Mesoscale Hydrodynamics of Capillary Imbibition under Nanoconfinement

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Summary: Understanding mesoscale hydrodynamics in confined geometries is critically important for numerous applications including lab-on-a-chip systems and drug delivery platforms. Exploring the dynamics of fluids at mesoscopic length and time scales remain very difficult to probe experimentally, and also bring unique challenges to both atomistic and continuum modelling techniques. Here we present a novel coarse-grained model that combines parameters calibrated for water with a dissipative particle dynamics thermostat for the purpose of investigating mesoscale hydrodynamics. The methodology is used for simulating fluid imbibition into a nanocapillary. Our results suggest that end effect may play a more important role in the loading process than previously believed, corroborating recent experimental results on nanochannels.

INTRODUCTION

Understanding the dynamics of fluids at the nanoscale is of great interest for researchers from a range of disciplines. This is because the behavior of fluids at small scales is strongly influenced by surface effects such as capillary forces in nanoscopic systems, which provides fundamental challenges to long standing macroscopic theories that aim to explain flow and mass transport phenomena. These deviations from the anticipated behavior not only govern the reliability and performance of nanoscale systems, but often also lead to new functionalities that have been enabled with the advent of nanotechnology. Examples of such systems include lab-on-a-chip systems, where the ability to control the motion of nanoscopic fluids is essential for the transport of particles of interest such as nanoparticles or biomolecules. Other applications include loading and unloading of active nanoparticles, novel adhesives, and thin films on nanopatterned surfaces such as nanopillars. Leveraging capillary and confinement effects may potentially lead to functional materials with dynamic surface properties arising from tunable hierarchical architectures[1]. Thus, improved understanding of capillary phenomena at the nanoscale is critical for advancements in broad range of nanoscale applications.

Recently there has been a great deal of interest in accurately modeling nanoscale fluid behavior. For very small systems, such as flow through carbon nanotubes, atomistic models have proven useful [2]. At length scales larger than a few microns, continuum descriptions can typically provide accurate models. However, many systems of interest lie in the mesoscopic (10nm-1um) range. At these length scales, system sizes are often too large to be modeled with all-atom models, yet continuum descriptions miss key physics that result from the discrete molecular nature of the fluid and solid interfaces. Therefore, new techniques capable of capturing mesoscopic fluid behavior are needed. For systems in equilibrium, such as simulations of biomolecules, where water acts as a solvent, coarse-grained molecular dynamics (CGMD) models have been shown to accurately reproduce the results of classical molecular dynamics (MD), while greatly reducing computational cost [3, 4]. For many transport problems, the solely the choice of potential parameters does not suffice to capture hydrodynamic details. In particular, for out-of-equilibrium conditions such as capillary imbibition and drainage, global thermostats like Nose-Hoover or Berendsen, which dissipate energy uniformly in the system, as well as local thermostats that rescale particle velocities relative to some stationary background (e.g. Brownian dynamics), fail to preserve momentum and thus are incapable of correctly capturing hydrodynamics. A popular solution to this issue is to use a dissipative particle dynamics (DPD) thermostat[5]. In a DPD thermostat, particle velocities are rescaled through pairwise interactions with neighboring particles in such a way that the system both satisfies the fluctuation-dissipation theorem and preserves momentum. In the following paper, we present a calibrated water model with a DPD thermostat that can be used for mesoscale fluid transport problems. The model is calibrated to match surface tension, density and viscosity of water accurately. The ability of this model to capture mesoscale hydrodynamics under nanoconfinment is demonstrated through a capillary imbibition simulation into a nanochannel.

RESULTS AND DISCUSSION

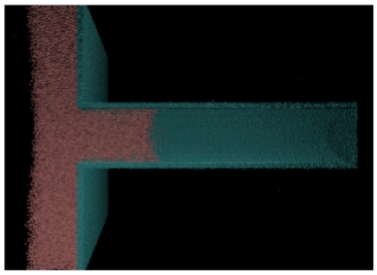

Figure 1. Capillary imbibition simulation

As a demonstration of the model's capability of capturing mesoscale hydrodynamic phenomena, fluid imbibition into a nanopore was simulated. The system (Figure 1) consisted of a cylindrical capillary 10nm in diameter and 50 nm in length in contact with a 50nm x 50nm x 10 nm reservoir of fluid. The reservoir dimensions were large enough compared to the capillary diameter so periodic boundary conditions could be used without any significant influence from neighboring pores on the filling dynamics. The capillary walls consisted of an fcc lattice of particles tethered to their initial position by linear springs with spring constant $k = \frac{k_B T}{a^2}$, where k_B is Boltzmann's constant and a is the fcc lattice constant. The walls were made to be hydrophilic so that the water completely wetted the surface. In separate simulations, the equilibrium contact angle between the water and the fcc surface was determined to be 0°. Initially, the capillary inlet was sealed and the reservoir was allowed to equilibrate for 1 ns. After equilibration, the inlet was opened and the fluid was drawn into the capillary through capillary suction.

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At the microscale, capillary imbibition can accurately be described through the Lucas-Washburn (LW) equation [6, 7] :

$$z(t) = \sqrt{\frac{\gamma R cos\theta_E}{2\eta} t}\ , \qquad (1)$$

where z is the imbibition length, γ is surface tension, R is the capillary radius, θ_E is the equilibrium contact angle and η is the fluid viscosity. However, applicability of this equation to nanoscale systems has remained a subject of much controversy, where several studies employed computational methods such as large-scale molecular dynamics (MD) to elucidate factors that may contribute to deviations from the theory for nanoscale capillaries. Martic et al. [8] simulated the imbibition of a Lennard-Jones fluid into a capillary and found that when the energy dissipation at the contact line is large compared with the viscous dissipation in the bulk fluid, as is often the case with nanoscale capillaries, the LW equation fails to accurately describe the penetration. In such cases, the LW equation must be modified to account for a dynamic contact angle (DCA). This result has been confirmed by a number of other studies using DPD[9, 10]. The derivation of the LW equation also neglects inertial effects. However, in the early stages of imbibition, the inertia prevails over viscosity. De Gennes [11] suggested that the timescale where inertia is significant is given dimensionally as $\frac{\rho R^2}{\eta}$, which for our case is ~1 nsec implying that inertial effects should not be ignored. In addition, several studies suggest that end effects can also contribute substantially to flow through nanochannels and pores [12]. Thus accounting for these effects, the force balance governing the imbibition dynamics becomes:

$$\frac{dp}{dt} = F_{cap} - F_f - F_{End}\ , \qquad (2)$$

where $F_{cap} = 2\pi r\gamma cos\theta_D$ is the capillary force, θ_D is the dynamic contact angle, $F_f = 8\pi\eta\dot{z}z$ is the resistive force due to wall friction, and F_{End} is force resulting from the pressure loss due to dissipation at the inlet. Sisan and Lichter [12] suggest the form for the pressure lost due to end effects is $\Delta P_{End} = \frac{3\eta}{r^3}Q$, where Q is the flow rate given by $\pi r^2\dot{z}$. Substituting into equation 2 gives the following equation of motion for the fluid front during the imbibition process:

$$\rho r^2(\dot{z}^2 + \ddot{z}z) = 2r\gamma cos\theta_D - 8\eta\dot{z}z - 3\pi\eta r\dot{z}\ . \qquad (3)$$

In order to use the above equation, the DCA must be known. To obtain a θ_D as a function of time, we extracted the value directly from the imbibition simulation. The resulting DCA, shown in Figure 2(a) as a function of time, is similar in form to that obtained in similar simulation in ref. [10], and is significantly different from the equilibrium contact angle ($\theta_E = 0$), adding credence to the importance of accounting for the DCA. A power law was fit to the DCA data, and equation 3 was solved numerically. The result is shown in Figure 2(b) along with the simulation data and the LW equation for comparison. Also included in Figure 2(b) is the solution for eqn. (3) with the end effects neglected. Our results suggests that the end effect play a substantial role in the early stages of capillary imbibition at the nanoscale and should be considered in the analytical model.

CONCLUSION

In this work we have developed a coarse-grained model for water using a DPD thermostat and a calibrated potential that allows for accurate simulation of hydrodynamics in confined geometries. Using the model to simulate the imbibition of water into a capillary, we observed that the end effects play a significant role in the dynamics of the fluid front. The model has the potential to be applied to a range of problems were mesoscale hydrodynamics and capillary forces are important.

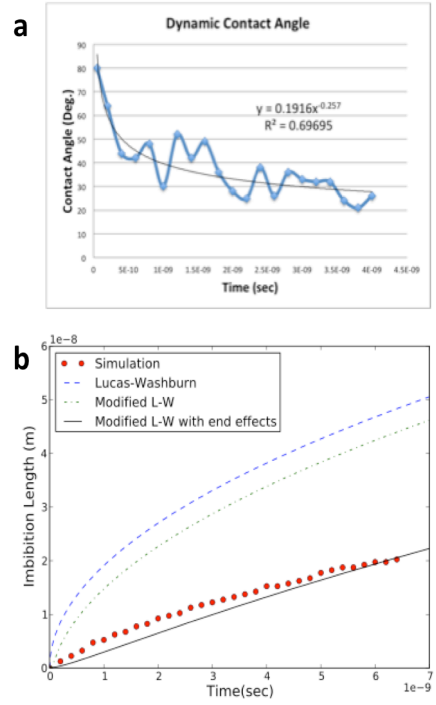

Figure 2. (a) Dynamic contact angle measurement and (b) capillary loading models.

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