DETERMINING HYDRODYNAMIC BOUNDARY CONDITION FROM EQUILIBRIUM FLUCTUATIONS

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Maxwell Equations vs. Navier-Stokes Equation

 In electrodynamics, Maxwell equations are solved with boundary conditions (BC) that can be derived from the equations themselves.

 In contrast, the hydrodynamic BC represents information that is additional to the Navier-Stokes equation, and necessary for its solution.

Non-equilibrium MD Simulation

 Non-equilibrium MD simulation has been widely used to calculate dissipation coefficients. For example,

(1) Fluid viscosity may be obtained by imposing on a bulk fluid system a share rate and measuring the stress, or vice versa.

(2) The surface frictional coefficient in nanoscale confined system may be obtained by imposing ether a Poiseuille flow in the channel and measuring the slip velocity and the surface frictional stress.

(3) Usually a Navier boundary condition is obtained: $v^{slip}\beta = \eta \dot{\gamma}$.

Non-equilibrium MD Simulation: An example



- Arbitrariness and difficulty in determining the position of hydrodynamic boundary, partially due to the large fluid density fluctuation in the boundary layers
- Macroscopically very large fluid velocity

Fluctuation-Dissipation Theorem (FDT)

- FDT links the macroscopic dynamic transport coefficient *L* to the thermal fluctuation of the corresponding flux *J* in equilibrium.
- FDT states that L can be calculated from the integral of the autocorrelation function of J in equilibrium

$$L = \frac{V}{k_B T} \int_0^{+\infty} \langle J(0)J(t)\rangle dt$$

Equilibrium MD Simulation

 FDT provides an approach to measure the fluid viscosity from equilibrium MD simulations, by calculating the stress-stress autocorrelation function

$$\eta = \frac{V}{k_B T} \int_0^{+\infty} \langle \tau_{xz}(0) \tau_{xz}(t) \rangle dt$$

 Several forms of FDT for confined fluid systems were also proposed. For example, Bocquet and Barrat (BB) proposed

$$\beta = \frac{1}{Sk_BT} \int_0^\infty F_{wf}(0) F_{wf}(t) dt$$

--Simulations based on the above formula yielded unphysical results that β is sample size dependent.

How to uniquely and consistently determine the precise location of the hydrodynamic boundary and the interfacial dissipation coefficient for a confined system in MD simulation?

We propose an approach by using the **Hydrodynamic Eigenmodes**.

Geometry of the System



Molecular view of a sample simulation system showing the definition of

- *H:* Position of atomic solid-liquid interface
- *h:* Position of hydrodynamic solid-liquid interface
- $\Delta = H h.$

Navier-Stokes Equation

• The fluctuating transverse (x) momentum density is defined as

$$J(z,t) = \rho_0 v(z,t)$$

where ρ_0 is the density of the fluid and v(z,t) is the transverse velocity • J(z,t) may be expressed as

$$J(z,t) = \sum_{n=1}^{\infty} j_n(z,t)$$

with the eigen-components $j_n(z, t)$ obtainable by solving the incompressible Navier-Stokes equation

$$\frac{\partial}{\partial t}j_n(z,t) = \frac{\eta}{\rho_0}\frac{\partial^2}{\partial z^2}j_n(z,t)$$

where η is the bulk viscosity of the fluid

Hydrodynamic modes

By writing the eigenmodes as

 $j_n(z,t) = Z_n(z)T_n(\Delta t)$

and considering only the anti-symmetric fluctuating modes, we have

$$Z_n(z) = A_n \sin(k_n z)$$
$$T_n(\Delta t) = T_n(0)e^{-\eta k_n^2 \Delta t/\rho_0}$$

with Δt the time relative to an arbitrary starting point. k_n 's are the eigenvalues of the hydrodynamic modes.

Eigenmodes contain information about the hydrodynamic boundary condition

• By introducing the slip length $l_{slip} = \eta/\beta$, we get the following equation for all the eigenmodes

$$\tan(k_n h) = -k_n l_{slip} \qquad Eq. (1)$$

- All the hydrodynamic modes are orthogonal to each other over the same spatial domain. This forms an over-determined system to uniquely locate the hydrodynamic boundary.
- It follow that the knowledge of k_n 's will enable (1) the determination of the location of the hydrodynamic boundary, and (2) the determination of the slip length.

Hydrodynamic Modes



Two hydrodynamic modes are also shown for $H = 13.2\sigma$, where σ is the size parameter in the Lennard-Jones potential. 2*H* is the channel width as defined by the solid-liquid molecular interface.

Yellow dashed lines indicate the hydrodynamic boundary.

Generalized Fluctuation-dissipation Approach



- $C(k, \Delta t)$: Normalized transverse momentum density autocorrelation function.
- $C(k_n, \Delta t) = \exp(-\eta k_n^2 \Delta t / \rho_0)$ Decay time $\tau_{Decay}(k_n) = \rho_0 / \eta k_n^2$.

• Deviation of the k value from k_n would introduce inconsistency with the boundary condition, thereby leading to a faster decay for $C(k, \Delta t)$.

 $-k_n$ can be identified as the location of local peaks in the decay time.

Molecu	Other Parameters				
		-Lennard-	Jones (LJ) fluid	r_c	2.5σ
$H_{\rm c} = 13.2\sigma$ $H_{\rm c} = 26.1\sigma$ $H_{\rm c} = 51.9\sigma$		-Confined	between two parallel	$ ho_f$	$0.81/\sigma^{3}$
		planar soli	d walls	$ ho_w$	$1.86/\sigma^{3}$
		-Two [001]	atomic layers each	Т	$2.8 \varepsilon/k_B$
		-Wall atoms constrained by a		NVT, Langevin thermostat	
$m_1 = 15.20, m_2 = 20.10, m_1$	13 – 51.70	harmonic s	spring potential	dt	$0.002\sqrt{m\sigma^2/\varepsilon}$
Force Field	Hydrophobic		Hydrophilic	m_w	m
Function Form (LJ)	$u_{ij}(r)$	$) = 4\varepsilon_{ij} \left(\left(\sigma_{ij} \right) \right)$	r) ¹² – $\delta_{ij} (\sigma_{ij}/r)^6$	m_{f}	m
\mathcal{E}_{Wf}		1.1			
\mathcal{E}_{ff}		8			
$\sigma_{\!ff}$		C			
σ_{wf}		1.0			
δ_{ff}		1			
δ_{wf}		1			

Implementation of the Projection Approach in MD

• From the MD trajectories, $C(k, \Delta t)$ was measured for different input values of k ranging from 0.001 to 1 in intervals of 0.001 (all in units of σ^{-1})

$$C(k,\Delta t) = \frac{\langle \left(\sum_{i=1}^{N} v_i(t=t_0) \sin(kz_i(t=t_0))\right) \cdot \left(\sum_{i=1}^{N} v_i(t=t_0+\Delta t) \sin(kz_i(t=t_0+\Delta t))\right) \rangle}{\langle \left(\sum_{i=1}^{N} v_i(t=t_0) \sin(kz_i(t=t_0))\right) \cdot \left(\sum_{i=1}^{N} v_i(t=t_0) \sin(kz_i(t=t_0))\right) \rangle}$$

 $z_i(t)$: z coordinate for atom i at time t *m*: the molecular mass

$C(k_n, \Delta t)$ from MD Simulations



Natural logarithm of the normalized auto-correlation functions measured from MD simulations for the three eigenmodes in the hydrophilic channel with $H_1 = 13.2\sigma$. The decay time can be evaluated from **the inverse of the slope** for each straight line.



Hydrophilic Case

- Figures A, B, and C are for channel widths $H_1 = 13.2\sigma$, $H_2 = 26.1\sigma$, and $H_3 = 51.9\sigma$, respectively.
- The positions of the peaks (marked by red arrows) were determined by using ORIGIN (inset of Fig. A), and remarkable agreement is achieved between MD measurement and hydrodynamic theory Eq. (1).
- Values of η obtained from the three simulations show excellent agreement, and differ only slightly from that evaluated from nonequilibrium MD simulations.

Data for the Hydrophilic Case

TABLE 1(k_n in units of $1/\sigma$)									
$H=13.2\sigma$, $h=10.9\pm0.1\sigma$, $\Delta=2.3\pm0.1\sigma$, $l_s=2.0\pm0.1\sigma$, $\eta=1.84\eta_{_0}$									
k _n MD	0.246 0.504				0.777				
k _n Theory	0.246	0.504				0.774			
$H = 26.1 \sigma$, $h = 23.8 \pm 0.2 \sigma$, $\Delta = 2.3 \pm 0.2 \sigma$, $l_s = 2.0 \pm 0.1 \sigma$, $\eta = 1.84 \eta_0$									
k _n MD	0.122	0.246	0.371	0.49	96	0.627	C).756	0.878
k _n Theory	0.122	0.245	0.369	0.495		0.622	C).75	0.879
$H=51.9\sigma$, $h=49.7\pm0.1\sigma$, $\Delta=2.2\pm0.1\sigma$, $l_s=2.1\pm0.1\sigma$, $\eta=1.81\eta_{_0}$									
k _n MD	0.061	0.121	0.182	0.244	0.304	4 0.3	367	0.428	0.489
k _n Theory	0.061	0.121	0.182	0.243	0.30	5 0.3	866	0.428	0.490
k _n MD	0.555	0.611	0.678	0.744	0.79	5 0.8	364	0.934	0.98
k _n Theory	0.552	0.614	0.676	0.739	0.80	1 0.8	364	0.926	0.989

- η , l_{slip} (thus β) & Δ determined from the three simulations are highly consistent, implying that they are intrinsic parameters that depend only on the physical and/or chemical properties of the specific bulk or interface, regardless of the system geometry.
- For the present hydrophilic case, l_{slip} is approximately equal to Δ . This coincidence makes the nonslip boundary condition, with the boundary set at the molecular interface, very accurate for most of the calculations.

The Position of Hydrodynamic Boundary



 $\left| \tan^{-1} \left(\frac{-z_n(z)/z_n'(z)}{l_s} \right) \right|$ with the k_n measured from MD simulations for each mode of the hydrophilic case with $H_2 = 26.1\sigma$. The multiple eigenmodes are seen to form an over-determined system for the unique determination of the hydrodynamic boundary position and l_s .



Hydrophobic Case

- Figure A, B, and C are for channel width $H_1 = 13.2\sigma$, $H_2 = 26.1\sigma$, and $H_3 = 51.9\sigma$, respectively.
- Same as in the hydrophilic case, remarkable agreement is achieved between the positions of the peaks measured by MD and those predicted by hydrodynamic theory.
- Values of η obtained consists with that obtained in hydrophilic case.

Data for the Hydrophobic Case

TABLE 2										
$(k_n \text{ in units of } 1/\sigma)$										
$H=13.2\sigma$, $h=10.8\pm0.2\sigma$, $\Delta=2.4\pm0.2\sigma$, $l_s=3.0\pm0.1\sigma$, $\eta=1.81\eta_{_0}$										
k _n MD	0.235			0.492			0.767			
k _n Theory	0.234	234 0.49			2 0.7			'67		
$H = 26.1 \sigma$, $h = 23.6 \pm 0.2 \sigma$, $\Delta = 2.5 \pm 0.2 \sigma$, $l_s = 3.0 \pm 0.1 \sigma$, η = 1.81 η_0										
k _n MD	0.119	0.242	0.367	0.49	1 (0.619	0.744	0.873		
k _n Theory	0.119	0.240	0.364	0.49	2 (0.621	0.751	0.882		
$H=51.9\sigma$, $h=49.7\pm0.2\sigma$, $\Delta=2.2\pm0.2\sigma$, $l_s=3.1\pm0.1\sigma$, $\eta=1.83\eta_{_0}$										
k _n MD	0.0593	0.12	0.179	0.24	0.301	0.365	0.421	0.489		
k _n Theory	0.0595	0.119	0.179	0.24	0.301	0.362	0.424	0.486		
k _n MD	0.55	0.609	0.677	0.736	0.804	0.866		0.983		
k _n Theory	0.548	0.610	0.672	0.735	0.798	0.861	0.924	0.986		

- η , l_{slip} (thus β) & Δ determined from the three simulations are highly consistent.
- l_{slip} exhibits a ~50% increase from the value of the hydrophilic case.
- This consistency, again, gives confidence in the location of the hydrodynamic boundary and the relevant parameter values using the current approach.

Location of the Hydrodynamic Boundary

- In both the hydrophilic and hydrophobic cases, the hydrodynamic boundary is located about 2.3^σ inside the fluid. Hence the hydrodynamic boundary is NOT the fluid-solid molecular interface. This is understandable from the point of view that there is always fluid structures at the molecular interface.
- The precise identification makes the value of the slip length meaningful.

Kubo-Greenwood Theorem for Confined



- Applies only to the domain where the hydrodynamic description is valid
- A thin lubrication layer next to the wall, with the thickness / (that will approach zero in the limit) and some artificial viscosity η_2
- No-slip at the interface between the wall and the boundary (lubrication) layers

FDT for Viscous Dissipation

- Incompressible Navier-Stokes equation is solved for the system by similar approach as in the previous case.
- We combine the bulk and interfacial dissipations into a single system for unified treatment by applying the FDT for viscous dissipation for each mode

$$2S \int_{0}^{+\infty} dt \int_{0}^{h} dz \left(\eta \left\langle \left(\frac{\partial j_n(z,t=0)}{\partial z} \right) \left(\frac{\partial j_n(z,t)}{\partial z} \right) \right\rangle \right) = \rho_0^2 k_B T$$

Separation of the Bulk and Interfacial Components

 In the limit of h/l>>1, we can separate out the interfacial component and the bulk component of the left hand side of the FDT equation

$$\begin{split} D_n^{boundary} &= 2S\beta(V_n^S)^2 \\ &\to \frac{\eta_1 k_n^2 \rho_0 k_B T}{1 + \frac{\eta_1 \beta}{h(\beta^2 + \eta_1^2 k_n^2)}} \times \frac{2\eta_1 \beta}{h(\beta^2 + \eta_1^2 k_n^2)} \\ D_n^{bulk} &= S\eta_1 A_n^2 k_N^2 \left(h - l + \frac{\sin(2k_n(h-l))}{2k_n} \right) \\ &\to \frac{\eta_1 k_n^2 \rho_0 k_B T}{1 + \frac{\eta_1 \beta}{h(\beta^2 + \eta_1^2 k_n^2)}} \times \left(1 - \frac{\eta_1 \beta}{h(\beta^2 + \eta_1^2 k_n^2)} \right) \end{split}$$

FDTs for Bulk and Interfacial Dissipations

• By defining a dimensionless boundary dissipation fraction

$$C_n = \frac{1}{2} \frac{D_n^{boundary}}{D_n^{bulk} + D_n^{boundary}} = \frac{\eta_1 \beta}{h(\beta^2 + \eta_1^2 k_n^2) + \eta_1 \beta}$$

The bulk FDT can now be written as

$$\int_{0}^{+\infty} dt \int_{0}^{h} dz \left\langle \left(\frac{\partial J(z,t=0)}{\partial z} \right) \left(\frac{\partial J(z,t)}{\partial z} \right) \right\rangle = \frac{\rho_{0}^{2} k_{B} T}{2S\eta_{1}} \sum_{n=0}^{\infty} (1 - 2C_{n})$$

And the boundary FDT is given by

$$\int_0^{+\infty} \langle J(z=h,t=0)J(z=h,t)\rangle dt = \frac{\rho_0^2 k_B T}{S\beta} \sum_{n=0}^{\infty} C_n$$

The Boundary FDT for a Finite System



- Numerical evaluation shows that $\sum_{n=0}^{\infty} C_n = \Xi \rightarrow 1/2$ as $h/l \rightarrow \infty$ when the interfacial FDT first presented by Bocquet and Barrat is recovered.
- The boundary and bulk dissipations are usually inseparable for finite systems, and the finite size simulation of the boundary FDT would lead to a clear size dependence.
- Separation of the two components, with size independence of the boundary FDT, is achieved only at the large h/l limit.

Conclusions

- We have uniquely determined the precise location of the hydrodynamic boundary, the interfacial dissipation coefficient, as well as the viscosity by using the wavenumbers and mutual orthogonality of the hydrodynamic eigenmodes. They can be unambiguously identified in MD simulations.
- Overwhelming consistency is observed between the microscopic simulations and the hydrodynamics description, even for the large k modes.
- In a confined system the hydrodynamic modes inherently contain the information about <u>both the bulk property and hydrodynamic boundary</u> <u>condition</u>.

Thank you for your attention!