

Computational Fluid Dynamics at the Nanoscale

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Introduction

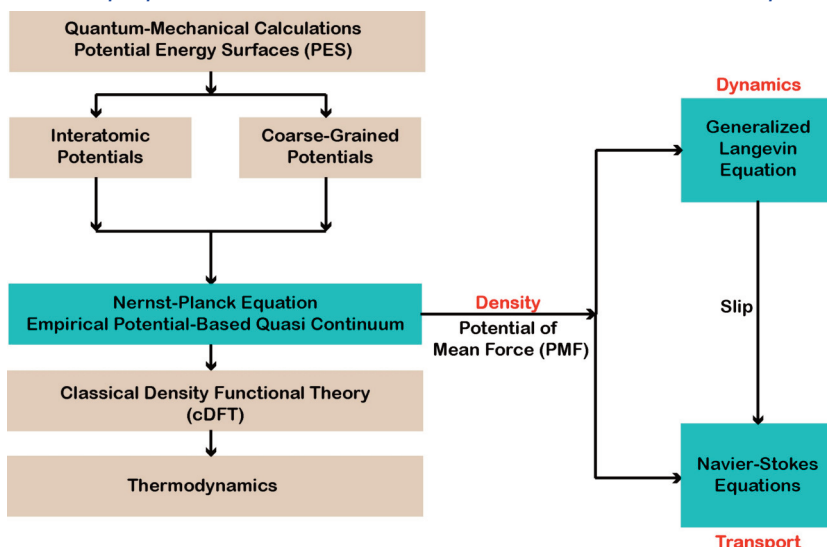
Computational fluid dynamics (CFD) has played a central role in enabling many important scientific and societal advances such as design of aircraft, understanding blood flow through arteries, electronics cooling for chip design, and simulation of complex manufacturing processes for product innovation. Classical CFD tools are built by solving the compressible and incompressible Navier-Stokes equations using a variety of sophisticated computational approaches. Often, depending on the application, the Navier-Stokes equations are combined with Maxwell's equations and their simpler forms to understand charged fluid transport. While compressible and incompressible Navier-Stokes equations are accurate for simulation of physical phenomena at larger length and time scales, an interesting question arises on the accuracy of these equations at the nanoscale. During the last couple of decades, fluid mechanics at the nanoscale (also referred to as nanofluidics) has gained a lot of prominence because of important applications such as clean water, clean energy, separations, nanomanufacturing, and selective transport of ions with important implications in disease diagnosis and drug discovery. As the critical dimension

encountered in nanofluidics ranges from a few Angstroms to several tens of nanometers, important deviations from classical hydrodynamics are observed [1]. For instance, density fluctuations near the interface, size dependent fluid properties, restricted translational and rotational motions of molecules, charge inversion where the net charge density at an interface is opposite in sign to the prediction from classical theory, flow reversal where the fluid moves in the opposite direction as that predicted from the classical theory, breakdown of classical constitutive relations, and several other important phenomena have been observed at the nanometer scale. As a result, the use of classical CFD tools to simulate fluid physics at the nanometer scale has been questionable.

To overcome the limitations of the classical theories for nanoscale fluid transport, quantum and atomistic approaches are widely used. However, these approaches are limited to small length and short time scales, and it makes it difficult to use them in a design environment for applications involving nanoscale fluid transport. An alternative approach is to develop multiscale approaches seamlessly incorporating atomistic physics into continuum theories to enable rapid simulation of nanofluidic systems. Over the last 1-2 decades, efficient multiscale approaches have been developed to accurately simulate hydrodynamics at the nanoscale. These multiscale simulation tools provide a robust computational fluid dynamics environment for nanoscale fluids. The rest of this article describes a multiscale framework that accurately describes fluid physics at the nanoscale.

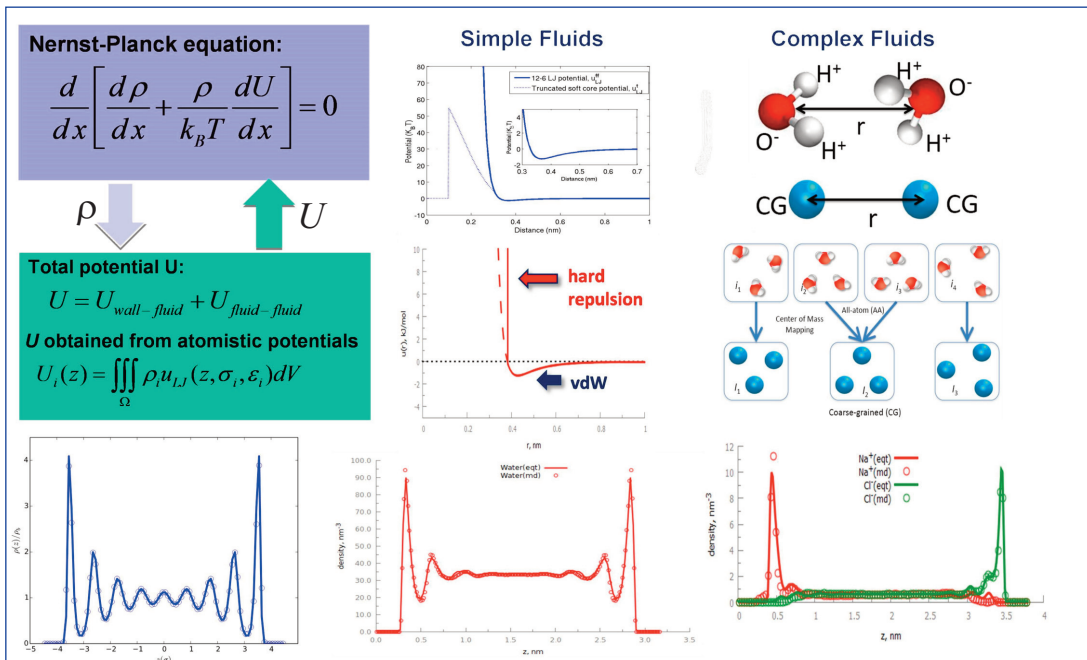
Figure 1:
Multiscale framework for nanoscale computational fluid dynamics (CFD). Structure (e.g. density profiles), dynamics (e.g., diffusion) and transport (e.g. velocity) – the essential components of nanoscale CFD are shown in cyan color boxes.

The quasi-continuum framework can be combined with the classical density functional theory to compute the thermodynamic properties of fluids confined in nanometer channels and pores



II - Multiscale Framework

IACM Expressions readers will note that authors are requested to submit articles with no equations. With this in mind, the basic ideas in multiscale modeling of nanofluidics are introduced using pictures and the mathematical details can be found in the references. Simulation of nanoscale fluid transport, including coupling to electric fields as driving forces, can be essentially reduced to computing the structure of the fluid (the focus here is primarily on density, but other structural aspects of the fluid are also



important at nanoscale), dynamics (for simplicity, the discussion here will focus on diffusion, but other dynamical properties are also of interest) and transport, primarily referring to the velocity of the fluid.

The multiscale framework to compute the structure, dynamics, and transport of nanofluidics is shown in Figure 1. To predict the structure of the fluid, the Nernst-Planck equation [2, 3] is used and the potential energy term in the Nernst-Planck equation is computed by using the atomistic potentials describing the atomic interactions in the fluid. The interatomic potentials and the coarse-grained potentials (as described in detail in Section III) can be obtained from quantum-mechanical calculations but this article will not delve into those details considering space limitations. Calculation of the structure is described in more detail in Section III. The solution of the Nernst-Planck equation provides the density profile as well as the potential of mean force (PMF) which serve as input to the generalized Langevin equation (for dynamics) and Navier-Stokes equations (for transport). The generalized Langevin equation is used to compute the trajectory of the fluid molecules using which the diffusion coefficient as well the slip velocity of the fluid can be computed.

The calculation of dynamical properties is described in Section IV. The multiscale framework described here can also be used to compute thermodynamic properties and this is also concisely summarized in Section IV. Using inputs from the Nernst-Planck and generalized Langevin equations, the Navier-Stokes equations are solved to compute the transport properties of the fluid. This is described in more detail in Section V.

Figure 2:

(top left) Quasi-continuum framework

to compute the structure of fluids;

(top middle) The fluid-fluid potentials are approximated by a soft-core (top) and hard repulsion (bottom);

(top right) Complex fluids (e.g., water) are represented by coarse-grained beads

(bottom left) comparison of density of argon from molecular dynamics (circles) and quasi-continuum theory (solid line)

(bottom middle) comparison of density of water from molecular dynamics (circles) and quasi-continuum theory (solid line)

(bottom right) comparison of density of ions (sodium and chloride ions) from molecular dynamics (circles) and quasi-continuum theory (solid line)

III - Structure

When a fluid is confined in a nanometer scale channel or pore, density inhomogeneity (layering of the fluid near the wall) is observed. The density oscillations, which arise due to the molecular interactions between the fluid with itself and with the wall, cannot be captured using classical theories. In addition, as shown in Figure 1, the density of a confined fluid is important to also understand dynamics and transport of the fluid. Instead of resorting to more expensive atomistic approaches, a quasi-continuum approach, where the interatomic potentials are directly integrated into the Nernst-Planck theory, can be used to compute the structure. The basic idea is shown in Figure 2. While quasi-continuum theories are prevalent in solid mechanics [4], for fluid mechanics it was first introduced in [5]. The potential energy term in the Nernst-Planck equation is computed using the atomistic interatomic potentials which are used to describe the fluid and wall in molecular dynamics – exceptions to this are discussed below. The various interactions

that contribute to the potential energy can be a function of the fluid density, so a simple iterative scheme is shown in *Figure 2* to self-consistently solve for the fluid density and the components of the potential energy. It is important to note that the potential energy dependence on density is highly nonlinear and good initial guesses (e.g., based on the Boltzmann distribution [6]) and effective nonlinear solvers are required to accurately compute the density profile.

Consider, first, simple fluids, which can be described by single-site isotropic pair potentials in atomistic simulations. In this case, van der Waals interactions [7] between fluid atoms (referred to as fluid-fluid interaction energy) and between the fluid and the wall (referred to as wall-fluid interaction energy) need to be considered. For most walls of interest, the wall-fluid interaction energy can be computed analytically by invoking the density of wall atoms (see [8] for more details). By invoking the density of a fluid, the fluid-fluid interaction energy can be computed by using the interatomic potential. However, the repulsive nature of the potential for short distances poses numerical difficulties. To overcome this, a mean-field approach, where a soft-core potential is used (see *Figure 2 (top middle)*) to approximate the repulsive part of the interatomic potential, a correlation-correction potential approach [9] where the pair correlation function is included in the formalism to overcome the mean-field approximation, and a fundamental measure theory where the repulsive part of the potential is approximated by a hard-sphere model (see *Figure 2 (top middle)*) are developed [10]. The unknown parameters in these approaches are determined by matching the potential of mean force (PMF) [11]. While all three approaches provide good accuracy, the fundamental measure theory-based approach is predictive and can be used for a variety of fluids with minimal effort (see *Figure 2 (bottom left)* for a typical result comparing molecular dynamics and quasi-continuum theory).

The quasi-continuum approach has also been extended to fluids with many-body interactions. For example, the charges on the oxygen and hydrogen atoms of water introduce electrostatic interactions which are long ranged. Since water molecules are represented by a density in the quasi-continuum approach, the charge information is not readily available. To address this challenge, each water is coarse-grained into a single spherical bead (see *Figure 2 (top right)*) and the interatomic potentials

describing water-water and water-wall are obtained by preserving some basic properties of the original all atom system. Some widely used approaches to develop coarse-grained (CG) potential for water and other complex fluids include iterative Boltzmann inversion (IBI) [12] – which preserves the bulk radial distribution function, force matching [13] – which preserves the forces between the all atom and CG systems, and relative entropy [14, 15] – which minimizes the information lost between all atom and CG systems. The CG potentials for water can be either directly incorporated or further coarse-grained before incorporation in the quasi-continuum framework. *Figure 2 (bottom center)* shows a typical result where the structure of water is compared between molecular dynamics and the quasi-continuum theory. The quasi-continuum framework can be extended to more complex fluids such as electrolytes, DNA, polymers, etc. For example, quasi-continuum treatment of electrolytes has been shown to effectively capture the charge inversion phenomenon (see [16]) which is missed by the classical theory.

IV - Dynamics, Thermodynamics

The dynamical properties of fluids (e.g., diffusion coefficient) at nanoscale can be different from their bulk properties. A straight-forward approach is to use molecular dynamics simulations. In molecular dynamics, the diffusion coefficient for the bulk fluid is usually determined by computing the mean-squared displacement (MSD) of the molecules, $\langle \Delta r(t)^2 \rangle$, as a function of time and fitting this behavior to the asymptotic time dependence predicted from the diffusion equation. For confined fluids, the diffusion coefficient can be anisotropic, i.e., the diffusion coefficient can be different along x-, y-, and z-directions. Furthermore, for inhomogeneous systems, where density layering is significant, molecules stay in the region of interest only for a finite time and then explore other regions. Thus, diffusion coefficient is expected to be different for different regions (spatial dependence of diffusion coefficient). Even though molecular dynamics simulations can be used to understand diffusion physics, they are expensive and limited to small systems.

The quasi-continuum framework can be combined with the memory function equation and generalized Langevin equation (GLE) (see *Figure 3 top*) to compute anisotropic and spatial variation of the diffusion coefficient [17]. In this multiscale approach, the density profile and the

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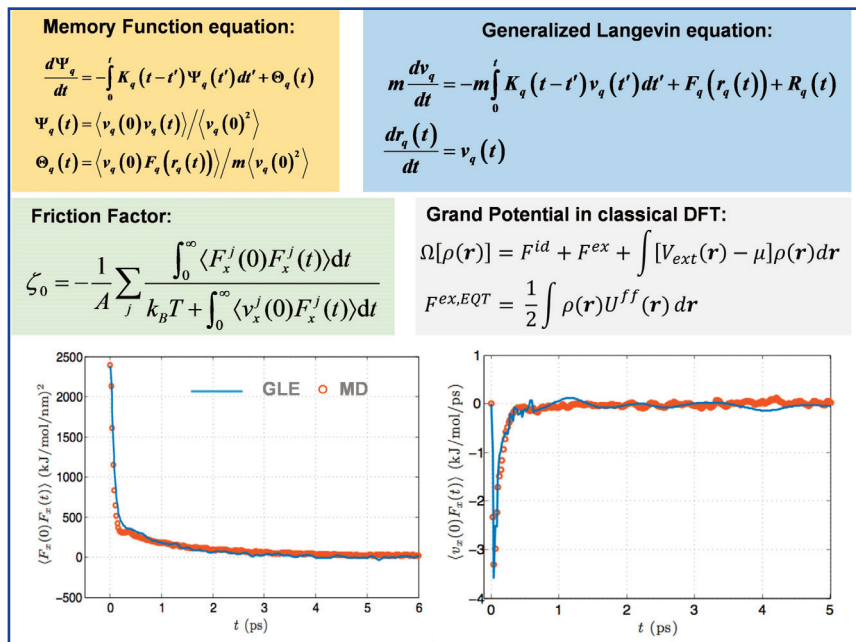
potential of mean force (PMF) are first computed by using the quasi-continuum theory. In a separate step, the memory function equation (see *Figure 3 top*), which is an integro-differential equation, is solved to determine the memory kernel. The dynamical variable (Ψ) describes normalized velocity autocorrelation function of a bulk fluid which is typically known, e.g., this can be obtained from molecular dynamics or experiments or via stochastic extension of the quasi-continuum theory. Once the PMF and the memory kernel are known, GLE can be solved to generate dynamic equilibrium trajectories of the fluid molecules. The generated trajectories can be used to compute quantities such as MSD and survival probabilities which can be used to estimate the diffusion coefficient. It is important to note that the solution of the memory function equation/GLE equation, with PMF obtained from the quasi-continuum theory, to obtain the diffusion coefficient is many orders of magnitude faster compared to the use of molecular dynamics. This is because the time step used in the generalized Langevin equation is much higher compared to that of the time step used in MD simulations.

A significant advantage of using the quasi-continuum/GLE approach, in addition to the fast calculation of the diffusion coefficient, is to estimate fluid-solid interaction properties such as the friction factor which can be used to calculate the slip velocity of a fluid on a solid wall. The friction factor, derived using linear response theory [18], is shown in *Figure 3 (middle)*. The expression for the friction requires the calculation of force autocorrelation and force-velocity cross correlation functions. Since forces and velocities as a function of time are obtained from the solution of GLE, the friction factor can be estimated easily. *Figure 3 (bottom)* shows force autocorrelation and force-velocity cross correlations for interaction of water with a silicon surface. The results from GLE compare well with those from MD. It is again important to note that the estimation of the friction factor using the GLE approach is orders of magnitude faster compared to using the molecular dynamics framework.

As shown in *Figure 1*, the multiscale framework can also be used to compute the thermodynamic properties of confined fluids. For fluids confined in nanometer channels and pores, the thermodynamic relationship between the grand potential and other thermodynamic properties such as entropy, temperature, pressure, etc. can be easily established. The classical density functional theory (cDFT) [19] provides a framework to

Figure 3:

- (top left) Memory function equation to determine the memory kernel (K_q);
- (top right) Generalized Langevin equation (GLE) describing the dynamics of particles;
- (middle left) Mathematical expression to determine the friction (and subsequently the slip of the fluid) that relies on force autocorrelation and force-velocity cross-correlation;
- (middle right) Definition of grand potential in classical density functional theory (cDFT); the excess free energy is computed by using the quasi-continuum potentials;
- (bottom left) Comparison of force autocorrelation from GLE and molecular dynamics (MD);
- (bottom right) Comparison of force-velocity cross correlation from GLE and MD



determine the grand potential in terms of the equilibrium density of the fluid (see *Figure 3 middle*). The excess part of the intrinsic Helmholtz energy accounting for non-bonded interactions is often difficult to compute, but quasi-continuum potentials can be used to accurately determine the excess part of the Helmholtz free energy. Thus, by combining the quasi-continuum framework with cDFT, thermodynamic properties such as adsorption, local pressure tensor, surface tension, and solvation force, of confined fluids can be computed (see [9] for more details).

V - Transport

The governing equations for nanoscale transport are the Navier-Stokes equations (see *Figure 4 (top)*). The classical Navier-Stokes equations, however, do not always accurately describe transport at the nanoscale because of complex interfacial physics – for example, two well known effects are the slip velocity and interfacial viscosity. Fluid-surface interactions and the

Navier-Stokes Equations:

$$\frac{D\rho_m \mathbf{u}}{Dt} = -\nabla P + \nabla \cdot (\boldsymbol{\mu} \nabla \mathbf{u}) + \mathbf{f}$$

$$u_x \left(-\frac{L}{2} + \delta \right) = u_x \left(\frac{L}{2} - \delta \right) = u_s$$

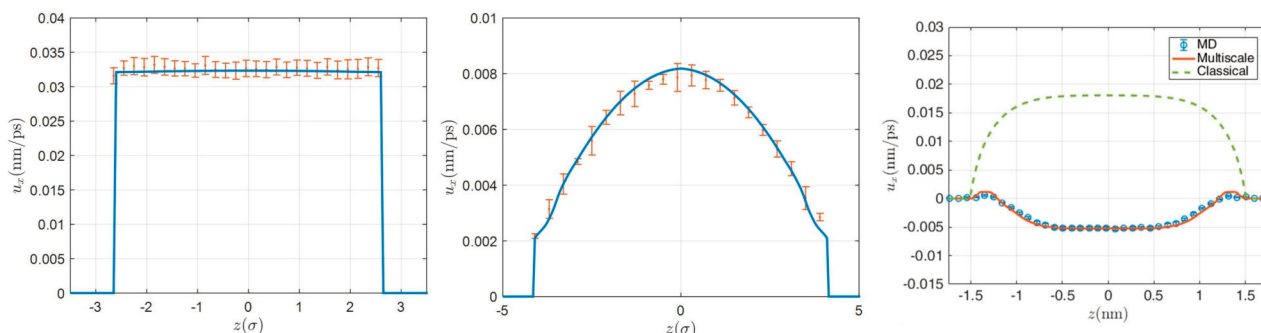
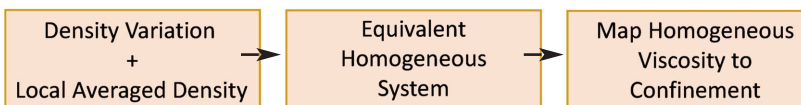
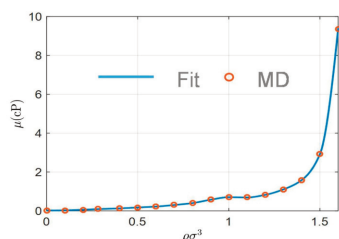


Figure 4:

- (top left)** Navier-Stokes equations along with the slip boundary conditions used for nanoscale transport;
- (top right)** Viscosity of water as a function of density
- (middle)** Approach used to determine viscosity of confined fluids
- (bottom left)** transport of water in graphene channels – solid line is multiscale simulation and error bars denote MD data
- (bottom middle)** transport of water in a silicon channel
- (bottom right)** electroosmosis of water; charge inversion causes flow reversal and multiscale theory accurately describes flow reversal

wall topology give rise to surface friction, which affects the collective motion of the fluid particles relative to the wall. The surface friction changes due to the potential corrugations, which changes due to the topology of the surface and the interaction potential between the fluid and the surface. It is important to account for surface friction effects which appear in the form of slip velocity in the transport model. It is also important to know where the slip velocity should be applied. Since there are essentially no fluid molecules at the wall, the slip velocity is applied at a distance from the wall where the density of the fluid is finite. This information is available from the quasi-continuum calculation of density profiles. The second aspect that is important is the viscous component of the flow. In macroscopic channels, viscosity is assumed to be constant in the entire channel. However, viscosity in confined channels can be different. Density layering near the surface introduces viscosity variation. As a result, viscosity can vary spatially in the nanochannel and it is important to account for this phenomenon. As shown in *Figure 1*

and described in the previous section, the slip velocity is computed using the generalized Langevin equation. The approach to compute the spatially varying viscosity is summarized in *Figure 4* (middle). Using the density from the quasi-continuum theory, a local averaged density is first computed. The local averaged density is then mapped to a bulk homogeneous system and the viscosity of the corresponding bulk system is computed. The bulk viscosity, corresponding to the local averaged density, is then used as the local viscosity of the

confined channel. This assumption works reasonably well for most nanochannels of interest. The bulk viscosity of most fluids as a function of density is known. In the absence of such relations, molecular dynamics can be used to compute density-viscosity relations. Shown in *Figure 4* (top right) is the density-viscosity relation for water. Once the various inputs to the Navier-Stokes equations are known (see *Figure 1*), the Navier-Stokes equations can be solved using well established methods to determine the velocity of the fluid.

The multiscale method described above has been used to investigate transport of a variety of fluids confined in nanometer channels [20]. Some representative results are shown in *Figure 4* (bottom). *Figure 4* (bottom left) shows the transport of water in a graphene channel. A significant slip velocity is observed in this system. The multiscale result (solid line) matches well with the molecular dynamics result (error bars). *Figure 4* (bottom middle) shows transport of water in a silicon channel where the slip velocity is not significant and viscous nature of the flow is observed in the central part of the channels. Again, a good comparison between multiscale method and molecular dynamics is observed. *Figure 4* (bottom right) shows an example where water and electrolytes are confined in a nanochannel. This is an example where charge inversion is observed, and the classical Navier-Stokes theory predicts that the water velocity is positive while molecular

dynamics predicts that the water velocity is negative. Multiscale theory, with inputs from the quasi-continuum theory for the density and the location of the slip velocity, the generalized Langevin theory for the slip velocity, and the local density approximation for the local viscosity, predicts that the water velocity is negative and the result matches reasonably well with the molecular dynamics result.

VI - Concluding Remarks

The multiscale methods described here to compute the structure, dynamics, thermodynamics, and transport of fluids confined in nanometer channels and pores are a point of departure from the classical CFD tools that are widely used at macroscale. Many important practical applications involve coupling of macroscale fluid mechanics with nanoscale fluid mechanics and efficient simulation of these problems is now possible via the multiscale methods described here. A number of issues such as the

development of coarse-grained potentials that are reliable at various thermodynamic states, seamless integration of structure, dynamics, thermodynamics and transport multiscale tools into one coupled computational environment, developing constitutive theories that are accurate and reliable at purely molecular limit, extraction of important transport parameters and properties such as slip and viscosity without resorting to coarse-grained theories are among the many challenges that will further push the frontiers on the development of multiscale methods for nanoscale hydrodynamics. ●

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