Long range correction for wall-fluid interaction in molecular dynamic simulations

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Abstract— **A new method is proposed for correctly modeling the long range interaction between a fluid and a bounding wall in atomistic simulations. This method incorporates the molecular structure of the solid substrate while allowing for a finite interaction cutoff by making a proper estimation of long range correction for the fluid-wall interaction. The method is then applied to a molecular dynamic simulation of a spreading droplet. Conparison to simulations using several other previously used methods shows that the long range correction can be significant in some circumstances.**

I. Introduction

Two methods have been widely used in the past to simulate the interaction between fluid and an adjacent solid substrate [1], [2]. In the first method solid substrates are modeled as layers of solid atoms that interact with fluid particles through appropriate potential typically cut off at some distance $r = r_c$. A second method ignores the molecular structure of the substrate and models the wall as a half space with a uniform density distribution. The wall-fluid interaction is then calculated by an integration of the interaction of a fluid particle with the uniformly distributed mass inside the substrate. This typically leads to a potential form that solely depends on the vertical distance (z) of the fluid particle to the fluid-substrate interface. For example, if the fluid and wall interact with the standard Lennard-Jones potential, this integration leads to a potential which is also associated with the van der Waals disjoining pressure in the fluid [3],

$$V(z) = -\frac{4\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{6z^3}, \tag{1}$$

where the repulsive term is omitted since fluid particles typically remain at fairly large distance from the wall and the attractive part of the potential dominates.

Although the first method above may be sufficient to qualitatively capture some aspects of the fluid-wall interface dynamics, the attraction on a fluid particle from an infinitely deep wall decays much slower than the intermolecular pair interaction. This long range effect can not be neglected in some cases. For example, as shown by de Gennes [4], the effect of van der Waals force on a spreading droplet can extend to distances of the order of 100σ from the wall-fluid interface and dominates the surface curvature term in the spreading dynamics at such intermediate regime. Distances of the order of 100σ are too large to be included within the cut off distance of wall-fluid interaction in current molecular dynamic simulations.

On the other hand, if the second method is used, at least two effects are ignored. One is the dynamical reponse of the wall, and the other is the atomic roughness of the wall. The latter aspect is sometimes included by choosing a potential that depends on the lateral location of the fluid particle [6]. These atomic scale effects can be important in some cases. One example is the case of wetting where atomic scale effects determine the dynamics of the precursor film which moves ahead of the macroscopic contact line of a droplet.

In their simulation of spreading droplets, Koplik and Banavar have combined the two methods [2]. In their approach, the long range potential (equation (1)) is added to all fluid particles, whereas several layers of wall particles are retained to interact with fluid particles through the general Lennard-Jones potential [2]. In this case, equation (1) becomes

$$V(z) = -\frac{4\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{6(z+z_1)^3}, \tag{2}$$

where z_1 is the "reference location" (depth below the wall-fluid interface) at which this continuum wall is assumed to start. Depending on this reference location, this method can either underestimate or overestimate the strength of the fluid-wall interaction. For example, if the location of the fluid-substrate interface is used ($z_1 = 0$), the interaction between explicit wall particles and the fluid particles within the simulation cutoff distance is double counted. On the other hand, if the location of the first layer of omitted wall particles is used, the interaction between a fluid particle and an explicit wall particle at distance $r > r_c$ will not be accounted for. For example, for fluid particles with $z > r_c$, the wall location is incorrectly represented at a further distance. This can lead to very different hydrodynamic behavior in at least some circumstances, such as the dynamics of spreading droplets [5].

In this paper we propose a method that retains the idea of using several layers of wall particles to include atomic scale roughness of the wall and its dynamic reponses, while correctly calculating the contribution of wall particles at longer distances from a fluid particle. Again we approximate the wall as a continuum medium with a uniform density distribution, but only for the part of the wall that's not within the cut off distance of the given fluid particle. We found that for a Lennard-Jones interaction, this long range correction takes a very concise form and it is easy to implement without significantly increasing the computational cost. In section II, we discuss this method in detail. Simulation results obtained using this method and comparisons to results from other methods will be presented in section III.

II. ATOMISTICALLY SIMULATED WALL-FLUID INTERACTION WITH LONG RANGE CORRECTION

Suppose a fluid-wall particle pair interacts with a potential of the form $V_{fw}(r)$, and there exist several wall particle layers such that the thickness of the explicitly simulated wall is greater than the cut off distance r_c^{wf} of this interaction. The long range correction for the wall fluid interaction can then be calculated for the following two different cases. Assuming the wall-fluid interface is located at $z = 0$, for a fluid particle with $z > r_c$, no interaction with the wall is accounted for from the explicitly simulated wall particles, and the long range correction for the potential must then be calculated through the integration,

$$V_{fw}^{lc}(z) = \int_0^\infty dz' \int_0^\infty dR \rho_w \, 2\pi R \, V_{fw}(\sqrt{(z+z')^2+R^2}), \tag{3}$$

where ρ_w is the density of the wall. The force on the fluid particle from the wall is along z direction and is given by

$$F_{fw}^{lc}(z) = -\frac{\partial V_{fw}^{lc}(z)}{\partial z}. \tag{4}$$

For fluid particles with $z < r_c$, the interaction from wall particles within a region of a spherical cap has been accounted for through explicitly simulated wall particles, so the integration equation for the potential needs to be corrected to

$$\begin{aligned} V_{fw}^{lc}(z) &= \int_0^\infty dz' \int_{\sqrt{min(r_c^2-(z+z')^2,0)}}^\infty dR \, \rho_w \, 2\pi R \times \\ &\qquad V_{fw}(\sqrt{(z+z')^2+R^2}), \end{aligned} \tag{5}$$

or,

$$\begin{aligned} V_{fw}^{lc}(z) &= \int_0^\infty dz' \int_0^\infty dR \, \rho_w \, 2\pi R \, V_{fw}(\sqrt{(z+z')^2+R^2}) \\ &\quad - \int_0^{r_c} dz' \int_0^{\sqrt{min(r_c^2-(z+z')^2,0)}} dR \, \rho_w \, 2\pi R \times \\ &\qquad V_{fw}(\sqrt{(z+z')^2+R^2}). \end{aligned} \tag{6}$$

For these particles, the long range correction for the force from the wall can no longer be calculated by differentiating equation (6). This is because when z changes the part of the wall involved in the integration (6) also changes. The correct way to calculate the force is by integrating the force directly,

$$\begin{aligned} F_{fw}^{lc}(z) &= \int_0^\infty dz' \int_{\sqrt{min(r_c^2-(z+z')^2,0)}}^\infty dR \rho_w \, 2\pi R \times \\ &\qquad \frac{\partial V_{fw}(\sqrt{(z+z')^2+R^2})}{\partial z}, \end{aligned} \tag{7}$$

or,

$$\begin{aligned} F_{fw}^{lc}(z) &= \int_0^\infty dz' \int_0^\infty dR \, \rho_w \, 2\pi R \, \frac{\partial V_{fw}(\sqrt{(z+z')^2+R^2})}{\partial z} \\ &\quad - \int_0^{r_c} dz' \int_0^{\sqrt{min(r_c^2-(z+z')^2,0)}} dR \rho_w \, 2\pi R \times \\ &\qquad \frac{\partial V_{fw}(\sqrt{(z+z')^2+R^2})}{\partial z}. \end{aligned} \tag{8}$$

Carrying out the calculation for a Lennard-Jones potential $V_{fw}(r) = 4\epsilon_{wf}(\frac{\sigma_{wf}}{r})^6$, where the repulsive part is ignored for $r > r_c$, we have

$$V_{fw}^{lc}(z) = \begin{cases} -\frac{4\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{6z^3} & ; z \geq r_c \\ -\frac{4\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{6r_c^3} - \frac{4\pi\epsilon_{fw}\sigma_{fw}^6\rho_w(r_c-z)}{2r_c^4} & ; z < r_c \end{cases} \tag{9}$$

for the long range correction for the potential, and,

$$F_{fw}^{lc}(z) = \begin{cases} -\frac{2\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{z^4} & ; z \geq r_c \\ -\frac{2\pi\epsilon_{fw}\sigma_{fw}^6\rho_w}{r_c^4}(3 - \frac{2z^2}{r_c^2}) & ; z < r_c \end{cases} \tag{10}$$

for the force. It can be verified that when $z < r_c$ the force in equation (10) is not the derivative of the potential in equation (9). One may also verify that long range corrections for both potential and force are continuous at $z = r_c$, as it is expected.

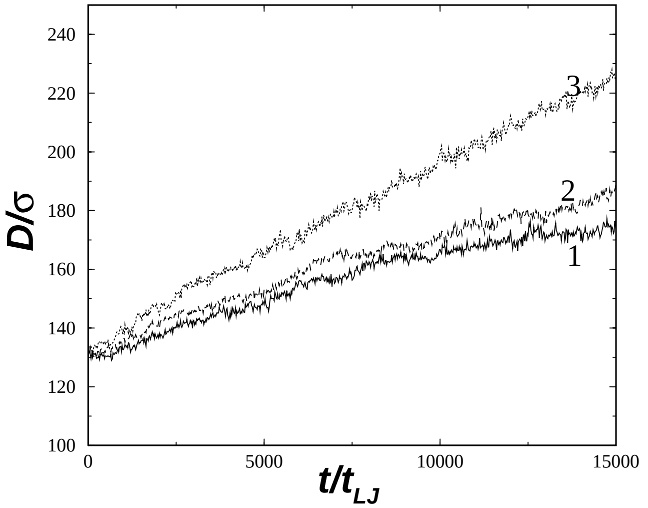

Fig. 1. Droplet radius as a function of time for a droplet spreading on a solid substrate. The droplet radius is measured at a height of $z = 3.1\sigma$ above the fluid wall interface. As shown in the plot, the partial correction usually applied in previous studies (denoted by number 2 in the figure) only corrects for a very small fraction of the long range effect of the potential.

III. COMPARISON WITH SIMULATIONS

We performed a comparison between the results obtained by using the different wall-fluid interaction schemes

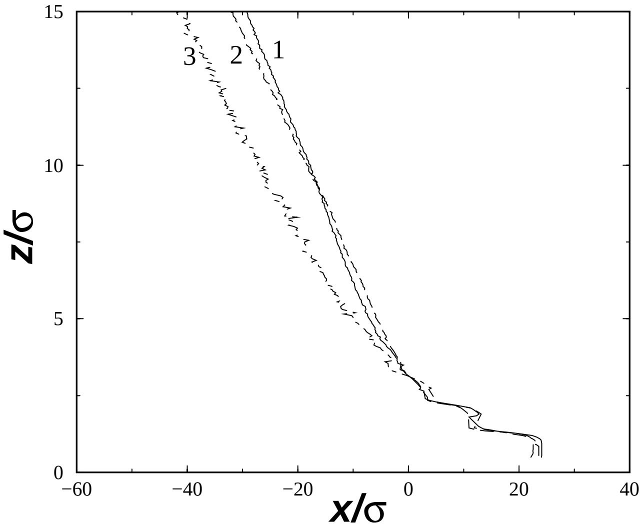

Fig. 2. Shape of the spreading droplet front. It is assumed that the droplet spreads quasistatically such that in a time segment of $\Delta t = 4000 t_{LJ}$. The droplet boundary is extracted every $40 t_{LJ}$, and then shifted to the nominal contact line at $z = 3.1\sigma$. As seen in the plot all three schemes predict similar structure close to the substrate. The much smaller contact angle in scheme 3 demonstrates that the droplet spreads faster than it does in the other two schemes.

discussed above. We simulated the wetting dynamics of a fully wetting cylindrical droplet on a flat substrate. The model droplet consists of 6799 linear chains of polymeric molecules. Each chain contains 4 Lennard-Jones monomers. Neighbouring monomers on the chain interacts with an additional Finite Extensible Nonlinear Elastic (FENE) potential,

$$V^{FENE}(r) = -\frac{1}{2} k R_0^2 \ln\left[1 - (r/R_0)^2\right], \qquad (11)$$

where $k = 30\epsilon\sigma^{-2}$, and $R_0 = 1.5\sigma$, have been widely used in many previous simulation studies on polymeric systems [8]. At our simulation temperature $k_B T = 0.793\epsilon$, the droplet remains in fluid state and there is almost no vapor present. The droplet has an initial contact angle of about 30° and an initial radius $R_0 \sim 67\sigma$. The width of the droplet in the third (periodic) direction is about 10.3σ. Since periodic boundary condition are applied in the plane of the wall-fluid interface, the system is translationally invariant in the axial direction of the cylindrical droplet at continuum level and no edge effects will be present.

Three wall-fluid interaction schemes are compared in this study. In all schemes, 4 layers of wall atoms with a density $\rho_w = 0.81$ are explicitly simulated. Wall atoms are tethered to lattices sites of an FCC lattice with its (111) surface facing the fluid. At $\rho_w = 0.81$, nearest neighbour distance of the lattice is $d_{nn} = 1.2\sigma$ and the thickness of 4 layers wall atoms is above 3σ, the cut off distance of atomically simulated wall fluid interaction. The tethering potential is also a nonlinear FENE potential with $k_w = 460\epsilon\sigma^{-2}$ and $R_0 = 15\sigma$. $k_w = 460\epsilon\sigma^{-2}$ is chosen according to the Lindemann criterion [7] for no melting which requires the root mean square distance of the oscillating wall atom around its tethering point to be much smaller than the lattice constant. With $R_0 >> r$, the FENE potential can be linearized to an elastic tethering potential $V(r) = -\frac{1}{2} k_w r^2$ used in several other studies [8], [9]. Wall atoms interact with fluid monomers through Lennard-Jones potential cut off at $r_c = 3.0\sigma$. With $\epsilon_{fw} = 4.0\epsilon$ and $\sigma_{fw} = 1.0\sigma$ the model polymeric fluid completely wets the substrates.

The difference of these wall-fluid interaction schemes lies in the different ways of applying the long range correction. In the first scheme, no long range correction is applied. The second scheme partially corrects for the long range interaction with a potential of the form in equation (1). In this scheme, z is measured from $z_0 = z_1 - h/2 = -\sigma$, where z_1 is the location of the furthest layer of explicitly simulated wall molecules, and h is the vertical distance between layers of the wall lattice. The third scheme uses the long range correction (9) and (10) derived in this paper.

In Fig. 1, we plot the evolution of the droplet diameter D as a function of time. It is measured as the width of the droplet at a distance 3.1σ above the fluid wall interface. This plot shows that adding a long range correction has an discernible effect on spreading. It is also very important to notice that scheme 2 only contributes a very small fraction of the total correction for the long range effects of the wall fluid interaction, accounted for by scheme 3.

In Fig. 2, we show the shape of the droplet at its spreading front. In order to supress the thermal fluctuations, we averaged the shape in time intervals of length $4000 t_{LJ}$ in the moving frame of the nominal contact line. Here $t_{LJ} = \sigma\sqrt{m/\epsilon}$ is the characteristic molecular timescale and m is the mass of a fluid monomer. Moving with the contact line assumes that during such a short interval, the droplet shape remains the same and it is only translated with the velocity of the contact line. As expected all three schemes predict similar layering structure close to the substrate. however, the smaller macroscopic contact angle exhibited by scheme 3 (at the same time) demonstrates again that the droplet spreads faster than it does in the other two cases.

IV. CONCLUSION

A new method is introduced for providing long range corrections for the wall-fluid interaction present in many physical problems. We have used this method to simulate the dynamics of a spreading droplet and demonstrated that the correction is not negligible. We also compared our scheme with another method that partially corrects for the effects and found that the latter only contributes a very small fraction of the overall correction.

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