Molecular hydrodynamics of the moving contact line

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Continuum picture

\[ \mathbf{v}_{slip} = 0 \]

Molecular picture

No-Slip Boundary Condition, A Paradigm

\[ \mathbf{v}_{\tau} \mathbf{n} = 0 \]
from Navier Boundary Condition (1823) to No-Slip Boundary Condition

\[ \nu_{\tau}^{slip} = l_s \cdot \dot{\gamma} \]

\[ \dot{\gamma} : \text{shear rate at solid surface} \]

\[ l_s : \text{slip length}, \text{ from nano- to micrometer} \]

Practically, no slip in macroscopic flows

\[ \dot{\gamma} \approx U / R \rightarrow \nu^{slip} / U \approx l_s / R \rightarrow 0 \]
Young’s equation: $\gamma \cos \theta_s + \gamma_2 = \gamma_1$
\[
\int_a^R \eta \frac{U}{x} \, dx \quad \xrightarrow{a \to 0} \quad \infty
\]

\[
\theta_d \neq \theta_s
\]

velocity discontinuity and diverging stress at the MCL
No-Slip Boundary Condition?

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

2. **Infinite Energy Dissipation**
   (unphysical singularity)

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 $S$?

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

Qian, Wang & Sheng,
PRE 68, 016306 (2003);
Ren & E, preprint

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

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**

\[ G_X^w, \quad G_X^f, \quad V_X^{\text{slip}} \]

as functions of \( X \)

**Stress from the rate of tangential momentum transport per unit area**
The Generalized Navier boundary condition

\[ \widetilde{G}_x^w = -\beta \nu_x^{slip} \]
\[ \widetilde{G}_x^w + \widetilde{G}_x^f = 0 \]

The stress in the immiscible two-phase fluid:

**viscous part**

\[ \sigma_{zx} = \eta [\partial_z \nu_x + \partial_x \nu_z] + \sigma_{zx}^Y \]

**non-viscous part**

**interfacial force**

GNBC from continuum deduction

\[ \beta \nu_x^{slip} = \widetilde{G}_x^f = \widetilde{\sigma}_{zx} = \sigma_{zx}^{visc} + \sigma_{zx}^Y \]

*static Young component subtracted*

\[ \text{uncompensated Young stress} \]

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

\[ \int_{\text{int}} d\tilde{x} \tilde{\sigma}_{zx}^Y = \gamma \cos \theta_d + \gamma_2 - \gamma_1 \neq 0 \]
\[ \sum_{s,d} = \int dx \sigma_{0,Y}^{\text{int}} \]

Diagram showing the nonviscous and viscous parts of the stress. The graph plots the tangential stress against \( \gamma \cos \theta_{d,s} (\varepsilon \sigma^{-2}) \) and \( x/\sigma \).
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

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

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

$$J_n \propto \partial_n \mu = 0 \quad \text{impermeability B.C.}$$
\[ F_{CH}[\phi(r)] = \int dr \left[ \frac{K}{2} (\nabla \phi)^2 + \left( -\frac{r}{2} \phi^2 + \frac{u}{4} \phi^4 \right) \right] \]

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

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

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

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

\[ \mu = \delta F_{CH}/\delta \phi \]

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

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

supplemented with

\[ \nabla \cdot \mathbf{v} = 0 \quad v_n = 0 \quad J_n \propto \partial_n \mu = 0 \]
**GNBC:**

an equation of tangential force balance

\[- \beta v^\text{slip}_x + \eta \partial_z v_x - K \partial_z \phi \partial_x \phi + \partial_x \gamma_{fs} = 0\]

\[\tilde{G}^w_x + \sigma^{visc}_{zx} + \sigma^Y_{zx} + \partial_x \gamma_{fs} = 0\]
Dussan and Davis, JFM 65, 71-95 (1974):

1. Incompressible Newtonian fluid
2. Smooth rigid solid walls
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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

Symmetric Couette flow

Asymmetric Couette flow

Diffusion versus Slip in MD
Symmetric Couette flow

$V = 0.25$

$H = 13.6$

near-total slip at moving CL

Boundary layer velocity profile

$v_x = 0$ for total slip

$v_x / V \rightarrow -1$

Symmetric Couette flow

$V = 0.25$

$H = 13.6$
$v_x(x)$ profiles at different $z$ levels

(a) symmetric Couette flow
$V=0.25$
$H=13.6$

(b) asymmetric 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).

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

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

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

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

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

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

rate of change of the free energy
Dissipation function (half the total rate of energy dissipation)

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

\[\Phi = \frac{1}{2} R_2 = \frac{1}{2} (R_1 + R_\phi) = \frac{1}{2} (R_v + R_s + R_d + R_\tau)\]

Rate of change of the free energy

\[\dot{F} = \int dr \left[\mu \frac{\partial \phi}{\partial t}\right] + \int dS \left[L \frac{\partial \phi}{\partial t}\right]\]

\[\int dr \left[\mu \ddot{\phi}\right] = \int dr \left[-\mu \nabla \cdot J\right]\]

kinematic transport of \(\phi\)

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

continuity equation for \(\phi\)

\[\int dr \left[\nabla \cdot (\mu J)\right] = \int dS \left[\mu J_n\right] = 0\]

impermeability B.C.

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

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

with respect to the rates \( \{v, J, \dot{\phi}\} \) yields

\[ -\nabla p + \eta \nabla^2 v + \mu \nabla \phi = 0, \]

Stokes equation

\[ \beta(\phi)v^{\text{slip}}_\tau = -\eta(\partial_n v_\tau + \partial_\tau v_n) + L(\phi)\partial_\tau \phi, \]

GNBC

\[ J = -M \nabla \mu, \]

\[ \dot{\phi} = \frac{\partial \phi}{\partial t} + \nu \cdot \nabla \phi = -\nabla \cdot J = M \nabla^2 \mu \]

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