Connecting the Motion of Atoms to Macroscopic Behavior

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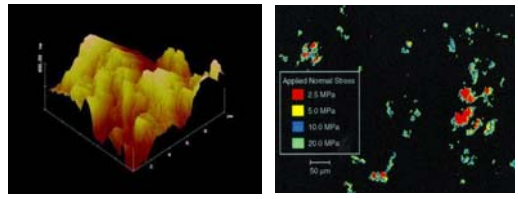
Scientific Goals

Nonequilibrium processes with a wide range of length and time scales: Contact, adhesion, friction, lubrication, multiphase flows

Self-affine fractal surface and distribution of contact areas

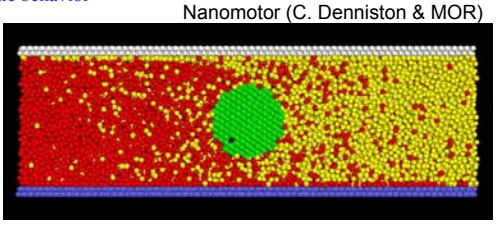


Scientific Goals

Nonequilibrium processes with a wide range of length and time scales: Contact, adhesion, friction, lubrication, multiphase flows

Problems where interfaces or small scale singularity affects large scale behavior

Nanomotor (C. Denniston & MOR)



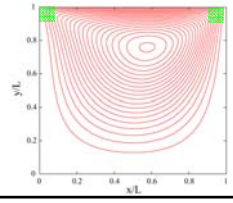
Require algorithms that are dynamic, finite temperature, nonlinear in continuum region, treat both solid and fluid phases and interfaces

Linking Atomistic and Continuum Regions

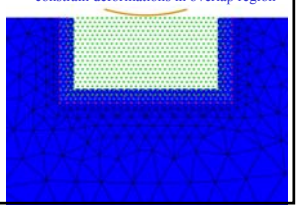
Three overlap regions where solve both continuum and MD
- Outermost → Continuum solution gives MD boundary condition
- Innermost → MD gives continuum boundary condition
- Middle → Two solutions equilibrate independently

Fluids: Apply boundary conditions to velocities
Solids: Apply boundary conditions to displacements

Streamlines in L~100nm channel with moving top wall. Atomistic solution in <1% of area (green) removes continuum singularity



Model contact region atomistically, elastic deformations with finite-elements, constrain deformations in overlap region



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Solids: Apply boundary conditions to displacements

Fluids: S. T. O'Connell & P. A. Thompson, Phys. Rev. E52, R5792, (1995)

Why not use forces instead of displacements/velocities?
E. G. Flekkoy, G. Wagner & J. Feder, Europhys. Lett. 52, 271 (2000)

Fluids – Position of boundary is undetermined
→ drifts in response to fluctuations or systematic errors

General – Any error in constitutive relation creates problems in overlap region
Less sensitive when match displacements
any global factor in stress is irrelevant

Fluid Continuum – Incompressible Navier-Stokes

$$\partial_t \mathbf{u} + (\mathbf{u} \bullet \nabla \mathbf{u}) = -\frac{1}{\rho}\nabla p + \nu \nabla^2 \mathbf{u}$$

$$\nabla \bullet \mathbf{u} = \mathbf{0}$$

Projection method (time splitting, staggered grid):

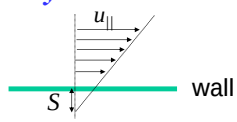
$$\frac{\mathbf{u}^* - \mathbf{u}^n}{\Delta t_{FD}} + \mathbf{u}^n \cdot \nabla \mathbf{u}^n - \nu \nabla^2 \mathbf{u}^n = 0$$

$$\frac{\mathbf{u}^{n+1} - \mathbf{u}^*}{\Delta t_{FD}} + \frac{1}{\rho}\nabla p^{n+1} = 0 \qquad \nabla \cdot \mathbf{u}^{n+1} = 0$$

$$\nabla p^{n+1} = \frac{\rho}{\Delta t_{FD}} \nabla \cdot \mathbf{u}^*, \qquad \mathbf{n} \cdot p^{n+1} = 0$$

Navier slip boundary condition

$u_{\parallel}|_w = S\,\partial_{\perp} u_{\parallel}|_w \propto$ stress



Slip length

Knowledge of S and μ completely characterizes a simple fluid.

Find can apply within atomic distance from solid and S ~ atomic size in most cases

Why parametrize instead of finding S, μ on the fly?
Substantial computational overhead → thermal fluctuations
When simple parameters aren't good, need explicit atoms

Atomistic Region → Molecular Dynamics

Truncated and shifted Lennard-Jones potential

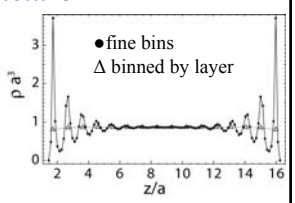
$$V^{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right]$$

σ: Characteristic length, particle diameter.
ε: Characteristic energy.
$\tau \equiv (m\sigma^2/\varepsilon)^{1/2}$: Characteristic time of the potential.
r_c: Cut-off distance, usually 2.2σ for fluids
Integrate with velocity-Verlet, time step $\Delta t_{MD} = 0.005\tau$

Determine parameters for fluid continuum model:
Temperature $1.1\varepsilon/k_B$, density $\rho = 0.81 m\sigma^{-3}$, viscosity $\mu = 2.14\varepsilon\tau\sigma^{-3}$.
Wall (111) surface of fcc crystal
Wall-fluid interaction ε_{wf} controls flow boundary condition (BC)
$\varepsilon_{wf} = 0.95\varepsilon$ → no-slip BC, S=0

Single Fluid Structure

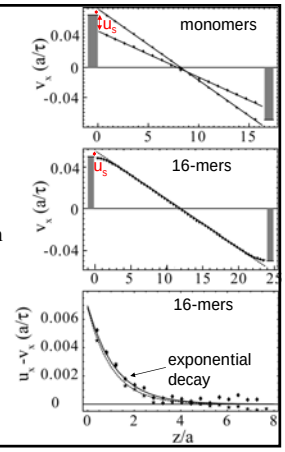
- Near walls – layering & in-plane order
- To compare with continuum average over layers
- Choice of wall position z_w is not unique at molecular level.
- Choose so total # of particles matches continuum



Single Fluid Slip

- Bulk flow extrapolates (lines) to $u(0) \neq u_{wall}$ (shaded bars)
  $u_s \equiv u(0) - u_{wall}$
- Define local η from local v
  $\eta \partial_z v_x(z) = \sigma_{xz}$
  (or finite difference)
- Then find Navier slip condition
  $$u_s = \int_b^w dz \partial_z (u - v) = L_s \sigma_{xz} / \eta_b$$
  $$L_s \equiv \int_w^b dz (\eta_b / \eta - 1)$$
- S> 0 slip, S< 0 stick
- S/a typically ~-2 – 20 can be much bigger for polymers

(Thompson & Robbins PRA41, 6830 (1990))



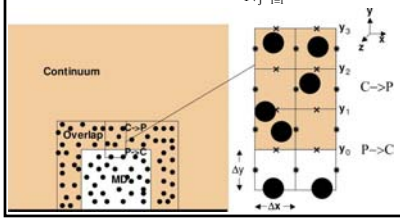
Hybrid Algorithm Applied to Fluids

Continuum: Incompressible Navier-Stokes (Projection method)
Atomistic: Molecular dynamics of Lennard-Jones atoms, no-slip
Potential: $U(r) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6]$; Units ε, σ

MD → Continuum $\quad u_J = \frac{1}{N_J}\sum_{i=1}^{N_J} v_i$

Continuum → MD $\quad \frac{1}{N_J}\sum_{i=1}^{N_J} v_i = u_J(t) \quad m\ddot{x}_i = F_i - \frac{1}{N_J}\sum_{k=1}^{N_J} F_k + m\frac{Du_J}{Dt},$

$$F_i = -\frac{\partial}{\partial x}\sum_k V_{ik}^{LJ}.$$



Potential confines particles at y_3

Insert/remove number of particles equal to net flux

Equation of Motion for Constrained Particle

The equation of motion for the particle *i:*

$$\ddot{\mathbf{x}}_i = \frac{\mathbf{F}_i}{m} - \frac{1}{N_J m}\sum_{i=1}^{N_J}\mathbf{F}_i + \frac{D\mathbf{u}_J(t)}{Dt}, \quad \mathbf{F}_i = -\frac{\partial}{\partial \mathbf{x}_i}\sum_j V_{ij}^{LJ}$$

Finite Difference Scheme for the equation of motion:

$$\frac{\mathbf{x}(t+\Delta t_{MD}) - 2\mathbf{x}(t) + \mathbf{x}(t-\Delta t_{MD})}{\Delta t_{MD}^2} = \frac{\mathbf{F}_i}{m} - \frac{1}{N_J m}\sum_{i=1}^{N_J}\mathbf{F}_i - \frac{1}{\Delta t_{MD}}\left(\frac{1}{N_J}\sum_{i=1}^{N_J}\mathbf{v}_i(t) - \mathbf{u}_J(t)\right)$$

$\Delta t_{FE} = 40\Delta t_{MD}$ → Staggered time grid
Average MD over Δt_{FE} to fix continuum boundary
Extrapolate continuum to integrate next MD interval

Particle Confinement and Mass Flux

External force *F* for $y_2 \le y \le y_3$

$$F_y = -\alpha p_0 \sigma \frac{(y-y_2)}{1-(y-y_2)/(y_3-y_2)}$$

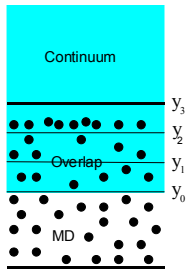
Maintain a mass flux by introducing particles *n(x,t)* near $y=y_2$

$$mn(x,t) = -A\rho u_y(x, y_2, t)\Delta t_{MD}$$

Langevin thermostat for $y_2 < y < y_3$:

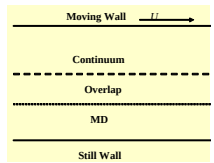
$$m\ddot{y}_i = \sum_{j \ne i} \frac{\partial V^{LJ}(r_{ij})}{\partial x_i} - m\Gamma \dot{y}_i + \zeta_i$$

$$\langle \zeta_i(t)\zeta_j(t') \rangle = \delta_{ij}\delta(t-t')2k_B T\Gamma$$

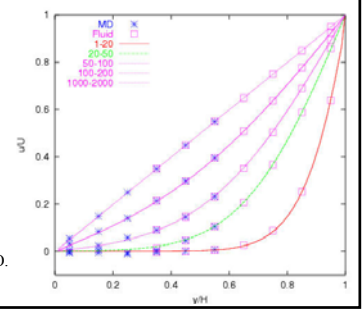


Dynamic Couette Flow

Schematic of simulation

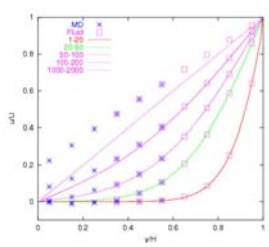


Hybrid solution (symbols) tracks full continuum (lines) as a function of time after motion starts

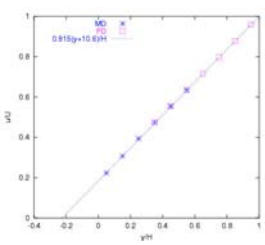


X. B. Nie, S. Y. Chen and M. O. Robbins, J. Fluid Mech. 2004.

Couette Flow with Velocity Slip



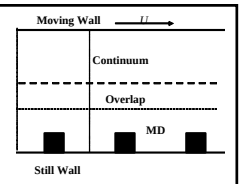
Hybrid vs. Continuum with no-slip

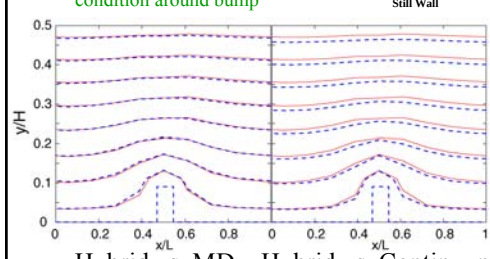


Hybrid vs. Pure MD

Flow past a rough wall

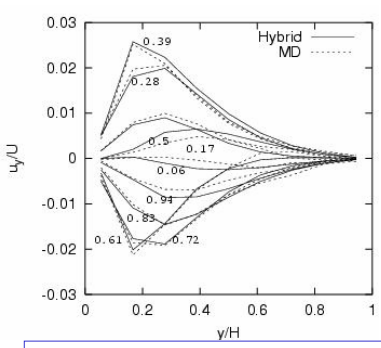
Streamlines from hybrid ≈ MD
includes flow between regions
Continuum fails because doesn't match complex boundary condition around bump





Hybrid vs. MD Hybrid vs. Continuum

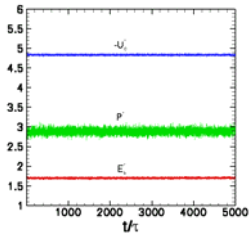
Vertical Velocity for Rough Wall



Statistical uncertainties are about $0.003\sigma/\tau$.

Including Heat Flux

$$\begin{cases} \nabla \cdot \mathbf{u} = 0 \\ \partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho}\nabla p + \frac{\mu}{\rho}\nabla^2 \mathbf{u} \\ \rho C_p \left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} \right) = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \mu \left[2\left(\frac{\partial u}{\partial x}\right)^2 + 2\left(\frac{\partial v}{\partial y}\right)^2 + \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)^2 \right] \end{cases}$$



Heat capacity C_p, for incompressible fluid

$$C_p^* = C_v^* = \frac{C_v}{Nk_B} = \frac{3}{2}\left[1 - \frac{2N}{3T^{*2}}\left\langle (\delta E_k^*)^2 \right\rangle\right]^{-1} = 2.42$$

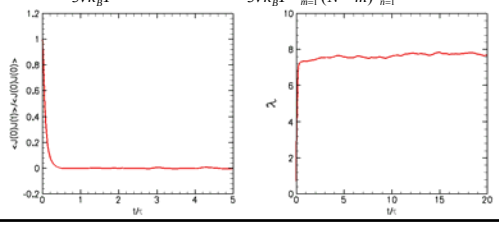
Determination of Thermal Conductivity λ

$$\mathbf{J}(t) = \sum_i \mathbf{v}_i \varepsilon_i + \frac{1}{2}\sum_{i,j,i\neq j} \mathbf{r}_{ij}(\mathbf{F}_{ij}\cdot\mathbf{v}_i)$$ Heat current

$$\varepsilon_i = \frac{1}{2}m_i|\mathbf{v}_i|^2 + \frac{1}{2}\sum_j \phi(\mathbf{r}_{ij})$$ Site energy

Thermal conductivity λ is calculated using Green-Kubo formula

$$\lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}(0)\cdot\mathbf{J}(t)\rangle dt = \frac{\Delta t}{3Vk_BT^2}\sum_{m=1}^{M}\frac{1}{(N-m)}\sum_{n=1}^{N-m}\mathbf{J}(m+n)\cdot\mathbf{J}(n)$$

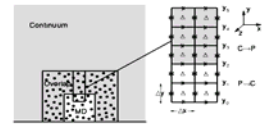


Coupling Scheme: Momentum and Energy

MD→Continuum :

$$\frac{1}{N_J}\sum_i \mathbf{v}_i = \mathbf{u}_{J,MD}(t)$$

$$\frac{1}{N_J-1}\sum_i \frac{1}{2}m(\mathbf{v}_i - \mathbf{u}_{J,MD})^2 = T_{J,MD}(t)$$



Continuum→MD (Constraint Dynamics and velocity rescaling):

$$\begin{cases} \frac{1}{N_J}\sum_i \mathbf{v}_i = \mathbf{u}_{J,C}(t) & \ddot{\mathbf{x}}_i = \frac{D\mathbf{u}_{J,C}(t)}{Dt} + \varsigma_i & \sum_i \varsigma_i = 0 \\ \varsigma_i = \frac{\mathbf{F}_i}{m} - \frac{1}{N_J m}\sum_{i=1}^{N_J}\mathbf{F}_i & \mathbf{F}_i = -\frac{\partial}{\partial x_i}\sum_{j\neq i} V^{LJ}(r_{ij}) & \\ \ddot{\mathbf{x}}_i = \frac{\mathbf{F}_i}{m} - \frac{1}{N_J m}\sum_{i=1}^{N_J}\mathbf{F}_i + \frac{D\mathbf{u}_{J,C}(t)}{Dt} & & \end{cases}$$

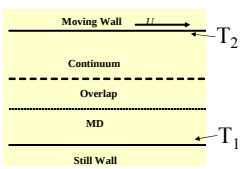
X. Nie et al. *JFM v500 55-64 (2004)*

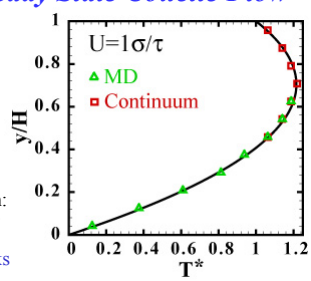
$$\mathbf{v}_i - \mathbf{u}_{J,MD} = \sqrt{\frac{T_{J,C}}{T_{J,MD}}}\times(\mathbf{v}_i - \mathbf{u}_{J,MD})$$

Mass flux across the interface :

$$n' = -A\rho u_y \Delta t_{FD}/m$$

Temperature in Steady State Couette Flow



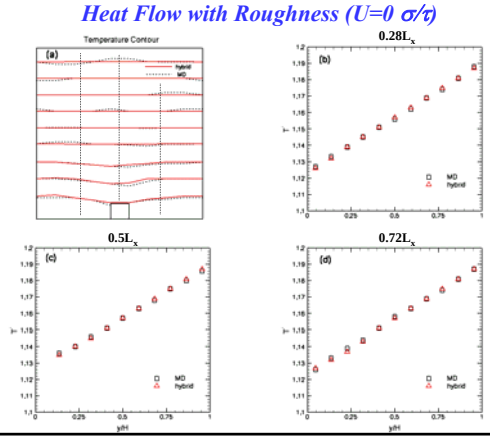


At boundaries of overlap region: rms MD veloc. ⇔ continuum T

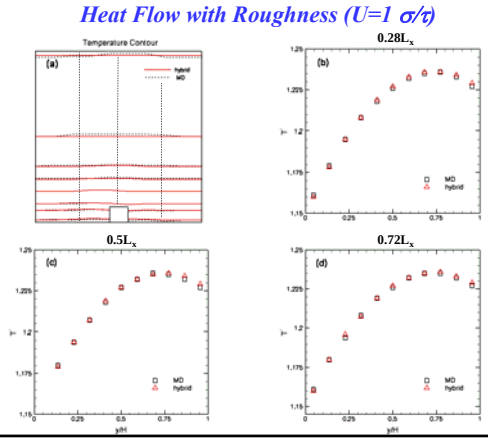
Hybrid solution (symbols) tracks full continuum (line)
Smooth variation in overlap region
Allows determination of Kapitza resistance at solid-fluid interface

$T^* = (T - T_1)/(T_2 - T_1)$

Heat Flow with Roughness (U=0 σ/τ)

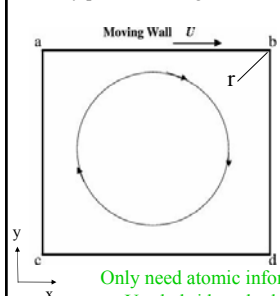


Heat Flow with Roughness (U=1 σ/τ)



Singular Cavity Flow

Continuum approach: Navier-Stokes + no-slip boundary condition (bc)
Usually phenomenological no-slip bc has little effect at large scales



Corner flow ⇒Molecular scale influences macroscopic forces

No-slip boundary condition is discontinuous at corners a, b
⇒Stress diverges as 1/r
⇒Log divergence in total force on wall

Only need atomic information near corners
⇒ Use hybrid method that treats bulk with continuum Navier-Stokes equations, corners with MD

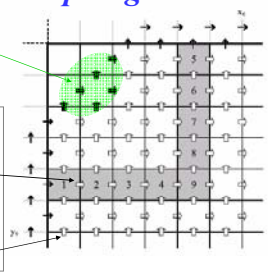
Coupling in Overlap Region

MD ⇒ Navier Stokes
Mean atomic velocity gives boundary condition to NS eqs.

Continuum ⇒ MD
1) Average tangential MD velocity in shadowed bins forced to NS value:

$$\ddot{x}_i = \frac{F_i}{m} - \frac{1}{mN_J}\sum_{j=1}^{N_J} F_j + \frac{Du_i}{Dt}, F_j = -\frac{\partial}{\partial x}\sum_k V_{jk}^{LJ}$$

2) Normal MD velocity constrained by matching mass flux at boundary



Have tested:
Agrees with pure MD calculations.
Independent of continuum grid 1, 3 and 6σ and specific set of constrained velocities (within MD noise)

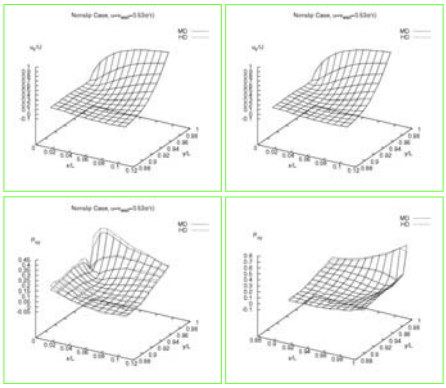
X.B. Nie, S.Y. Chen and M. R. Robbins, Physics of Fluids 2004.

Comparison With Full MD Near Corners

$L = 125\sigma$
$U = 0.53\sigma/\tau$

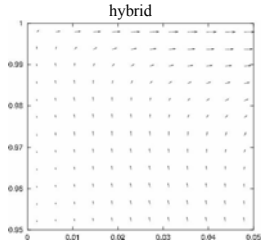
Velocity

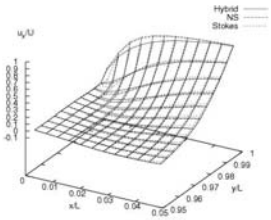
Stress



NS and Hybrid Velocities Near Corners

hybrid





Effect *like* slip BC on scale S
S is larger of ~2σ and U/0.1σ/τ

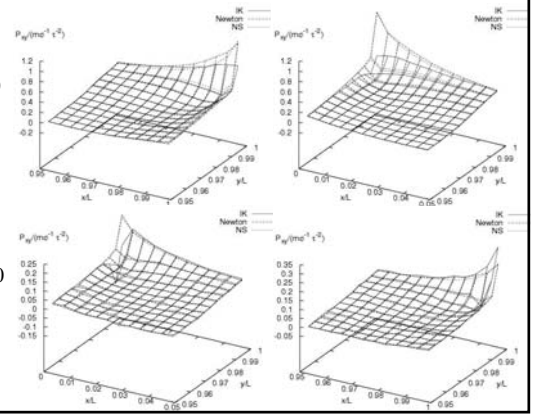
discreteness shear-thinning

Hard to use effective Navier BC: spatially varying, nonlinear

Stresses Near Corners

$R_e = 50$

$R_e = 10$



Treating Large Range of Length Scales

Problem: Size of atomistic region independent of system size L
BUT time to equilibrate NS flow field grows with L.
Initial approach limited to L~0.1μm.

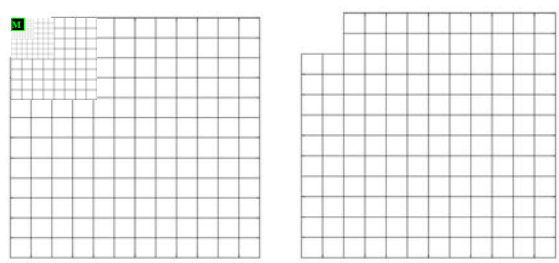
Solution: Multigrid and time approach
Integrate to steady state at each scale with optimum time step.
Iterate between scales till self-consistent (~10 times).

Result: Size limited only by onset of non-steady, turbulent flow
Show results for 0.1mm cavities.
> 10 orders of magnitude faster than fully atomistic
~ 20 minutes per iteration
Use average over 16 MD representations to accelerate

Schematic of Local Refinement

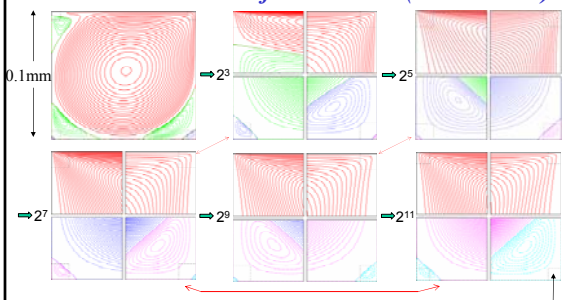
Coarse ->Fine: Prolongation.

Fine->Coarse: Restriction.



Flow at each scale reaches steady state at its own characteristic time

Multiscale Solution for Re=6400 (U=0.068σ/τ)

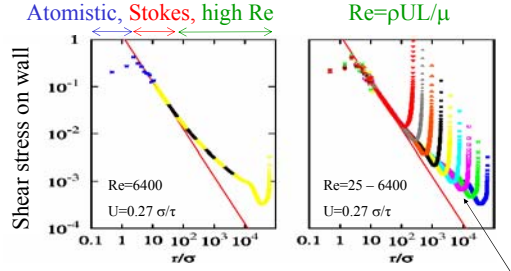


- Ten grid levels, largest 256x256, others 64x64, smallest mesh 0.95σ
- Dashed lines: the regions expanded in successive plots. Final plot → MD region
- Stokes equations→ bottom corners self-similar under mag. by ~16 (red arrows) This scaling is cut off by atomic structure.
- Computational time saving more than 10^{10} over fully atomistic.

Stress along the moving wall

Three regions contribute to force F:

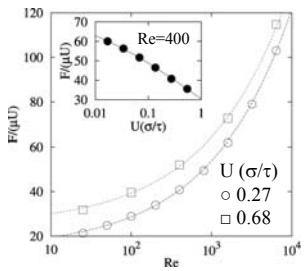
Atomistic, Stokes, high Re Re=ρUL/μ



Breakdown of Stokes for r<S – atomistic or r>R_I ≡μ/ρU – inertial
Little change for r < R_I as increase Re by increasing L
Large r contribution gives change in F for fixed U, atomic props.

Total Force on the Moving Wall

Re - only parameter in continuum theory
Find strong variation with U at fixed Re, atomic model



$$\frac{F}{\mu U} = f_S + f_{Stokes} + f_{Re}$$

r<S S<r<R_I R_I<r

$$f_S = 4.3$$

$$f_{Stokes} = \frac{8\pi}{\pi^2 - 4}\ln(R_I / S)$$

$$f_{Re} = 3.85 + 1.98\mathrm{Re}^{0.434}$$

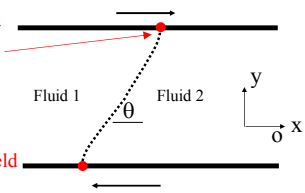
f_S given by assumption that stress saturates at S
S= 0.3+ 7U$t_{L,I}$; f_{Re} is phenomenological fit

Moving Contact-line Problem

No-slip condition also leads to 1/r singularity at moving contact line

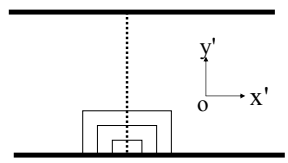
Interface bent by viscous stress
θ(r)=$θ_0$ + Ca (Q+ln(r/S))
where Ca=μU/γ, Q, S, consts.

Contact line affects entire flow field



Solve in transformed coordinate system with fixed multigrid

Interface: x_s=f(t,y_s)
x'=x-f(t,y), y'=y



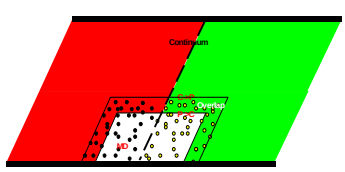
Hybrid Scheme for Two Phase Flow

Must fix interface angle, position in addition to velocity

P⇒C: Find location where concentration changes to determine angle & position

C⇒P: Add forces that enforce interface position at outer edge Displace atoms to maintain location in middle

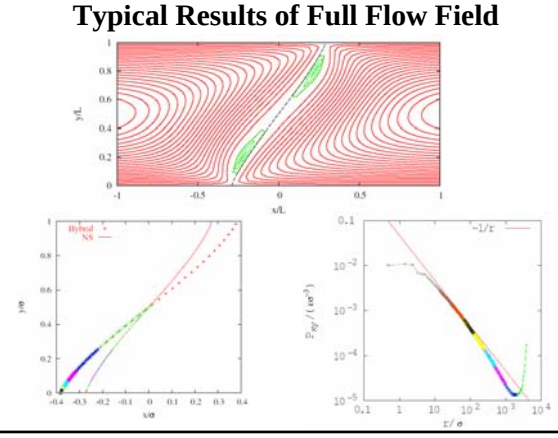
Originally C had no-slip at fluid-fluid interface, but found slip length ~5.5σ. Had to change C code



Procedure to get steady MD solution:

1) Fix the boundary shape, let system reach steady state.
2) Correct boundary shape according to the new interface and then repeat the first step until the the boundary and interface shapes are consistent.

Typical Results of Full Flow Field



Summary for Fluid Flow

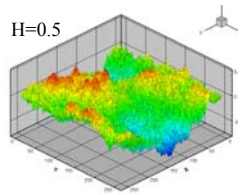
- We have developed a multiscale hybrid method that can simulate a macro-length scale flow while still resolving the atomistic structure in a small region. Treats mass and heat flux
- The ability to resolve the stress on all scales enables the first calculation of the drag force on the moving wall in cavity flow. The force depends on three dimensionless numbers:

$$Re = \frac{\rho UL}{\mu}, \quad I = \frac{U\tau}{\sigma} \text{ and } R_m = \frac{S}{r_l} = \frac{\rho US}{\mu}.$$

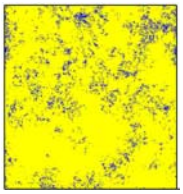
- Algorithm adapted to dynamic interfaces
  Initial results for contact line motion will be extended to study interface shape and stress over wide range of length scales.

Multi-scale modeling of contacts between self-affine surfaces

Contact geometry and stresses central to friction & adhesion
Real surfaces often rough on many scales → self-affine
Surfaces steeper at smaller scales, fractal contact regions, most connected regions of contact at resolution of calculation
⇒Not clear continuum mechanics applies

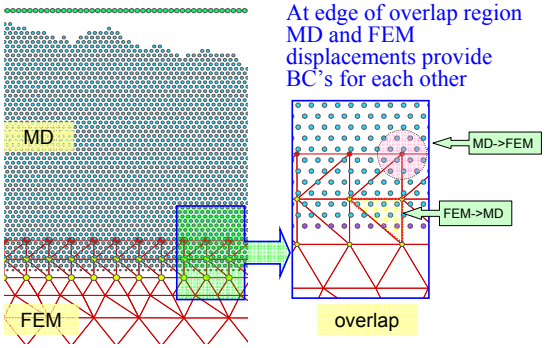


Self-affine surface



Contact (blue) of self-affine surface

Hybrid model for 2d self-affine surfaces
Easily treat volumes with ~10^8 atoms



At edge of overlap region MD and FEM displacements provide BC's for each other

Continuum Treatment of Solid

- Linear finite elements
- Explicit dynamics for nodes
- Newmark method $\Delta t_{FE} \sim 10\ \Delta t_{MD}$, Langevin thermostat
- Staggered time grid as for fluids
- Constitutive law – quadratic in strain
  – accurate to 2% in each strain component

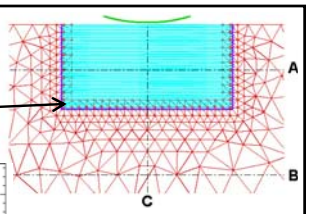
Atomistic Treatment of Solid

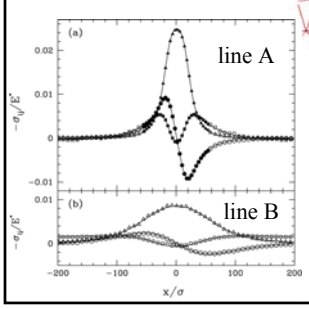
- Two dimensional triangular lattice
- Lennard-Jones interactions between neigbors
- Velocity Verlet, Langevin thermostat

Show low T results to minimize noise, but works at high T

Quasistatic Test Cylindrical Contact

Mesh, atomistic & overlap



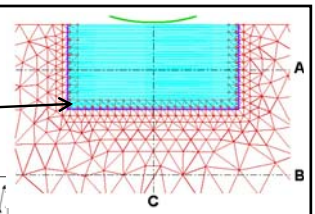


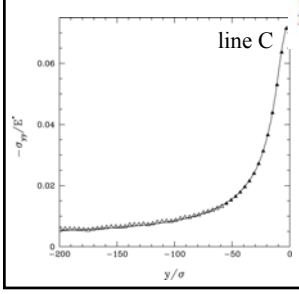
Lines – pure MD

Symbols – hybrid
Filled – MD region
Open – FEM region
▲ - σ_{yy} ● - σ_{xx}
■ -σ_{xy}

Quasistatic Test Cylindrical Contact

Mesh, atomistic & overlap





Lines – pure MD

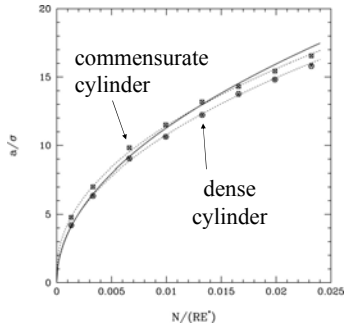
Symbols – hybrid
Filled – MD region
Open – FEM region
▲ - σ_{yy}

Scaling of Contact Width a with Load

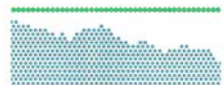
— Continuum theory
□,○ All MD
x,* Hybrid

Excellent agreement of hybrid with MD

Deviate from continuum due to anelastic response and atomic discreteness



Contact Area vs Load for Self-Affine Fractal



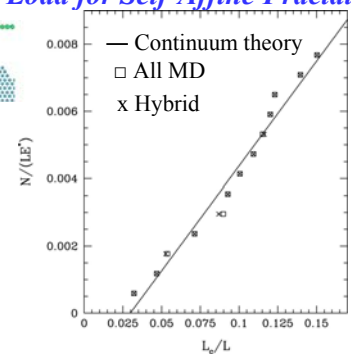
1024 atomic spacings in each dimension

Roughness exponent 0.6

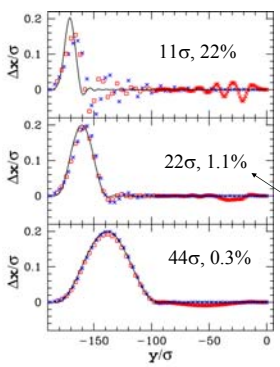
Voss midpoint algorithm

Excellent agreement of hybrid with MD

Only deviation due to activated plastic event. See fluctuations in time of occurrence for all MD



Multiscale simulation of shear wave in solid



— Full MD
□ Hybrid
x FEM

Deviations from full MD are like those caused by coarse resolution in FEM.

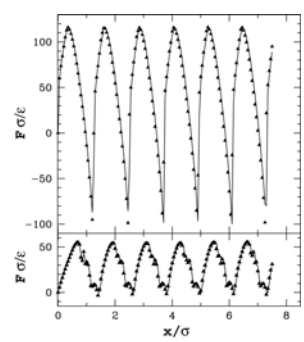
Percentage of energy reflected at overlap region comparable to that from resolution change in FEM

Small for pulse > ten times mesh size 4σ

Multiscale simulation of dynamic friction

— Full MD ▲ Hybrid

L=1024 d_{nn} U=0.01σ/τ
N=204.8ε/σ

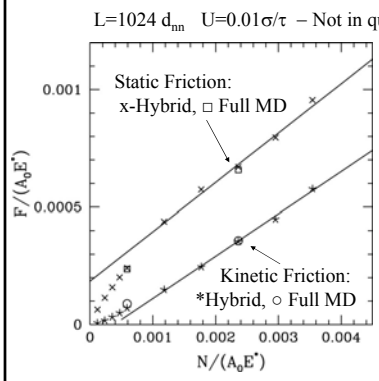


Flat on flat geometry

Flat on self-affine rough surface

Friction vs. Load for Rough Surface

L=1024 d_{nn} U=0.01σ/τ – Not in quasistatic limit

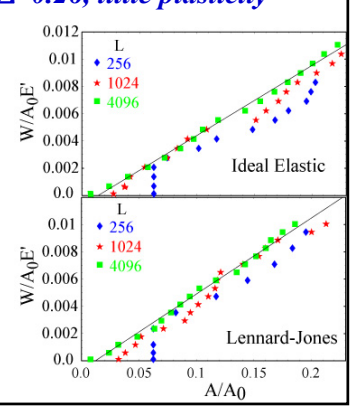


Smooth surfaces, Δ=0.26, little plasticity

Δ=rms surface slope
L= # atoms on side

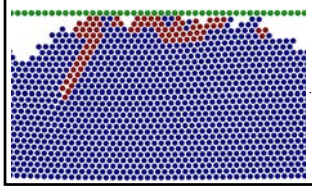
Results nearly converged for L=4096 atoms ~1μm

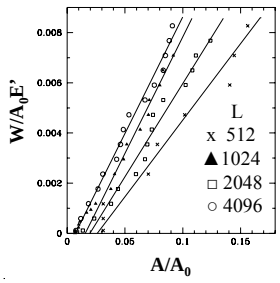
Find A ∝ W, but ratio 2-3 times continuum



Plastic results for Δ=0.78 show size effects

- Still have A∝W, but L dependent
- Surface flattening before dislocations important

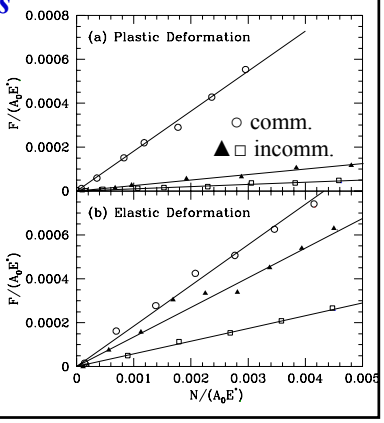




Friction forces

commensurate:
plastic ≈ elastic

incommensurate:
plastic < elastic
because contacts bigger, forces average to zero



Conclusions for Hybrid Method

- Have robust multiscale method for both fluids and solids
- Implemented for quasi-2D flows near solids
  → lengths to ~1μm for dynamic cases, ~1mm for quasistatic
- Implemented for quasi-2D contact between self-affine surfaces
- Incorporated heat flux for sheared fluids
- Comparisons to MD and continuum results show limitations of continuum approximation at interfaces
  →Position and rate dependent slip near solids
  →Sensitivity of contact area and stress to atomic scale structure, unexpected mode of plastic deformation at interface
- First calculation of drag force in singular corner flow
  → integrate stress over 5 orders of magnitude in length
- First calculation of atomistic effects in self-affine contact
  → rough over 4 orders of magnitude in length scale