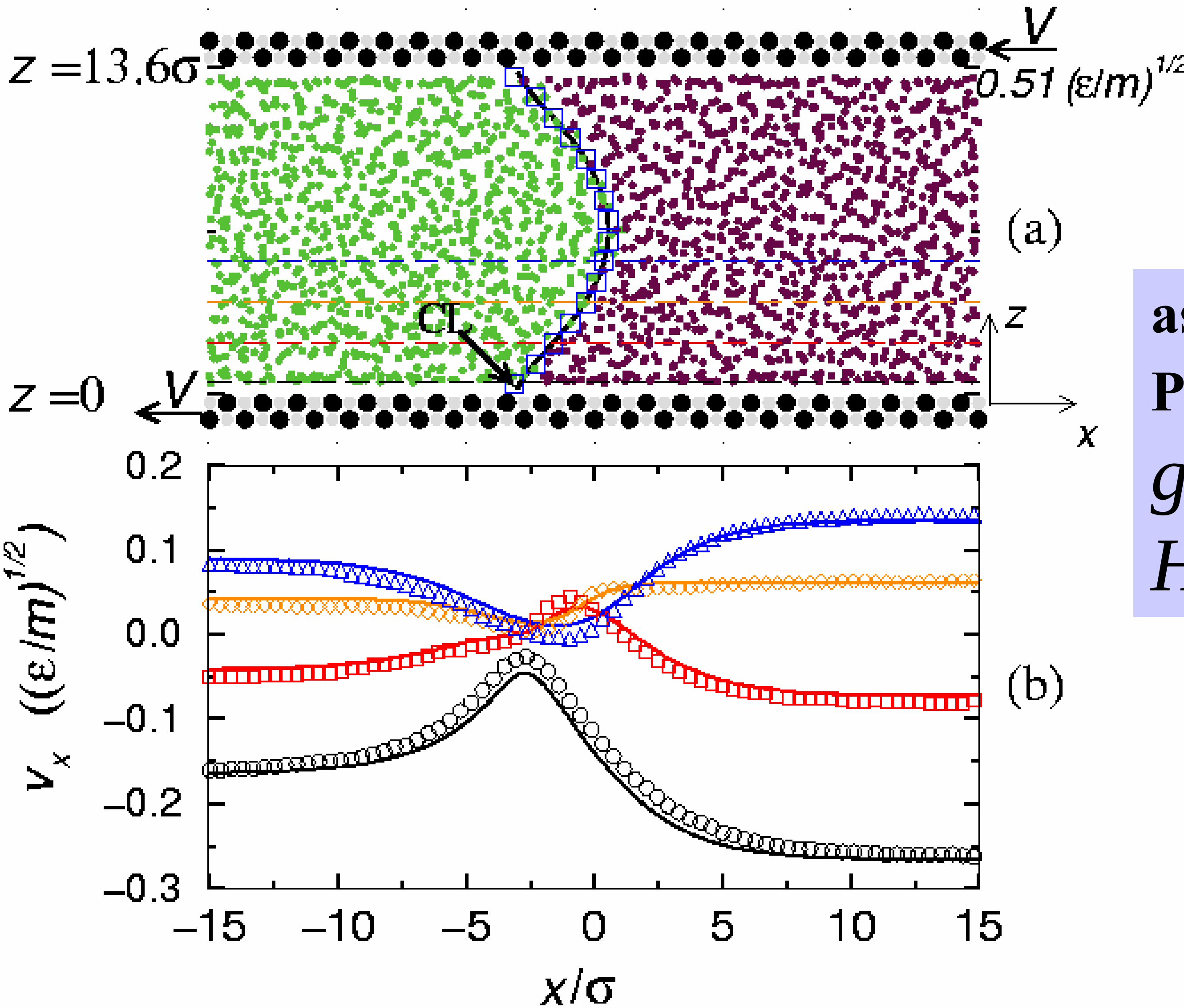
a symmetric case of immiscible Couette flow ($V = 0.05(\epsilon/m)^{1/2}$ and $H = 27.2\sigma$)



an asymmetric case of immiscible Couette flow ($V = 0.2(\epsilon/m)^{1/2}$ and $H = 13.6\sigma$)



an asymmetric case of immiscible Couette flow ($V = 0.1(\epsilon/m)^{1/2}$ and $H = 27.2\sigma$)



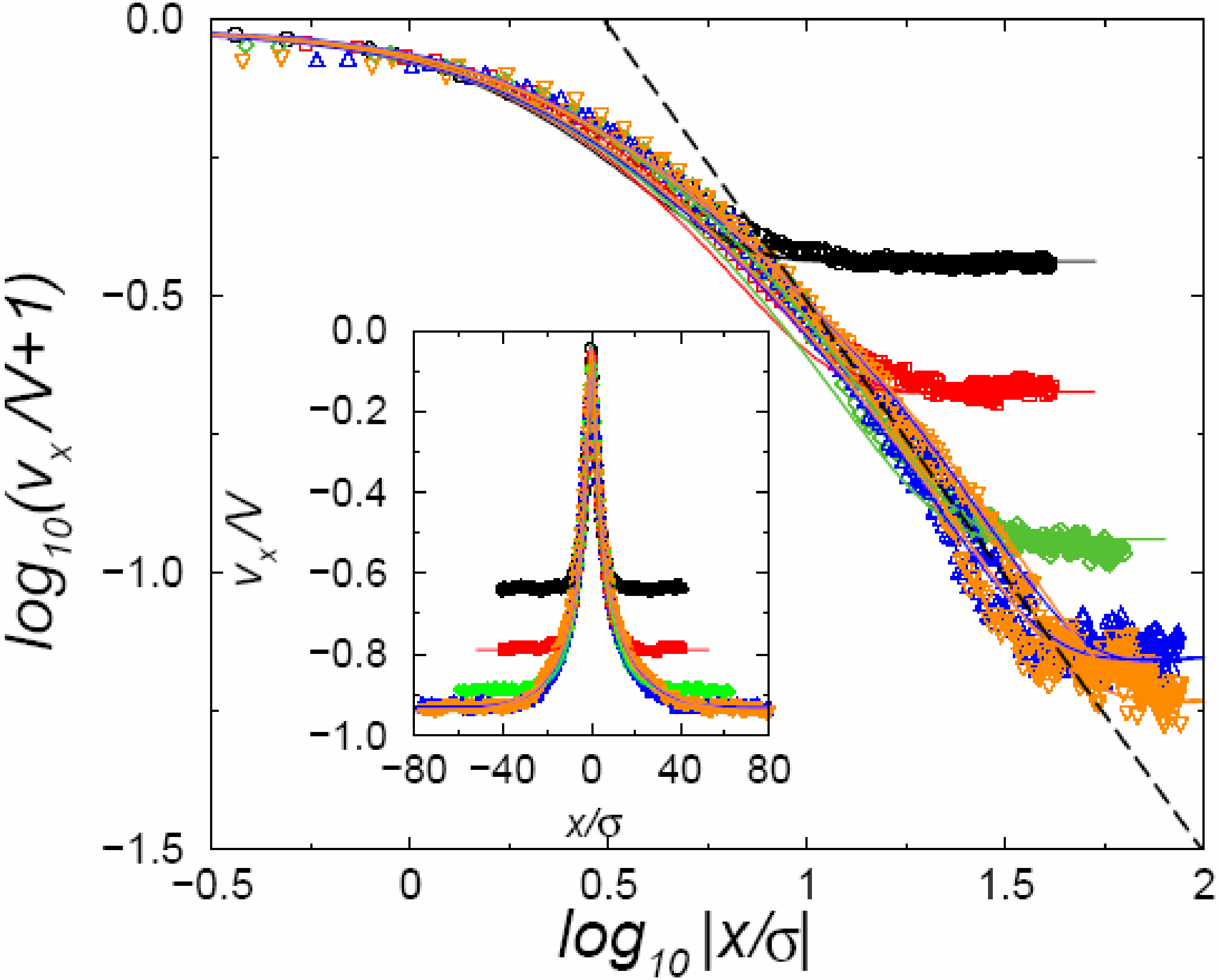
asymmetric Poiseuille flow

$g_{ext}=0.05$

$H=13.6$

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

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

Onsager 1931
Onsager-Machlup 1953

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

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

for the statistical distribution of the noise (random force)

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

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

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 <u>fixed</u> 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:

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

From velocity differential to velocity difference

$$\nabla \mathbf{v} \rightarrow v^{slip}$$

Transport coefficient: from viscosity η to slip coefficient β

$$\eta = \frac{1}{V}\frac{1}{k_{\mathrm{B}}T}\int_0^{\infty} dt \left\langle F_\tau(t) F_\tau(0) \right\rangle_{eq}$$

Green-Kubo formula

$$\beta = \frac{1}{S}\frac{1}{k_{\mathrm{B}}T}\int_0^{\infty} dt \left\langle F_\tau(t) F_\tau(0) \right\rangle_{eq}$$

J.-L. Barrat and L. Bocquet, *Faraday Discuss*. **112**, 119 (1999).

Generalization to immiscible two-phase flows

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

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

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

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

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

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

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

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:

$\boxed{\mu = Const.}$ $\boxed{L = 0}$ (Young's equation)

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

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

DISSIPATION

F. Brochard-Wyart and P. G. De Gennes, Adv. in Colloid and Interface Sci. **39**, 1 (1992).

Dissipation function: half the rate of energy dissipation

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

$$\int \mathrm{d}\boldsymbol{r}\left[\frac{\eta}{4}(\partial_i v_j + \partial_j v_i)^2\right]$$

outside of $x_{\min}$

viscous dissipation $\rightarrow T\dot{S}_{\mathrm{wedge}} = \dfrac{3\eta}{\theta} U^2 \ln \dfrac{x_{\max}}{x_{\min}}$

$$\int \mathrm{d}S\left[\frac{\beta}{2}\left(v_\tau^{slip}\right)^2\right]$$

inside of $x_{\min}$

surface dissipation due to slip,
concentrated around the real contact line $\rightarrow T\dot{S}_{\mathrm{tip}} = CU^2$

Mechanical effects of the fluid-fluid interfacial tensions
in the bulk and **at the solid surface** (sharp interface limit)

$$\begin{aligned}\mu\nabla\phi &= [-K\nabla^2\phi - r\phi + u\phi^3]|\nabla\phi|\mathbf{m} \\ &= -K\nabla_t^2\phi|\nabla\phi|\mathbf{m} + [-K\partial_m^2\phi - r\phi + u\phi^3]|\nabla\phi|\mathbf{m}\end{aligned}$$

$$\mu\nabla\phi \approx -K\nabla_t^2\phi|\nabla\phi|\mathbf{m}$$

$$\kappa = -\nabla_t^2\phi/|\nabla\phi|$$

$$\mu\nabla\phi \approx K|\nabla\phi|^2\kappa\mathbf{m} \approx \gamma\kappa\delta(l_m)\mathbf{m}$$

Young-Laplace curvature force

$$\gamma \approx \int dl_m K\left(\nabla\phi\right)^2 \approx \int dl_m K\left(\partial_m\phi\right)^2$$

$$\int_{int} dx\,[L(\phi)\partial_x\phi] = \int_{int} dx\,[(K\partial_n\phi + \partial\gamma_{fs}/\partial\phi)\partial_x\phi]$$

$$\int_{int} dx\,[(K\partial_n\phi)\partial_x\phi] = \gamma\cos\theta$$

$$\gamma\cos\theta_s + \gamma_{fs}(\phi_+) - \gamma_{fs}(\phi_-) = 0$$

Uncompensated Young stress (net tangential force)

$$\int_{int} dx\,[L(\phi)\partial_x\phi] = \gamma\cos\theta_d + \gamma_{fs}(\phi_+) - \gamma_{fs}(\phi_-) = \gamma(\cos\theta_d - \cos\theta_s),$$

Energetic variational derivation of the complete form of stress, from which the capillary force and Young stress are both obtained.

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

Anisotropic stress tensor $\delta F_{\mathrm{CH}} = \int dr \left[\sigma^{Y}_{ji} \partial_j \delta x_i \right]$

$$\boldsymbol{\sigma}_{\mathrm{CH}} = -K \nabla \phi \otimes \nabla \phi + \left[\frac{K}{2} (\nabla \phi)^2 + \left(-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 \right) \right] \mathbf{I}$$

Capillary force density

$$\nabla \cdot \boldsymbol{\sigma}_{\mathrm{CH}} = \mu \nabla \phi$$

Young stress

$\sigma^{Y}_{zx} = \left[\sigma_{\mathrm{CH}} \right]_{zx} = K \partial_n \phi \partial_x \phi$ (outward surface normal n = -z)

Wetting: statics and dynamics

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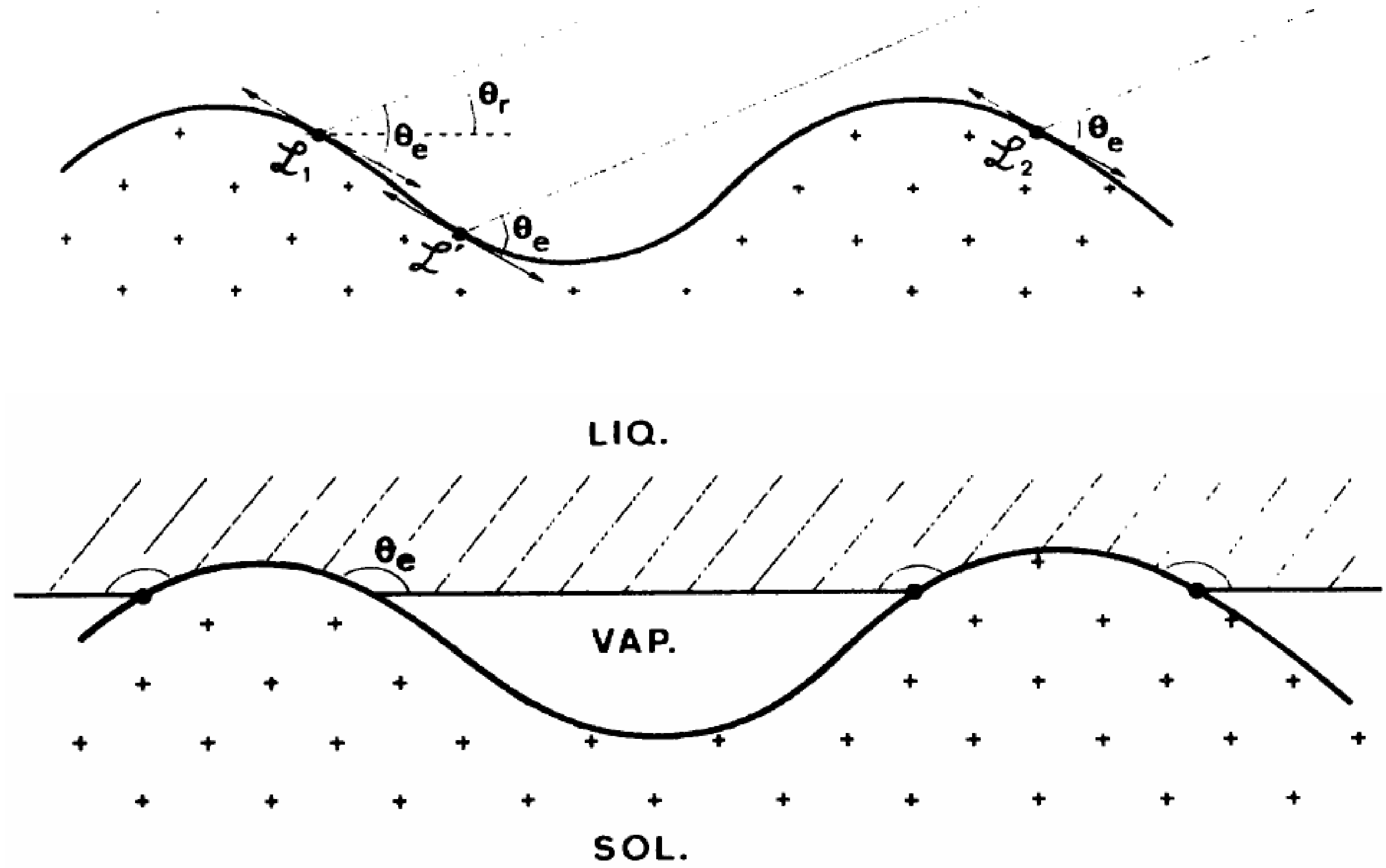
The wetting of solids by liquids is connected to physical chemistry (wettability), to statistical physics (pinning of the contact line, wetting transitions, etc.), to long-range forces (van der Waals, double layers), and to fluid dynamics. The present review represents an attempt towards a unified picture with special emphasis on certain features of "dry spreading": (a) the final state of a spreading droplet need not be a monomolecular film; (b) the spreading drop is surrounded by a precursor film, where most of the available free energy is spent; and (c) polymer melts may slip on the solid and belong to a separate dynamical class, conceptually related to the spreading of superfluids.

Reviews of Modern Physics, Vol. 57, No. 3, Part I, July 1985

Models with parallel grooves



Reviews of Modern Physics, Vol. 57, No. 3, Part I, July 1985

Moving contact line over undulating surfaces:

(f) $t = 43.75.$

complete displacement

(g) $t = 50.$

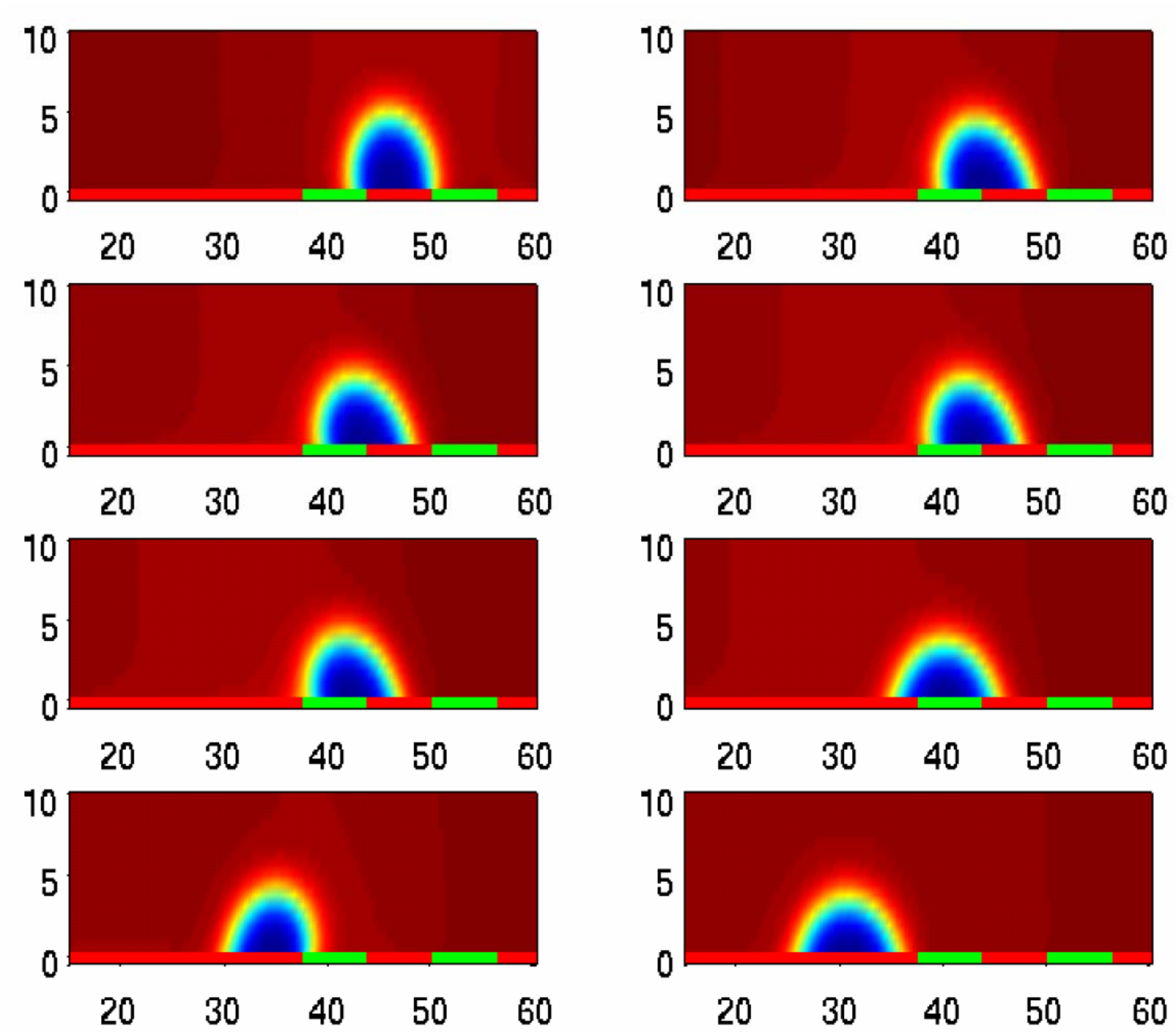
(f) $t = 43.75.$

incomplete displacement

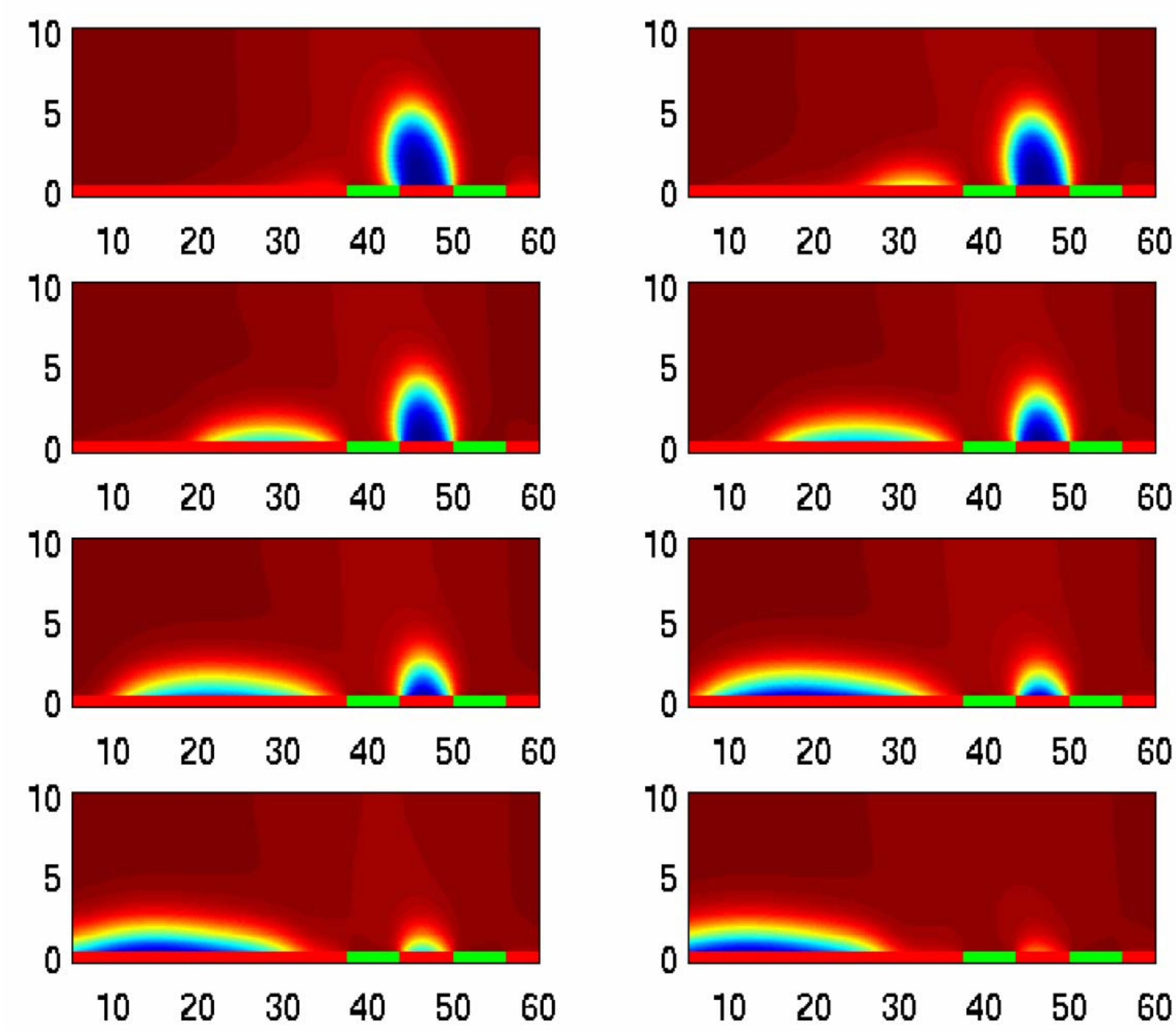
(g) $t = 50.$

Moving contact line over <u>chemically patterned surfaces</u>:

(a) Low wettability contrast



(b) High wettability contrast (minimum dissipation)



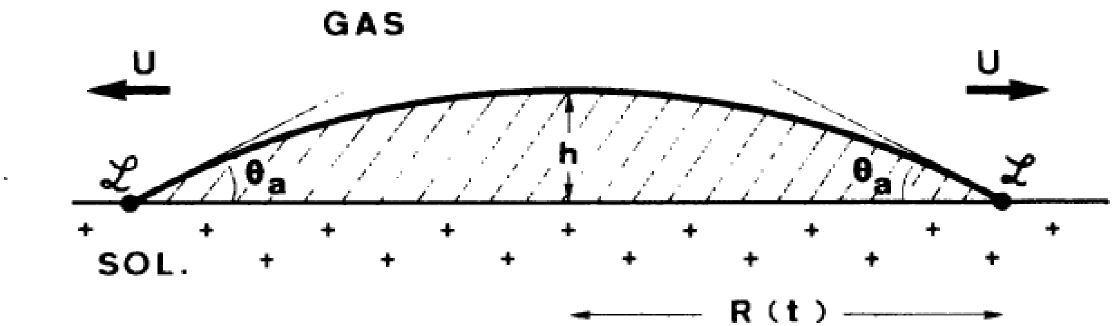


FIG. 28. A nearly flat droplet spreading on a solid: the macroscopic picture.

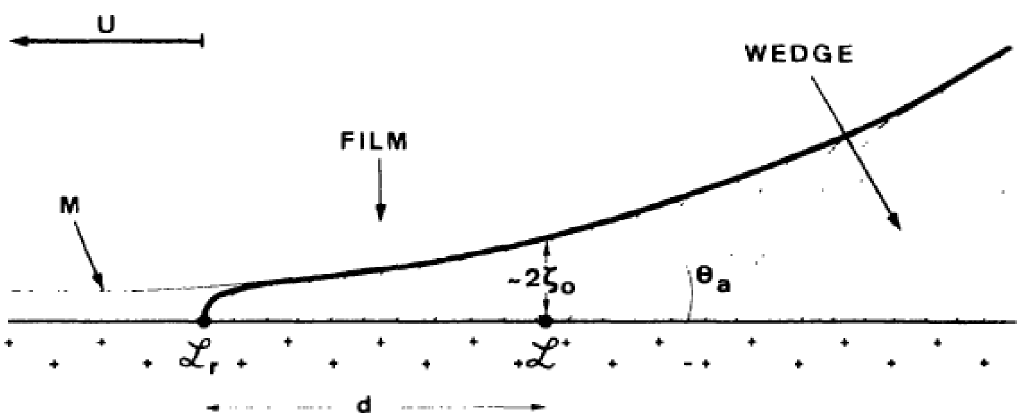


FIG. 30. A nearly flat droplet spreading on a solid: the microscopic picture.

van der Waals energy (per unit volume of liquid) between liquid and solid

$$W(z) = -\Pi(z) = -\frac{A}{6\pi z^3}$$

$$\frac{3\eta U}{\zeta^2} = \frac{d}{dx}\left[-\gamma\frac{d^2\zeta}{dx^2} + W(\zeta)\right]$$

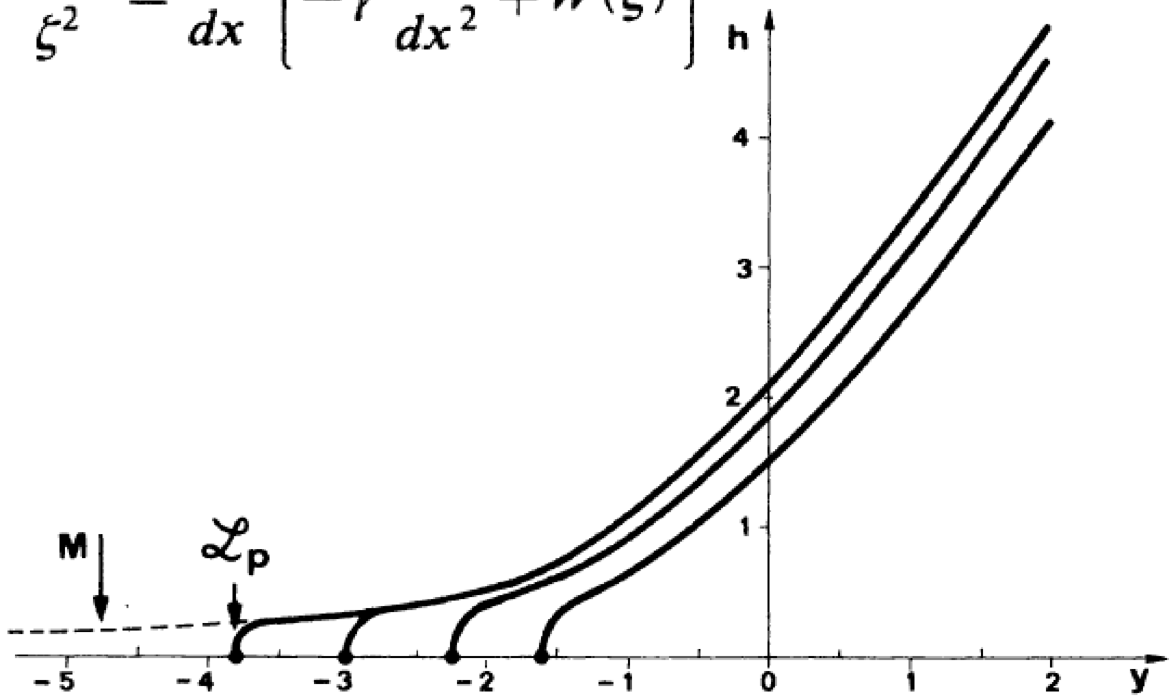


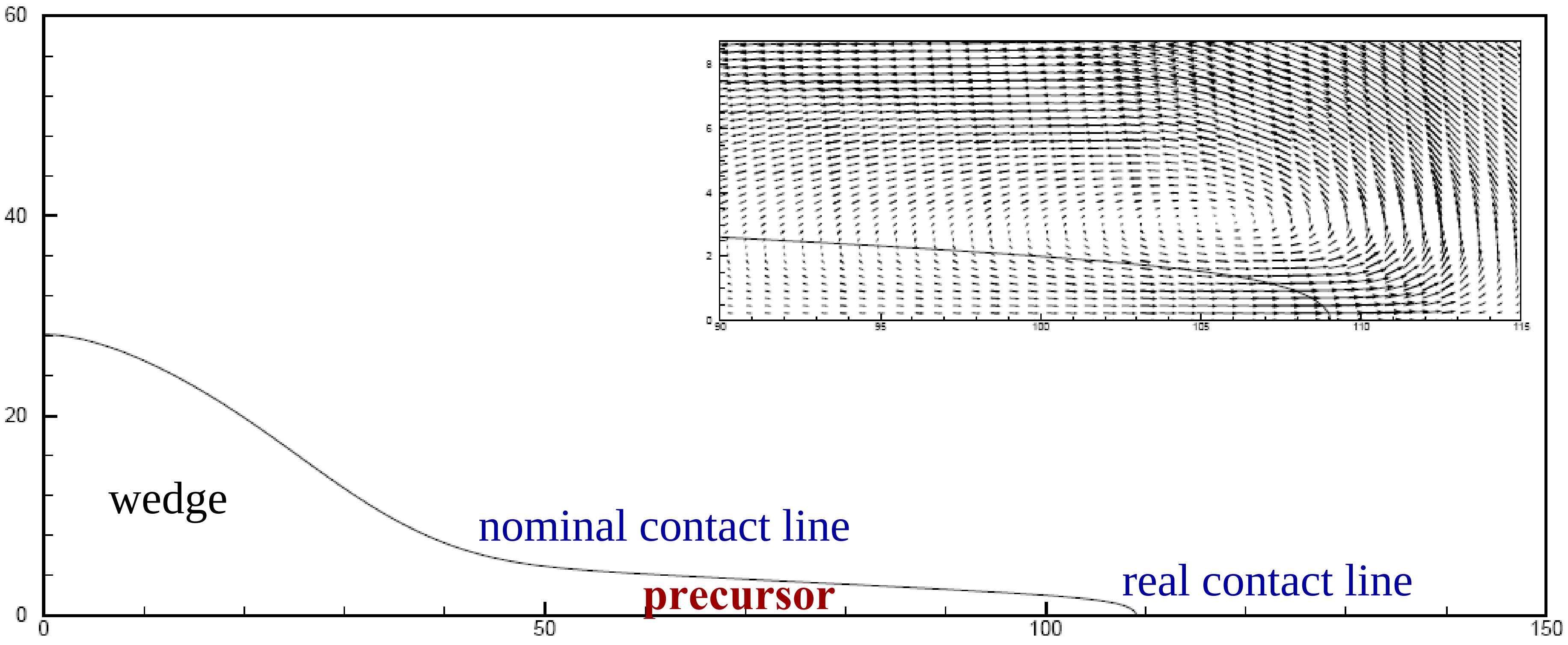
FIG. 33. A few numerical solutions of the film equation (4.33) for various values of the spreading parameter S (after Hervet and de Gennes, 1984). The larger S values correspond to the larger films.

Reviews of Modern Physics, Vol. 57, No. 3, Part I, July 1985

Spreading driven by the attractive van der Waals force:
Development of the precursor film in the complete wetting regime

Spreading coefficient $S = \gamma_1 - [\gamma_2 + V_{VW}(\infty)] - \gamma$

$S > 0$ with the van der Waals interaction taken into account



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 <u>the fluid-solid interfacial dissipation</u>.
- 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