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MOLECULAR DYNAMICS SIMULATION ON THE MOBILIZATION OF DEPOSITED NANOPARTICLES BY A MOVING INTERFACE

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ABSTRACT OF THE DISSERTATION

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It is now generally accepted that aside from liquid and gaseous phases, the solid phase is also responsible for contaminant transport in subsurface media. Understanding the mobilization of colloidal particles induced by moving interfaces is relevant to contaminant spreading and water purification in the subsurface. The transport and fate of particles in the presence of dynamic interfaces, present in the unsaturated subsurface or vadose zone, is one of the considerable uncertainties in predicting particulate mobilization. Although forces and torques are relatively well characterized for a particle at an interface near thermodynamic equilibrium, non-equilibrium effects due to moving interfaces and contact lines on the re-mobilization of a colloidal particle deposited on a solid surface remain not entirely understood. A better understanding of the mechanisms driving the transport of particulates in unsaturated porous media would contribute to the design of water purification processes and the management of contamination risk.

Using molecular dynamics simulations, we investigate the transport and fate of a nanoparticle deposited on a solid surface as a liquid-liquid interface moves past it,

depending on the wetting of the solid by the two liquids and the magnitude of the driving force. The particle, the wall, and the fluids are all modeled as atomic systems, where the wetting properties of fluids are determined by the interactions between liquid and solid atoms. We explore how the interfacial transient dynamics alters the equilibrium deposition of particles to a solid surface by a moving fluid-fluid interface in parallel plates channel by looking into the driving force and static contact angles. The deposited particle interacts with two types of interfaces: an advancing interface where the wetting fluid replaces the non-wetting fluid and a receding interface that the non-wetting fluid invades the wetting one.

Theoretically, for a static force balance model, when the vertical upward net force is positive, lifting of colloid from the solid substrate can be observed, otherwise, particle remains attached to the substrate or sliding along the substrate occurs based on the horizontal forces. In this work, particle interfacial pinning is observed at sufficiently small values driving forces that below a critical value predicted by a static force balance. Above the critical driving force for pinning and for large contact angle values we observe stickslip motion, with intermittent interfacial pinning and particle sliding at the interface. At low contact angles, we observe that particle rolling precedes detachment, which indicates the importance of dynamic effects not present in static models. Dynamic effects associated with particle rotation and the observed stick-slip and sliding motion can result in the remobilization and removal of nanoparticles for driving forces that are much smaller than the critical value predicted by conventional static models. The findings in this work indicate that critical forces for particle mobilization and removal efficiencies by liquid-liquid interfaces can be significantly underestimated by static models.

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Chapter 1 Introduction

1.1 Introduction

Colloids are dispersed particles with size ranging from 1nm to 1000nm in characteristic diameter. In the natural subsurface, there exist an assortment of inorganic and organic colloids, including mineral precipitates (iron, aluminum, calcium and silicates), rock and mineral fragments, broccoloid (viruses, bacteria and protozoans), micro-emulsions of non-aqueous phase liquids, and macromolecular components of natural organic matter [1]. The colloidal particles in the subsurface can be released from the rock matrix [2], [3] and may perform as pollutant carrier if the containments strongly sorb to the colloids and less associate with the immobile solid phase. This rapid pathway for contaminants transport is referred to as 'colloid-facilitated contaminant transport in literature. Figure 1.1 presents a schematic of the colloid-facilitated transport of contaminants has been proved to be one of the important mechanisms of contaminant migration in groundwater in recent years [4]–[8]. Understanding the transport of colloidal particles is important due to its applications in water purification [6], contaminant spreading [8] and public health [9].



Figure 1.1 Schematic of colloid-facilitated transport in a saturated porous medium in the subsurface. Contaminates (black dots) can be adsorbed to the surface of mobile and immobile solid phase or dissolved in the liquid phase. Figure from Ref. [10].

Mobile colloids are ubiquitous in the vadose zone, which is the unsaturated subsurface with the presence of air/water interfaces. Investigation of colloid transport in the vadose zone can help address several issues, including contaminant transport [11]–[13] and pathogenic micro-organisms movement [14]–[16]. However, the predictions of colloid transport in the vadose zone are further complicated compared to saturated porous media [17]. The mechanisms driving colloid mobilization are still not fully understood and quantified, with challenges in the interactions of colloids with air/liquid and solid interfaces. The key features affecting colloid movement in the vadose zone are the presence of air-water interfaces, transients in flow and soil structure as shown in Figure 1.2. One of the considerable uncertainties in the colloids mobilization unique to the vadose zone is the transport and fate of particles in the presence of moving air-water interfaces as water infiltrates or drains from the system. Moving air-water interfaces in the subsurface occur during imbibition and drainage and can result in the detachment of soil or sediment particle from the stationary solid. Colloids could also be pinned to air/water/solid contact line by

water films, causing colloid retention and immobilization (Figure 1.2). The fluctuation on the level of groundwater by rainfall and evaporation may cause imbibition and drainage, resulting in the movement of air-water interfaces. A better understanding of the mechanisms driving the transport of particulates in unsaturated porous media could lead to new paradigms in the design of water purification processes, the management of contamination risk, the development of remediation strategies, and would facilitate the recovery and recycling of technological nanomaterials.

Considering the effect of moving interface on the remobilization of deposited particles, one of the natural phenomena related to interactions between particle and air-water interface is called "Lotus-Effect" where dust particles can be removed from the lotus leaves by the rolling of droplets [18]. Inspired by this phenomenon, the possibility of particle removal by moving interfaces are studied. Particles attached to liquid/liquid or gas/liquid interface experience capillary force depending on the position of the interface[19], [20]. The capillary force is the summation of surface tension force and Laplace pressure force caused by the curvature of the interface. As a moving air-water interface pass a deposited particle, the capillary force will act at the contact between them. The colloids which are initially attached to a solid surface can be removed by a moving air-water interface through surface tension force[21]–[23]. It has been proposed as a silicon wafers cleaning method in microelectronics because of its efficiently on colloids removal [21]. Leenaars and O'Brien found that the capillary force can scale with the particle radius when using this cleaning method to remove particles with size smaller than 10 µm, and the capillary force is more relevant as a detachment force as particle size decreases.





Figure 1.2 Illustration of colloid transport in the vadose zone. Colloid deposition mechanism includes grain attachment by physicochemical filtration, attachment to immobile air-water interface or three phase contact line, pore straining attachment and thin film straining attachment during drainage. Colloid mobilization mechanisms include particle dispersed by chemical perturbation. Colloid released by film expansion during imbibition, air-water interface scouring during imbibition and drainage, and shear mobilization. Figure from Ref. [24].

A moving air-water interface has two different processes depending on the direction the interface moves: (1) Drainage (receding), where a non-wetting invading fluid displaces a wetting fluid, and the opposite case, (2) Imbibition (advancing) occurs when a wetting fluid displaces a non-wetting fluid, as shown in Figure 1.3. The angles through wetting fluid at the three-phase line during these two processes are known as advancing and a receding contact angle. Mobilization of the particle by moving air-water interface during imbibition

and drainage processes in the vadose zone was first studied by El-Farhan et al. [25] and Saiers et al [26]. They found colloid mobilization are related to irrigation patterns, such as interface velocities and the number of AWI passages. The detachment of deposited particles has been demonstrated to be more efficient as AWI velocity decreasing, the number of AWI passages increasing and with solid-colloid attractive force [27], [28]. The colloid detachment was found to be significantly affected by colloid shape, that edged particles were detached more than smooth spherical particles [29]. Lazouskaya et al.[30] showed that due to the surface tension force, deposited colloid to the substrate can be mobilized and retained at the contact line by moving air-water interface at pore scale, a detailed look is presented in Figure 1.3. Armark et al.[29] found by experiment that colloid detachment from the substrate by dynamic interface for all tested colloid shapes. The colloids mobilization are different for imbibition and drainage fronts due to the difference on dynamic contact angles and interfacial shape at the contact line [31].

Theoretically, in the presence of an external force, a deposited particle will remobilize when this external force exceeds the adhesion force between the particle and solid surface or net torque by these forces exerting at the contact point is larger than zero [32]–[34]. Depending on the forces and torques balance on the attached particle, the mobilization of a particle includes desorption from the substrate, sliding along the substrate and rolling. Theoretical conceptualization of particle removal from the solid substrate using surface tension force by the passage of moving interface was first developed by Leenaars.[21], [35] Major forces and torques acting on a single particle at the contact line include adhesion,

drag, friction and surface tension forces. The attached particle can be mobilized via sliding, lifting or rolling process through the forces and torque[31]. Gómez Suárez et al.[22] showed theoretically that the detachment force (surface tension force) is related to both particle-air-water and surface-air water contact angles and particles experience larger detachment forces at advancing interface than receding interface. Ahmadi [36] found that in the turbulence flow rolling as the dominant detachment mechanism for deposited spherical particles in the presence of capillary force. Instead of air/water interface, a moving fluid/fluid interface (water/fluorinert) can also result in the remobilization of attached colloid by the domination of surface tension force [37], [38].



Figure 1.3 Images of the microfluidic channel acquired with the confocal microscope and the schematic cross-section in two regimes: (a) imbibition front (advancing interface) and (b) drainage front (receding interface). Figure from Ref. [30]

The particles interacting with moving interface reported in previous studies were at micron scale, however, the fate and transport of nano-sized particles in the vadose zone are limited reported to date. Nanomaterials, which are defined as particle sized between 1 to 100nm in at least one dimension, may cause potential risks to the environment and public health.[39], [40]. One of the most important applications of nanotechnology in the petroleum industry

to help locate bypassed oil and enhance oil recovery [41]. The way of silica nanoparticles transport in rock is found similar to colloid particles when the adhesion to the wall is weak [42]. The stability of nanoparticles at interface differs due to the unique properties, such as larger surface area and higher reactivity, thus may introduce new mechanisms on the transport behavior. According to the DLVO theory (Derjaguin-Landau-Verwey-Overbeek), which is the sum electrostatic double-layer force, the van der Waals force, and short-range or steric forces, the transport of nano-sized particles have strong relevance with particle size [43]. It predicts the interaction energy between a colloid with an interface (air/water interface or solid/water interface) or other colloids as a function of separation distance. However, several studies have raised doubts on whether the DLVO theory is applicable to the nanoparticle, particularly extremely when the particle size is smaller than 10nm [44], [45]. Non-DLVO interactions may occur, including hydration and solvation, which may result in the failure of DLVO prediction. The release of deposited particles at a few nanometers separation distance cannot be quantitatively described by DLVO theory due to the significant contribution of other types of interactions [46]. The DLVO theory is discussed in a lot of experimental studies when measuring the adhesion force of deposited particles. In this work, we focus more on the wettability and dynamic effects on the transport of particle by moving interfaces, the particles we used are neutral charge, thus we will not apply the DLVO theory to our model.

1.2 Theory background

1.2.1 Particle at equilibrium position without external forces

The most common way to understand wetting is to deposit a liquid droplet onto a solid surface. At equilibrium state, the three surface tensions (liquid/solid γ_{LS} , solid/vapor γ_{SV} and liquid/vapor γ_{LV}) acting at the three-phase contact line, determine the contact angle θ of the liquid on the solid, as shown in Figure 1.4. The contact angle can then be calculated by Young's equation,

$$\gamma_{LV}\cos\theta + \gamma_{LS} = \gamma_{SV}. \tag{1.1}$$

The vapor phase could also be replaced by another immiscible liquid phase, and the equation becomes $\gamma_{SL_1} = \gamma_{SL_2} + \gamma_{L_1L_2} \cos\theta$, where γ_{SL_1} is the surface tension between solid and liquid 1, γ_{SL_2} is the surface tension between solid and liquid 2, and $\gamma_{L_1L_2}$ presents the surface tension between two liquids.



Figure 1.4 Illustration of Young's equation for contact angle θ of a liquid droplet spread onto a solid surface, where γ_{LS} , γ_{SV} and γ_{LV} are the interfacial energies (i.e. the surface tensions) of liquid/solid, solid/vapor and liquid/vapor respectively.

The same analysis leads to the definition of the contact angle of a particle at a liquid/liquid or gas/liquid interface, and the position of the particle at the interface can be determined by the balance of the interfacial energies. Specifically, if we neglect the weight of a smooth spherical particle, the equilibrium at an interface is determined by minimizing the net interfacial energies of the liquid/particle, gas/ particle and gas/liquid interfaces. Figure 1.5 presents a spherical particle at an interface at equilibrium state, where the interface is generated by two immiscible phases (phase 1 is non-wetting and phase 2 is a wetting phase with respect to the solid particle), R is the particle radius and h denotes the distance between the top of the particle and the interface. The angle between the interface and the tangent plane of the sphere at the three-phase contact line is defined as the particle contact angle θ_p . By convention, the particle contact angle in this work is measured from the wetting phase. Thus, a hydrophilic particle, would be mostly immersed in the wetting phase and $\theta_p < 90^\circ$. If the particle is hydrophobic, it would be mostly exposes to the non-wetting phase and the contact angle is $\theta_p > 90^\circ$.



Figure 1.5 Illustration of the particulate at phase1/phase2 interface, where h is the distance from the top of the particle to the interface in the less wetting side, R is the particle radius and θ_p denotes the particle contact angle. γ_{12} , γ_{1p} and γ_{2p} correspond to the surface tension of phase1/ phase2, phase1/particle and phase2/particle.

If the interfacial energy is denoted by γ_{12} for the phase1-phase2 interface, γ_{1p} for the phase1-particle interface and γ_{2p} for the phase2-particle interface, then the particle contact

angle can be determined from these quantities by the Young's equation as: $\gamma_{12}\cos\theta_p + \gamma_{2p} = \gamma_{1p}$. For a spherical particle, the contact angle θ_p can also be determined based on its equilibrium position, which is related to the height h indicating the part of the particle submerge in the less-wetting phase and particle radius, given as $\cos\theta_p = 1 - h/R$. When $\theta_p = 90^\circ$, the particle shows no preference to either phase and the geometrical relation is h=R. This case is called the neutrally-wetting.

The adsorption free energy is the change of system total interfacial energy as a particle moves from the interface to one side of the bulk. When a particle is completely immersed in phase 1, the total energy can be written as

$$E_1 = \mathcal{A}_P \gamma_{1P} + \mathcal{S} \gamma_{12}, \qquad (1.2)$$

Where 1 and 2 are immiscible phases components, P denotes the particle, A_P presents the surface area of the particle, *S* is the surface area of the interface and γ is the surface tension. As the particle is attached to the interface, the total energy of the system is

$$E_2 = A_{1p}\gamma_{1p} + A_{2p}\gamma_{2p} + (S - A_{12})\gamma_{12}, \qquad (1.3)$$

where A_{12} is intersection area of particle and interface when the particle is attached to the interface, and A_{1p} and A_{2p} are the surface area of the particle exposed to phase 1 and phase 2, as shown in Figure 1.5. If we assume E_2 to be the total energy when the particle is at its equilibrium contact angle, by subtracting (1.2) from (1.3) and combine with Young's equation, the particle adsorption energy can be written as:

$$\Delta E_p = -\pi R^2 \gamma_{12} (1 \pm \cos\theta_p)^2 \tag{1.4}$$

The \pm signs denote the particle position corresponding to the interface: positive sign indicates the particle moves from phase 1 (less wetting phase) to the interface, and negatives sign means particle starts form phase 2, corresponding to the more wetting phase. The particle is attached to the interface and hard to escape if the adsorption energy ΔE_p is larger than the thermal energy k_BT [47], where k_B is the Boltzmann constant and T is the temperature. In general, the adsorption energy of a micron sized particle is around of the order 10⁶k_BT which explains that adsorption of colloidal particles is irreversible. However, when scaled down to nanoparticles, the binding of the nano-sized particle to liquid interfaces would be more complex [21] because of the stability of nanoparticles at interfaces is much weaker. Figure 1.6 presents the adsorption energy ΔE_p difference between nano-sized and micro-sized particle as a function of particle contact angle θ_p for particle size 10nm and 1µm, and it shows huge differences in adsorption energy between nanoparticles and microparticles. From equation (1.4), the adsorption energy is found to increase with R^2 , so when scale down the radius of the particle to even smaller value 1nm from 10nm, ΔE_p would decrease 100 times. These values for nanoparticles are much smaller than the thermal energy, indicating the adsorption of nanoparticle would be reversible.



Figure 1.6 Adsorption energy of the particle at interface, ΔE_p , as a function of particle contact angle θ for particle radius R=10nm (a) and R=1 μ m (b) at 25°C ($\gamma = 50 \text{ mN/m}$).[48]

1.2.2 Equilibrium with external forces acting on the particle

When an external force is acting on a particle as an interface moving it away from its equilibrium position, the particle experiences a capillary force (F_c) acting normal to the interface orientation, which is the sum of a Laplace pressure force (F_L) and a surface tension force (F_{γ}). To investigate the wetting processes of small particles, gravity forces can be neglected. In addition, when the particle as at a flat interface, the Laplace pressure force is zero, because there is no curvature on the interface, thus only interfacial forces are considered. To balance different external forces, the surface tension force would change depending on the position of the interface relative to the particle.



Figure 1.7 Schematic of the position of colloid as a force acting on it. (a) a particle at equilibrium position without external force ($\phi = \theta_p$), (b) force pulling particle from wetting fluid ($\phi > \theta_p$), (c) force pushing particle to wetting fluid ($\phi < \theta_p$).

Figure 1.7a shows a spherical particle sitting on the air/water interface at the equilibrium position, where R is the particle radius, θ_p is the contact angle of the spherical particle, and ϕ is the filling angle denoting the position of the particle at the interface. The filling angle is the angle between the vertical center line of the particle and the line from the center point of the particle to any point at the contact line, and it is measured with respect to the non-wetting phase side. For a particle at equilibrium state on the interface, the filling angle ϕ is equal to the particle contact angle θ_p , and there is no surface tension force acting on the particle. The filling angle ranges from 0° to 180° as the particle moves away from its

equilibrium point by an external force acting on the particle and causing the deformation of the interface near the contact line. As shown in Figure 1.7b, when the external force is upward, moving the particle to the non-wetting phase, the filling angle increase from θ_p to 180°. Whereas, if the force is downward as Figure 1.7c, the filling angle decreases from θ_p to 0°, pushing the particle towards the wetting fluid. From the thermodynamic view, the steady state of a system can be reached when the free energy is minimized. In principle, for any filling angle and any position of the particle at the interface, the particle contact angle remains constant and equals to θ_p .

Let us consider the surface tension force acting on the particle. Due to the symmetry of the system, the net surface tension force is only acting on the vertical direction and is given by [48], [49]

$$F_{\gamma} = 2\pi R \gamma \sin \phi \sin(\theta_p - \phi), \qquad (1.5)$$

where γ is the liquid/liquid or gas/liquid surface tension.

The normalized surface tension force $F_{\gamma}/2\pi R\gamma$ as a function of filling angle ϕ for different particle contact angles is presented in Figure 1.8. When the particle is fully immersed in the wetting phase, $\phi = 0^{\circ}$, and when it is completely in the non-wetting phase, $\phi = 180^{\circ}$. As an external force is pulling or pushing the particle from one side of the bulk to the other side, ϕ changes from 0° to 180° (or 180° to 0°) during which passes its equilibrium position $(F_{\gamma}/2\pi R\gamma = 0)$ and the surface tension force experiences two magnitude maxima. In the figure, the positive (or the negative) value stands for the particle position below (or above) its equilibrium state. According to the surface tension force from equation (1.5), at $\phi =$ $\theta_p/2$, the maximum surface tension force is $2\pi R\gamma sin^2(\theta_p/2)$ and the other maximum occurs at $\phi = \theta_p/2 + 90^\circ$ which equals to $2\pi R\gamma sin^2(\theta_p/2 + 90^\circ)$. As a particle moves from the wetting phase to the non-wetting phase, it first experiences a maximum surface tension force at $\phi = \theta_p/2$ with the direction pulling it away from the wetting phase, and as it passes the equilibrium position, it would experience another maxima pushing it back to the wetting phase.



Figure 1.8 Calculation of surface tension forces as a function of filling angle ϕ at various contact angles θ_p from equation (1.5).

1.2.3 Release of a deposited particle from a solid interface

The capillary force that acts between colloids and the air-water interface can result in the detachment of initially deposited colloids from a solid surface. Figure 1.9 shows a spherical particle attached to a solid surface with different water levels. At small water content, the

particle is pinned to the surface by capillary force. As the water content increase, the curvature of air/water changes from concave to convex and the capillary force acts as a lifting force against the adhesion force between the particle and solid surface. When this capillary force is larger than the adhesion force, the detachment of the particle from the surface would occur.



Figure 1.9 Schematic of capillary force acting on a colloid for different height of liquid/liquid interface. (a) small water content with a pinning capillary, (b) large water content with lifting pinning capillary, (c) particle at equilibrium point of air/water interface after removing from the surface.

In the case of liquid/liquid interface bounded to a solid surface at one end, the interface is tilted by the liquid/liquid/solid contact angle θ . If the particle is not at the equilibrium position, the surface tension force acting normal to the tilted interface can be separated into
two components, where $F_{\gamma,\parallel}$ is the component along the substrate and $F_{\gamma,\perp}$ is the surface tension force perpendicular to the substrate as shown in Figure 1.10.



Figure 1.10 Schematic of surface tension force acting on a colloid at a tilted interface with a substrate contact angle θ . $F_{\gamma,\parallel}$ and $F_{\gamma,\perp}$ are the components of the surface tension force along and normal to the solid surface. For a particle at the tilted interface, the components of the surface tension force also depend on the substrate contact angle θ , and are determined as

$$F_{\gamma,\parallel} = 2\pi R\gamma sin\phi sin(\theta_p - \phi)sin\theta \tag{1.6}$$

$$F_{\gamma,\perp} = 2\pi R\gamma sin\phi sin(\theta_p - \phi)cos\theta \tag{1.7}$$

Figure 1.11 shows a schematic view of a colloid particle attached to a solid substrate interacting with advancing and receding interfaces. The dashed line represents the particle/interface at equilibrium state, and the solid line denotes the interface position as it moves past the equilibrium position due to an external force acting on the fluids. When the wetting phase invades the non-wetting fluid, the interface is defined as an advancing interface, and when the non-wetting fluid replaces the wetting fluid, there is a receding interface. Since the interfaces are moving in the positive x-direction, they tend to be at the solid line positions. In addition to the capillary force (F_c), the adhesion force (F_A) and the

particle friction force (F_F) are also acting on the particle for both advancing and receding interfaces as shown in the figure.



Figure 1.11 (Color online) Schematic of the force analysis on a spherical particle attached to a wall for an advancing interface (left; solid line) and a receding interface (right; solid line) with wall contact angle θ . The view corresponds to a cross-section of the system. Red dashed lines denote the interface equilibrium positions. At the liquid-liquid interface, the particle experiences surface tension forces (F_{γ}), in addition to the adhesion (F_A) and particle friction forces (F_F).

As an interface pass by an attached particle, the surface tension force acting on the particle changes with the filling angle and has two maxima with one before the equilibrium position and one after. For an advancing interface, the particle will first experience a maximum surface tension force as equation (1.8) and (1.9) before equilibrium position, if not mobilized, it will then reach another maximum force according to equation (1.10) and (1.11), and the direction of the surface tension force changes from towards the wetting fluid to the non-wetting fluids These maximum forces are reversed as a receding interface is passing by the particle. The following are the maxima expressions of surface tension force corresponding to Figure 1.11, where the interfaces are all located after their equilibrium positions.

For advancing interface:

$$F_{\gamma,\parallel,max} = 2\pi R\gamma sin^2(\theta_p/2)sin\theta \tag{1.8}$$

$$F_{\gamma,\perp,max} = 2\pi R\gamma sin^2 (\theta_p/2) cos\theta \tag{1.9}$$

For receding interface:

$$F_{\gamma,\parallel,max} = 2\pi R\gamma \cos^2(\theta_p/2)\sin\theta \tag{1.10}$$

$$F_{\gamma,\perp,max} = 2\pi R\gamma \cos^2(\theta_p/2)\cos\theta \tag{1.11}$$

The Laplace pressure is the pressure difference across a curved interface from a nonwetting phase to a wetting phase. The Laplace pressure is determined by the Young– Laplace equation, given by

$$\Delta p = \gamma(\frac{1}{R_1} + \frac{1}{R_2}), \tag{1.12}$$

where R_1 and R_2 are the principal radii of curvature. In the absence of confinement, there is no contribution of Laplace pressure force to the capillary force. There is no pressure difference across the interface far away from the particle, since the interface is flat. The deformation of interface can be found near the contact point, Because of the saddle shape of the interface near particle, the curvature is balanced by $R_1 = -R_2$, leading to $\Delta p = 0$ across the interface. However, if two immiscible fluids are confined between two infinite long parallel plates with the interface connected to both ends, the pressure in the nonwetting phase is larger than in the wetting phase. In this case, the shape of the interface is part of the surface of a cylinder. For an interface with cylindrical shape, the curvatures $R_1 = r_c$ and $R_2 = \infty$, given the pressure difference $\Delta p = \gamma/r_c$, where r_c is the radius of the cylindrical interface. If the height of the channel is H, then the curvature of interface can be written in terms of surface contact angle θ ,

$$r_c = \frac{H}{2\sin(\theta - \pi/2)},\tag{1.13}$$

When a particle interacts with the cylindrical interface, due to the pressure difference, the particle experiences a Laplace pressure force, which is related to the intersection area between the spherical particle and interface. For a particle attached to the interface with a filling angle ϕ , the Laplace pressure force is expressed as $F_L = \Delta p \pi R^2 sin^2 \phi$, where $\pi R^2 sin^2 \phi$ is the intersection area between the spherical particle and the interface. By combining this with the expression for Δp and eq. (1.13), the Laplace pressure force can be written as,

$$F_L = \frac{2\pi R^2 \gamma}{H} \cos\theta \sin^2\phi. \tag{1.14}$$

Thus, the capillary force acting on a deposited particle with a curved interface is the summation of surface tension force and Laplace pressure force,

$$F_c = 2\pi R\gamma [\sin\phi \sin(\theta_p - \phi) + \frac{R}{H}\cos\theta \sin^2\phi].$$
(1.15)

According to the equation, whether the Laplace pressure or the surface tension forces dominate the capillary force depends on the ratio of particle radius to channel height. When R/H is relatively small, the effect of Laplace pressure force can be neglected. Whereas, if R/H is large, the Laplace pressure force should be taken into consideration as one of the main forces acting on the particle.

Let us now consider the balance of forces acting on the particle when the interface is away from the equilibrium position. The conditions for the different pinning, sliding, or lifting interactions of the particle by the interface can be determined from a force analysis on the particle in the directions along and normal to the substrate. In the horizontal direction, the major forces are drag, friction forces and the x-component of the surface tension force. The balance of these forces will determine whether the particle is pinned on the wall or sliding along the wall. First, the pinning of particle condition occurs when $F_{\gamma,\perp,max} + F_A < 0$ and $F_{\gamma,\parallel,max} < F_F$. Then, if $F_{\gamma,\parallel,max}$ becomes larger, sliding may occur as $F_{\gamma,\perp,max} + F_A < 0$ but $F_{\gamma,\parallel,max} > F_F$. Finally, the change on the positive vertical net force on the particle would lead to particle lifting is $F_{\gamma,\perp,max} + F_A > 0$. From the force analysis, we observed that when the interface is located at the after-equilibrium position, the surface tension force at a receding interface is always pushing the particle towards the substrate, whereas for the advancing interface, surface tension force is lifting the particle away from the substrate.



Figure 1.12 (Color online) Schematic of the torque analysis on a spherical particle attached to a wall for an advancing interface (left; solid line) and a receding interface (right; solid line) with wall contact angle θ . As particle starts to rotate at point O, the particle experiences torque by surface tension forces (I_{γ}) and the torque by adhesion force (I_A).

In addition to the forces, we should also consider the torque acting on the particle. Figure 1.12 illustrates the torque analysis on a spherical particle attached to a wall for an advancing and receding interface. Point O denotes the contact point around which the rotation of particle occurs, and all torques are calculated with respect to this point. Rolling at point O may occur when $|F_{\gamma}I_{\gamma}| > |F_AI_A|$ for both advancing and receding interfaces, where I_{γ} and I_A are the lever arms corresponding to the surface tension and adhesion forces shown in the figure, respectively. Lazouskaya et al. [31] points out that this approximation has two limitations: the torque due to the surface tension force should oppose the resisting torque

due to the adhesion force. The maxima of surface tension force is $2\pi R\gamma sin^2(\theta_p/2)$ for advancing interface and $2\pi R\gamma cos^2(\theta_p/2)$ for receding interface as shown in Figure 1.12, that only forces after equilibrium are taken into consideration. However, the conditions before the equilibrium state are not taken into consideration. Second, the adhesion contact I_A does not take into account the load due to the normal component of the surface tension force, which is not sufficiently accurate.

It is also important to mention that previous studies considering the force balance on the particle are all based on static considerations, few discussed the dynamics effects on particle remobilization. The dynamics effect, such as the rotation motion of such small particles is hard to be examined in experiments.

1.3 Motivation & Objective

As discussed in the previous section, the development of predictive models for the transport and fate of colloidal particles in the vadose zone has proven especially elusive [1], [51]– [53]. Some of the most challenging knowledge gaps that remain in the description of particulate transport are unique to the vadose zone, and stem from our limited understanding of the motion and fate of particles in the presence of dynamic interfaces. Previous work mostly focused on energetic considerations and static interactions. The outof-equilibrium dynamics of particles that interact with moving interfaces has received little consideration, except for a few recent studies [28]–[31] that actually highlight our limited capabilities to predict the behavior of deposited particles. Here, we explain the outline of this thesis concerning the effect that interfacial dynamics have on the re-entrainment of deposited particles. The overall goal of this thesis is to study particle transport and fate in the presence of moving liquid/liquid interfaces in unsaturated porous media under non-equilibrium conditions. We will perform Molecular Dynamics simulations with atomic detail using LAMMPS [54]–[56], which will provide insight of mechanistic understanding and widen the scope of the investigation in parameter space, including surface tension values, wetting properties and contact angles. The advantage of using MD simulations is that it can provide information by revealing details of particle-wall-fluids contact angles, the specific interactions between the particle and fluid/fluid interface and the orientation of the particle. These details which are hard to measure using experimental methods can help us better understand the detachment mechanism of the particle. The specific objective is to study the effect of wettability on particle detachment from a solid surface by a moving liquid/liquid interface.

First, we started from simple systems: liquid/liquid and liquid/solid interface and measure the surface tension for various interaction parameters. We investigated the contact angle for the planar and spherical shape of solid with different methods. The interaction energy is studied to help us better understand the attraction parameters when a particle is adsorbed to a liquid/liquid or liquid/solid interface. Second, under equilibrium conditions, when the particle is in a static system without any external force acting on the fluid, particle adsorption on the solid surface is found to have a dependence on the wetting properties of the liquid. We present results for a particle immersed in a single fluid with various wetting properties and released from the center of a channel. As the liquid changes from less wetting to more wetting, we investigated if particle adsorption to the solid surface can be observed, where the particle and substrate are treated as the same material. Then, we studied whether switching the liquid wetting properties in a system with a deposited particle will result in the desorption of the particle to see if this adsorption process can be reversed. Furthermore, we looked into the motion of the attached particle by an external force acting on it in the direction normal or parallel along the wall, which is equivalent to measure the friction force and detachment force of the particle, respectively.

The non-equilibrium effects, such as the flow rate and the velocity of the contact line, have been poorly considered on the motion of a particle attached to a solid surface. In real systems, there are both advancing and receding contact lines moving on the solid walls. We studied the effect of non-equilibrium flow and contact-line velocity by adding an external force acting on the fluids, to see how this influence the desorption of particles in the presence of advancing and receding interfaces. Additionally, surface tension force of the liquid/liquid interface is related to particle contact angle. In our case, in the presence of solid walls, this force is also influenced by wall contact angle. Theoretically, when the normal component of surface tension force is larger than the adhesion force between particle and wall, desorption of the particle can be observed. We considered different contact angles for particle and wall to see the effect of the re-entrainment of a particle from a solid surface by moving a liquid/liquid interface. Moreover, we studied how the rolling of the particle can help particle desorption from solid walls in the presence of moving liquid/liquid interface. As a particle interacts with a moving fluid/fluid interface, rollinginduced detachment of the particle could occur even in unfavorable cases, that is when the vertical component of the surface force pushes the particle towards the wall and the net force on particle is, a prier, also towards the solid surface. Simulations will provide a

particle-level detail of forces and motion during these processes and can be used to elucidate the boundaries in parameter space between all the different regimes discussed so far. In our simulations, we would be able to determine if an advancing interface or a receding interface would be able to scavenge the particles or if they would remain deposited on the walls.

Chapter 2 Simple Liquid/Liquid & Liquid/Solid Systems

2.1 Introduction

Due to the fundamental importance of interfacial properties on many technology processes, extensive experimental and theoretical studies have been carried out to help understanding the interfacial properties of fluids. However, there still exists challenges and difficulties on current experimental methods. In recent years, molecular dynamics simulation has been complementing our understanding of the properties of liquid/vapor, liquid/liquid and fluid/solid interfacial behavior [57]–[61]. The classical pure atomic Lennard-Jones (LJ) 12-6 fluid has been most employed by molecular dynamics simulation to study the equilibrium of liquid/vapor of liquid/liquid coexistence system [54], [62], [63]. The LJ fluid model, considering much of the essential physics, is the best studied continuous potential by far which reasonably describes the properties of nonpolar real fluids.

The main objective of this chapter is to characterize the basic systems which are used in our work on moving interfaces and particles. Here, we will briefly introduce some previous studies on the simulations of liquid/liquid and liquid/solid systems using MD method with the LJ model. Theoretical studies of liquid-vapor interfaces investigate surface tension, interface thickness, capillary waves [64]–[66]. Extensive progress has been made on the simulation of liquid-gas systems for the calculation of surface tension during the last two decades. The initial simulation on gas/liquid interface for simple LJ fluids has been extended to molecular fluids. Also, simulation on liquid/liquid and solid/liquid systems have been studied. There have been a number of studies on the surface tension of a planar vapor-liquid interface of 12-6 Lennard-Jones potential [67]–[70], where the surface tension is by calculated by the virial Kirkwood-Buff formula [71]. The studies on properties of the liquid/liquid interface, which are important to biological systems [72]-[74], technical applications [75], [76], as well as the theoretical studies [77] have received significantly less attention compared to vapor/liquid system. Meyer [54] simulated a liquid/liquid interface with a range of temperature and pressure near the triple point using Molecular dynamics method. The atoms of two types of liquids interact via a modified Lennard-Jones potential functions, where an extra interaction parameter is introduced to describe the miscibility between the two liquids. He found that different interfacial tensions and miscibility can be obtained depending on the interaction parameters between the liquids. Molecular dynamics simulation of a planar liquid/liquid interface in a binary mixture of simple liquids at low temperatures was studied by Stecki et al. [62]. They demonstrated the existence of a vacuous gap between liquid slabs, which is not limited to the pure repulsion simulations. Thus, in our simulations, the interaction parameter applied should ensure the immiscibility of two liquids, at the same time, the gap to be relatively small compared to the size of the nanoparticle, so that the vacuous space will not cause a problem as the interface interacting with the particle.

Numerous studies on the nanoscale wetting properties of a liquid droplet on the solid surface have been reported using MD simulation governed by LJ interactions, and compared to Young's equation with macroscopic systems. These studies mainly simulated atomistic smooth planar surface that atoms in solid phase are fixed on lattice sites. Nijmeijer et al. [78], [79] compared the contact angle measured by visual inspection of the meniscus of the interface to the value calculated by Young's equation where solid-vapor, liquid-vapor and solid-liquid surface tensions are obtained by MD simulation. They found there exists discrepancy on these methods due to the use of live wall, which particles are not fixed on lattice site, but have a good agreement when the wall is replaced to a rigid wall. Ingebrigtsen and Toxvaerd [80] studied the contact angle of liquids and droplet on planar surfaces interacting via 9-3 LJ potential. They pointed out due to the fluctuation on liquid density at the liquid/solid interface, the validity of Young's equation at nanoscale should have a length scale of at least \sim 5nm to eliminate the short-range interactions. They found that the observed contact angles in nanoscale deviated from the corresponding contact angles obtained by Young's equation for macroscopic systems, especially for strong attractions with small contact angles. Grzelak et al. [81] employed LJ interaction to study the anisotropic wetting by simulating liquid in contact with [100], [110] and [111] of FCC (Face-Centred Cubic), BCC (Body-Centred Cubic) and SC (Simple Cubic) lattices for three different substrate-fluid interactions. They found that the contact angle is significantly influenced by the structure of solid atoms and is the most diverged for the strongest substrate-fluid interaction. Becker et al. [82] examined the influence of liquidsolid interactions, temperatures and solid density on the contact angles of sessile drops in LJ systems by MD simulations. For larger systems consisted of at least 10000 particles, the contact angles are found to converge to a constant value, contrarily, contact angles decrease with smaller system size. In order to eliminate the effect on contact angles caused by system size. In our work, we employed a system which is about 10 times larger than the ones suggested by the author.

In this chapter, we will use molecular dynamics simulation to study the interfacial properties of planar liquid/liquid and liquid/solid interface with a simple LJ fluid model. First, the surface tension of the liquid/liquid interface with various immiscibility is measured through Kirkwood-Buff theory and compared with available data from the literature. Second, the liquid/solid interactions are considered with single fluid with different wetting properties confined between two parallel plate solid walls. Third, we studied a liquid/liquid/solid system with two immiscible fluids of different wetting properties in parallel plates. The contact angles are calculated via direct measurement and Young's equation where the surface tensions between each two phases were measured using Kirkwood-Buff theory. These simulations will provide detailed information, such as surface tension values, wetting properties, and contact angles, to help us better understand the mechanisms of particles interacting with moving interfaces in parameter space.

2.2 Molecular Dynamic Simulation

Molecular Dynamics (MD) simulation is used to determine the evolution of a classical many-particle system, where atoms and molecules interactions are based on Newton's Law [83]. In classical molecular dynamics simulations, the new positions and velocities of atoms are calculated according to Newton's equation of motion from their previous conditions,

$$m_i \frac{d^2 r_i}{dt^2} = F_i, \quad i = 12, \dots, N.$$
 (2.1)

where r_i , v_i and m_i are the position, velocity and mass of atom i, respectively. F_i is the total force acting on the atom, derived from the potential energy $V(\{r_1, r_2, ..., r_N\})$,

$$F_i = -\frac{dV}{dr_i}.$$
 (2.2)

In the MD simulation, the quantity changes in a time step Δt is based on the forces and velocities of particles in the system from a previous time step. The choice of the value for Δt should meet the efficiency in computing and the accuracy in energy conservation at the same time.

In this thesis, we use a molecular dynamics simulation package, 'Large-scale Atomic/Molecular Massively Parallel Simulator' (LAMMPS), which is an open-source code focusing on material modeling using the MD method. This package allows users to easily extend and modify additional features based on their need and can be run on parallel processors. In the LAMMPS package, the Verlet algorithm [84] is used, that in this algorithm the velocity at the midpoint of two timesteps ($v\left(t + \frac{\Delta t}{2}\right)$) is calculated by the previous velocity at $\left(t - \frac{\Delta t}{2}\right)$ according to the acceleration rate at the this time step t. This scheme is in principle time-reversible, and can be expressed as

$$v_i\left(t + \frac{\Delta t}{2}\right) = v_i\left(t - \frac{\Delta t}{2}\right) + \frac{F_i(t)}{m_i}\Delta t, \qquad (2.3)$$

$$r_i(t + \Delta t) = r_i(t) + v_i\left(t + \frac{\Delta t}{2}\right)\Delta t, \qquad (2.4)$$

where Δt is the timestep.

2.2.1 Lennard-Jones interaction potential

A popular choice to represent the interaction between a pair of atoms or molecules is the Lennard- Jones potential. The LJ potential was first proposed for liquid argon system, and is given by,

$$V(r_{ij}) = 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - \left(\sigma/r_{ij} \right)^{6} \right], \qquad (2.5)$$

where r_{ij} is the separation between atoms, ϵ and σ define the energy strength and length scale, respectively. The LJ potential passes through 0 at $r_{ij} = \sigma$ and reaches its minimum value ϵ at $r_{ij} = r_m = 2^{1/6}\sigma$, as shown in Figure 2.1. With appropriately chosen parameters σ and ϵ , the LJ potential model can be used to simulate interatomic interactions and physical quantities for specific materials.



Figure 2.1 12-6 Lennard-Jones potential, where r is the distance between two atoms. At $r_m = 2^{1/6} \sigma \approx 1.122\sigma$, the potential reaches its minimum.

The reduced units for LJ potential, also called MD units, are widely used to investigate the general properties of liquids and solids. Table 2.1 lists the physical quantities in reduced units and the corresponding values for liquid argon.

Physical quantity	Parameters	Reduced units	Value for Ar
Mass	m	m ₀	$6.69 \times 10^{-29} kg$
Distance	r	$r^{*}=r/\sigma$	3.405Å
Energy	U	U*=U/ ϵ	$1.65 \times 10^{-21} J$
Time	t	t*=t ($\epsilon/m/\sigma^2$)1/2	$2.17 \times 10^{-12} s$
Temperature	Т	T*= k_B T/ ϵ	120 <i>K</i>
Velocity	V	v*=v τ/σ	157m/s
Force	F	$F^*=F\sigma/\epsilon$	$4.85 \times 10^{-12} N$

Table 2.1 Reduced Lennard-Jones physical quantities in MD simulation and the corresponding values for liquid argon.

The use of reduced units can convert the very small values in the common macroscopic units to numerical values in the order of unity. It also simplifies the equations of motion, ensuring a consistent set of all the units in the simulation.

2.2.2 Periodic boundary conditions

Using Periodic boundary conditions, the simulation box is replicated at each side of the original one to form an infinite lattice with copies of the central box. With these periodic boundary conditions, each atom or molecule located near surface sides will experience interactions with other atoms surrounding it, which can be the atoms from the central box and the copies of images. If one atom moves in the central box, its periodic images from other copies of boxes will have the same trajectory. As an atom leaves from one side of the box, it will enter from the opposite side. Normally, a spherical cutoff region (r_c) is

considered, such that the interaction calculation for a given particle is performed only with other particles located in this region instead of the whole system, as shown in Figure 2.2.



Figure 2.2 Schematic representation of periodic boundary conditions. An atom in the center box interacts with other atoms surrounding it, which may be from the same, as well as the copied images. Beyond the cutoff radius r_c , the interaction is ignored.

2.2.3 Nose-Hoover thermostat

The Nose-Hoover thermostat is a method to control the temperature in NVT ensemble, which was first proposed by Nose [85] and further improved by Hoover [86]. A thermodynamic friction coefficient ξ is introduced to represent a heat bath. The physical meaning of the coefficient is to slow down or accelerates atoms until the system reaches the target temperature T_0 . Then the equation of motion can be written as

$$m_i \frac{d^2 r_i}{dt^2} = F_i - \xi m_i v_i, \qquad (2.6)$$

$$\frac{d\xi}{dt} = \frac{T - T_0}{Q} = \frac{1}{Q} \left[\sum_{i=1}^{N} \frac{m_i v_i^2}{2} - \frac{3N + 1}{2} k_B T_0 \right], \qquad (2.7)$$

where T is the instantaneous temperature of the system, N is the number of atoms in the original system, (3N+1) is the new number of degree of freedom by adding the friction coefficients ξ and the coupling constant Q, which determines the relaxation of the dynamics of ξ . From eq. (2.7), the kinetic energy of the system is $\frac{(3N+1)}{2}k_BT_0$ at steady state.

2.3 Liquid/liquid system

In the liquid/liquid system, the interaction between two liquids is described by a dimensionless attraction parameter A which determines the surface tension between the two immiscible liquids. With a large A, liquids experience strong attractions. We first consider a two-component mixture of Lennard-Jones fluids in a simulation box of volume $L_x \times L_y \times L_z$ (160 $\sigma \times 40\sigma \times 20\sigma$). The box contains two slabs of liquids with liquid 1 in the left region and liquid 2 in the right region as shown in Figure 2.3. The initial orientation of the interface is perpendicular to the x-direction and the initial position is located at x=0, which us the center of the box. Periodic boundary conditions are applied to the system. Both liquids have the same density $\rho_L = 0.8\sigma^{-3}$. The atoms i and j in the system interact via L-J potentials as

$$V_{\alpha\beta}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - A_{\alpha\beta} \left(\sigma/r_{ij} \right)^{6} \right], & r_{ij} \le r_{c} \\ 0, & r_{ij} > r_{c} \end{cases}$$
(2.8)

where r_{ij} is the interatomic separation, σ and ϵ are the length scale and energy scale respectively, and $A_{\alpha\beta}$ is a dimensionless attraction parameter that controls the attraction between the various atomic species in the system. The attraction coefficient for atoms in the same fluid are set as $A_{11} = A_{22} = 1.0$, while atoms between two fluids varies to simulate different miscibility ($A_{12} = 0.1 \sim 1.0$).



Figure 2.3 Schematic of two immiscible fluids with box size $L_x \times L_y \times L_z = 160\sigma \times 40\sigma \times 20\sigma$. L1 (red atoms) and L2 (green atoms) both have 50266 atoms with the same number density of $0.8\sigma^{-3}$. Peroxidic boundary conditions are used in three directions.

As mentioned before, the molecular dynamics simulations are performed using LAMMPS. In LAMMPS, the Lennard-Jones potential is written in the basic form as eq. (2.5). Thus, to implement the dimensionless attraction parameter $A_{\alpha\beta}$ in a LJ potential of the form from eq. (2.8), we use a Lennard-Jones interaction in which we modify the two parameters of the potential, ϵ' and σ' , as follows:

$$\epsilon' = (A_{\alpha\beta})^2 \epsilon, \tag{2.9}$$

$$\sigma' = (A_{\alpha\beta})^{-1/6}\sigma, \qquad (2.10)$$

resulting in the desired interaction. If the interaction parameter is chosen as $A_{\alpha\beta} = 0.2$ for the system, it is equivalent as $\epsilon' = 0.04\epsilon$ and $\sigma' = 1.31\sigma$ used in eq. (2.5). In all cases, we implement a global cutoff radius $r_c = 2.5\sigma'$. The calculations are done in the canonical ensemble (NVT), with temperature maintained at T = $1.0 \epsilon/k_B$ using the Nose-Hoover thermostat. The equations of motion are integrated by Verlet's algorithm with a time step $\Delta t = 0.01$. The simulation starts with fluids atoms initially placed as solid-like FCC lattice with a density of $\rho_L = 0.8\sigma^{-3}$, followed by an equilibration process of 10,000 timesteps before we start collecting data.

First, we measured the density variation across a planar liquid/liquid interface. The density of the fluids is measured by equally dividing the domain into several layers or bins which are parallel to the plane of the interface, and then averaging the number density of fluids atoms in each layer over 15,000 timesteps. Figure 2.4 shows the fluids number density profile as a function of x, which is the direction perpendicular to the interface. The density of each fluid rapidly drops to zero at the center of the domain and keeps constant in the other half of the box. This confirms the immiscibility of the two fluids and the position of the fluid/fluid interface. Given the periodicity of the simulation box, this density drop can also be observed at the ends of the box, which forms another interface. Away from the interfaces, the number density of the fluids is close to the setting value of $0.8\sigma^{-3}$. The two liquids are equivalent, and as a result their density profiles are symmetric with respect to the x=0 position. The total density $\rho_{L1} + \rho_{L2}$ is also plotted in Figure 2.4 as a function of x, showing that it decreases from $0.8\sigma^{-3}$ to $0.5\sigma^{-3}$ as we go from the bulk to the interface. We also observe that there exists a density gap caused by the immiscibility of the two fluids which is around 8σ in width for $A_{12} = 0.2$. It is measured between the points where the slope of two liquids density profiles derivates away from zero. Such density gap between immiscible fluids has also been observed in others literatures using molecular dynamics simulations [54]–[56].



Figure 2.4 Equilibrium density distribution of two immiscible liquids as a function of the position x for $A_{12} = 0.2$. The density distribution for liquid 1 is given in solid black line, liquid 2 in solid red line and the total density is in dashed blue line.

The density gap for different values of the attraction coefficient A_{12} was also studied. By varying the value of A_{12} from 0.1 to 1.0 between the two-fluid species, the fluids become more miscible because of the stronger attraction. Figure 2.5 shows the total density profile as a function of x, near the interface, and for different values of A_{12} . We find that the region near the interface becomes less dense as the attraction between the two fluids is weaker. For $A_{12} = 0.2$, the minimum number density is $0.55\sigma^{-3}$. As A_{12} is increased to 1.0, in which case the two fluids are equivalent, we observe they are totally mixed and that the density in the center is similar to the density far away, that no interface is formed in such case. The stronger attraction between the two species leads to a larger concentration of the fluid atoms near the interface. These results are similar to Rezvantalab's studies [56].



Figure 2.5 Density distribution for two immiscible liquids as a function of position x for different attraction coefficients A_{12} near the liquid/liquid interface.

Next, the liquid/liquid surface tension is measured for different values of attraction coefficients. The surface tension is defined as the isothermal work per unit area of interface based on the thermodynamic definition. Using statistical mechanics, Fowler developed a relation between the surface tension and the intermolecular forces. Specially, the surface tension is calculated as the integral across the interface of the difference between the normal and tangential components of the pressure tensor,

$$\gamma = \int_{-\infty}^{\infty} dy \{ P_N(x) - P_T(x) \},$$
 (2.11)

where P_N is the normal component of the pressure tensor, P_T is the tangential component of the pressure tensor and ∞ denotes the location in the bulk which is infinity far away from the interface. In the case of our system with two interfaces due to periodicity, the surface tension is calculated as half of the integral. The infinite sign can be approximately replaced by the finite system size, since the pressure difference is zero far away from the interface. Then, equation (2.11) can be written as $\gamma = \frac{1}{2} \int_{-L_X/2}^{L_X/2} dy \{P_N(x) - P_T(x)\}$, where Lx is the length of the simulation box in the x-direction perpendicular to the interface. The pressure tensor component $P_{\alpha\beta}$, with Cartesian coordinates α and β is defined by Kirkwood-Buff theory [71] as,

$$P_{\alpha\beta} = \rho k_B T \boldsymbol{I} + \frac{1}{V_s} \langle \sum_{i=1}^{N-1} \sum_{j>i}^{N} (r_{ij})_{\alpha} (f_{ij})_{\beta} \rangle \qquad (2.12)$$

where **I** is the unit tensor, ρ is the number density which equals to N/V_s , V_s is the volume of the system, k_B is the Boltzmann constant, T is the absolute temperature, r_{ij} is the vector between atom i and j and f_{ij} denotes the intermolecular force. For a planar interface perpendicular to y direction, the normal pressure is defined as $P_N(x) = P_{xx}(x)$, and the tangential component is given by $P_T(x) = (P_{yy}(x) + P_{zz}(x))/2$. In order to obtain the integral in eq. (2.11), the system is sliced into slabs parallel to the YZ plane and the normal and tangential components of pressure tensors of each slab are calculated from eq. (2.12) as

$$P_N(x) = \rho(x)k_BT - \frac{1}{V_{slab}} \left\langle \sum_{ij} \frac{x_{ij}^2}{r_{ij}} \frac{dV(r_{ij})}{dr_{ij}} \right\rangle$$
(2.13)

$$P_T(x) = \rho(x)k_B T - \frac{1}{V_{slab}} \langle \sum_{ij} \frac{y_{ij}^2 + z_{ij}^2}{2r_{ij}} \frac{dV(r_{ij})}{dr_{ij}} \rangle$$
(2.14)

where $\rho(x)$ and V_{slab} are the density and volume of each slab and $V(r_{ij})$ is the potential energy of the atomic pair i and j. The angle brackets indicate the average of all atoms located in the slab at x over an ensemble.

Figure 2.6 shows the normal and tangential components of the pressure as a function of x, obtained by averaging 15,000 timesteps. Figure 2.6a corresponds to an attraction coefficient between the two liquids of 0.2 and Figure 2.6b corresponds to an attraction coefficient of 0.5. The jump in pressure across the interface is much smaller for the normal component compared to the tangential component. The normal and tangential components of the pressure tensor can be calculated from eq. (2.13) and (2.14), respectively. By integrating the difference ($P_N - P_t$) from -80 σ to 80 σ in the x direction, the surface tension between two fluids γ_{12} can be obtained. Due to the periodicity of the system, there are two liquid/liquid interfaces, so the value of γ_{12} is half of the integral of the pressure difference. The oscillations exhibited in the pressure profiles corresponded to the oscillatory behavior of the density profiles. Moreover, a decrease in the tangential component P_T at the interface position is observed.



Figure 2.6 Local pressure profile: Normal (black), tangential (red) and the difference in normal and tangential pressure of two immiscible liquids (blue) as a function of x for $A_{12} = 0.2$ (up) and $A_{12} = 0.5$ (down).

Using this method with MD simulations, we measured the surface tension between liquids for different attraction coefficients A_{12} ranging from 0.1 to 1.0. From Figure 2.7, we find that surface tension decreases as the attraction between the atoms in the two kinds of liquids increases. We compared our results (empty symbols) to the data from available literature [54], [56] (solid symbols). A truncated LJ potential with a cutoff radius 3.0 σ was used in ref. [54], and the shift-force LJ with $r_c = 2.5\sigma$ is applied in ref. [56]. Even though there is a slightly difference in the simulated model, we find a good agreement with our results. The Lennard-Jones potential we employed is the truncated model with a cutoff radius $r_c =$ 2.5 σ in pink empty symbols, truncated LJ with $r_c = 3.0\sigma$ in circle empty symbols and shifted-force LJ model for $r_c = 2.5\sigma$ in black square symbols. The shifted-force Lennard-Jones potential is given by

$$V(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - A_{\alpha\beta} \left(\sigma/r_{ij} \right)^{6} \right] - V(r_{c}) - \left(r_{ij} - r_{c} \right) \frac{dV}{dr} \Big|_{r_{ij} = r_{c}}, & r_{ij} \le r_{c} \\ 0, & r_{ij} > r_{c} \end{cases}$$
(2.15)

These simulations with different cutoffs show similar results, which indicate that the truncated model with a cutoff radius $r_c = 2.5\sigma$ in the simulation of a particle interacting with moving interfaces would be a reasonable choice, similar to larger cutoff distances.



Figure 2.7 Liquid/liquid surface tension as a function of attraction parameter A_{12} at T = 1.0 ϵ/k_B . First three sets of data are from our simulation with a domains size $160\sigma \times 40\sigma \times 20\sigma$. Solid symbols are the surface tension from references.

2.4 Liquid/solid system

To study the surface tension of a liquid/solid interface, a rectangular box is used as the simulation domain. In the domain, a single fluid is enclosed between two parallel solid walls as shown in Figure 2.8. The atoms *i* and *j* in the system interact via LJ potentials as $V_{\alpha\beta}(r_{ij}) = 4\epsilon \left[(\sigma/r_{ij})^{12} - A_{\alpha\beta} (\sigma/r_{ij})^6 \right]$, with a cutoff radius at $r_c = 2.5\sigma$. The solid wall is assumed to consist of three layers of an FCC (face centered cubic) lattice with a reduced density $1.0\sigma^{-3}$. The plane in contact with the fluid is the [1 0 0] surface. The system contains about 100,000 liquid atoms and 7000 solid atoms, with a distance between

solid walls Ly=40 σ , lateral cell dimensions Lx=160 σ , Lz=20 σ and wall thickness 2.5 σ . All simulations are carried out at a constant temperature 1.0 ϵ/k_B with a Nose-Hoover thermostat in the canonical ensemble. For same species of atoms, $A_{\alpha\beta}$ is 1. We measured the solid/liquid surface tension while varying the attraction coefficient between solid and liquid atoms, labeled as A_{ls} . All the data are collected after the system reaches equilibrium state, using 50,000 timesteps for equilibration. The system initially contains one wall. After periodic boundary conditions are applied, the wall from another image can be considered as the upper wall of the original domain.



Figure 2.8 Schematic of single liquid enclosed between two solid walls where green points are solid atoms and pink points are liquid atoms. This configuration of the wall was formed by three layers FCC lattice consisted of 7538 atoms ($\rho_{wall} = 1.0\sigma^{-3}$) at each side.

Density and surface tension are sampled by equally dividing the y-direction of the simulation box into multiple slabs. The surface tension is evaluated by calculating the difference between tangential and normal components in each slab using equations (2.11) – (2.14), in a way analogous to the calculations in liquid/liquid systems. The density profile of the fluid enclosed by two planar walls along the y-direction for different attraction coefficients is shown in Figure 2.9. We used walls of two different reduced densities, $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$. To obtain the interface density distribution, 134 bins in the y direction were used and the width of each bin is about 0.3σ . As -22.5~20.0 σ is occupied

by rigid wall atoms, the fluid density in this region is zero. The density profiles show large oscillations near the interfacial region with a range of about 10σ for both wall densities, which is owing to the fact that liquid atoms are orderly distributed near the solid interface due to strong attractions. We are able to capture this effect because the size of bin is smaller than the molecular diameter. This oscillatory characteristic of the density profiles are also reported in Refs. [87]–[90]. The density reaches a peak value and the oscillations gradually decay to a constant value corresponding to the bulk density at the middle section of the channel. The nominal density of liquid atoms is $0.8\sigma^{-3}$ if there is no wall effect. However, due to the adsorption layers of liquid atoms by the wall, the density of the bulk liquid is lower than the nominal value. The width of the bulk liquid and interface region, where its local density deviates from the bulk value, remain basically the same for different attraction coefficients. We also observe that with a strong attraction between the wall and the fluid atoms, the first peak in number density is clearly higher. For high interactions, for example for $A_{ls} = 0.9$, the density peaks are about $1.4\sigma^{-3}$ and $2.0\sigma^{-3}$ for wall density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$, respectively. Whereas, for a lower interaction 0.5, the density peaks are about $1.25\sigma^{-3}$ and $2.25\sigma^{-3}$ for wall density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$, respectively. It shows that the density variation in the interface regions become smaller with reducing A_{ls} , and the interfacial layer structure was less prominent, leading to the bulk liquid closer to its nominal value.





Figure 2.9 Density profile of liquid as a function of normal distance from the solid interface plane $\rho_{wall} = 1.0\sigma^{-3}$ (up) and $\rho_{wall} = 4.0\sigma^{-3}$ (down) for different A_{ls} (0.2, 0.5, 0.7 and 0.9).

The pressure tensor is calculated using the same method as when calculating the liquid/liquid surface tension discussed in 2.3 and using equation (2.14). The only difference is that the solid/liquid interface is normal to the y-direction. By integrating the $P_N(y) - P_T(y)$ term from the surface of the wall to the center of the bulk liquid, the surface tension between wall and liquid γ_{ls} can be obtained.

Note that since the wall atoms were arranged by FCC lattice in a box with size $160\sigma \times 2.5\sigma \times 20\sigma$, the center positions of the first layer of the wall which is in contact with the fluid atoms are y=-20.7 σ for density $1.0\sigma^{-3}$ and y=-20 σ for density $4.0\sigma^{-3}$.



Figure 2.10 Local pressure profile: Normal (black), tangential (red) and the difference in normal and tangential pressure of liquid/solid (blue) as a function of y for $A_{ls} = 0.5$ and $A_{ls} = 0.9$ with different wall densities.

The surface tension γ_{ls} is plotted as a function of attraction coefficient A_{ls} Figure 2.11. As the attraction increases, fluid properties change from partial wetting to complete wetting to the wall and the surface tension γ_{ls} decreases. We also find that the solid phase formed by same species of atoms or molecules show lower surface tension for higher density.



Figure 2.11 Solid/liquid surface tension as a function of attraction coefficient A_{ls} for wall density $\rho_{wall} = 1.0\sigma^{-3}$ and $\rho_{wall} = 4.0\sigma^{-3}$. Each data point is evaluated by four independent runs.

2.5 Liquid/liquid equilibrium adjacent to a solid wall

2.5.1 Direct measurement method

We consider the system with two immiscible fluids confined between parallel plates as an atomic system interacting with a 12-6 LJ potential. The two fluids are in a domain size of $160\sigma \times 40\sigma \times 20\sigma$ with a 2.5 σ thick solid substrate perpendicular to the y-direction as shown in Figure 2.12. The atoms of the solid substrate are constructed by an FCC lattice with a reduced density of $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$. To ensure the immiscibility of the two liquids, the liquid/liquid interaction between non-wetting and wetting fluid is $A_{12} = 0.2$

with density $\rho_L = 0.8\sigma^{-3}$ for both fluids. The attraction coefficient for liquid 2/substrate varies from 0.1 to 0.9 and for liquid 1/substrate the attraction coefficient is always set to be 0.5. All simulations are carried out at a constant reduced temperature of 1.0 with a Nose-Hoover thermostat.



Figure 2.12 a) Snapshot of the simulation setup for liquid/liquid equilibrium adjacent to a solid wall, where the pink region is solid atoms, red and green region are liquid 1 and liquid 2. b) Schematic of wall contact angle θ as two immiscible fluids enclosed by parallel plates.

We performed the direct contact angle measurements by fitting a circle to the liquid/liquid interface. The wall contact angle is the angle between the tangent line of the line connected from the center of the fitting circle to the three-phase contact point and the wall surface to the more wetting liquid side. When liquid 1 is less wetting than liquid 2, θ <90°, when liquid 1 is more wetting than liquid 2, θ >90°. The liquid/liquid interface is flat when both liquids have the same interaction with the solid. Snapshots for contact angle of wall density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$ with different wetting properties are shown in Figure 2.13.



Figure 2.13 Snapshots of two immiscible enclosed by parallel plate where $A_{12} = 0.2$, $A_{1s} = 0.5$ and $A_{2s} = 0.5 \sim 0.9$. The atoms in red are liquid 1 (less wetting) and the atoms in blue are liquid 2 (more wetting).

We overserved that a large discrepancy in the wetting of two fluids results in lower contact angle at the wall, as expected. Under the same wetting conditions, the solid density also has an effect on the contact angles. The wall with higher density, which has a stronger attraction with fluids, results in lower contact angle for the same combination of attraction coefficients. When A_{2s} is larger than 0.7 for wall density of $\rho_w = 4.0\sigma^{-3}$, the more wetting fluid formed a thin film on the wall, which broke the connection between the fluid/fluid interface with the wall. The wall contact angle is zero in such cases. By
controlling the attraction coefficients between two species and the density of the solid, we can get arbitrary contact angles.

2.5.1 Young's equation

As mentioned in Chapter 1, the wetting properties of a substrate/liquids combination can be described by Young's equation:

$$\cos\theta = \frac{\gamma_{1s} - \gamma_{2s}}{\gamma_{12}} \tag{2.16}$$

where γ_{1s} and γ_{2s} are the surface tension of the wall with liquid 1 and of the wall with liquid 2, respectively, and γ_{12} is the corresponding fluid/fluid surface tension. The surface tension between two phases was independently measured by means of the integral over the pressure tensor difference between the normal and tangential components using equation (2.11). In this section, we calculated the contact angles for two fixed attraction parameters: wall/liuiqd1 interaction A_{1s} is 0.5, liquid/liquid interaction is 0.2 and varying the interaction between liquid 2 and wall, which are the same set of parameters used in the direct measurement method section.

$ ho_w \left[\sigma^{-3} \right]$	A_{12}	A_{1s}	A_{2s}	θ [°]
1	0.2	0.5	0.6	86±1
1	0.2	0.5	0.65	$84{\pm}1$
1	0.2	0.5	0.7	82 ± 1
1	0.2	0.5	0.75	79±1
1	0.2	0.5	0.8	76 ± 1
1	0.2	0.5	0.85	73±1
1	0.2	0.5	0.9	$68{\pm}1$
4	0.2	0.5	0.6	80 ± 1
4	0.2	0.5	0.7	67±1
4	0.2	0.5	0.8	48 ± 2
4	0.2	0.5	0.9	3 ± 2

Table 2.2 Wall particle contact angle (θ) from Young's equation for $A_{12} = 0.2$, $A_{1s} = 0.5$ and $A_{2s} = 0.5 \sim 0.9$ with different wall densities.

From Table 2.2, we present the wall contact angle values calculated by Young's equation, where the values of surface tension are obtained from previous simulations for wall density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$. We found that the wall contact angle decreases as the fluid becomes more wetting. For wall density $4.0\sigma^{-3}$ and $A_{2s} = 0.9$, the contact angle drops to 3° that liquid 2 is almost completely spreading on the surface of the wall, which is in agreement with what we observed using direct measurement method shown in Figure 2.11.

Chapter 3 Particle in Static Systems

3.1 Introduction

Understanding the transport and fate of nano-scale particles through porous media, such as the adsorption of particles at solid-liquid interface in fluid-filled nanochannels, has attracted considerable attention recently, due to its importance in emerging areas in nanotechnology. Both experiments and numerical studies on single fluids at fluid-solid interfaces at the nanoscale showed that the wetting properties of the fluid play an important role at the solid-liquid interface [91]–[94]. Molecular dynamics simulations have been used with simple Lennard-Jones liquids to study the hydrodynamic behavior of single fluids in a nanochannel, where the wetting properties of the liquid were controlled by the strength of liquid-solid interactions [94], [95]. In previous work, our group has also used MD simulations to investigate the motion of nanoparticles suspended in a single fluid inside a cylindrical nanochannel. They found that for poorly wetting fluids, a particle initially moving along the center of a nanochannel can be adsorbed onto the tube wall and remains stationary at the solid interface or slips along the wall afterward (see Figure 3.1 taken from Ref. [96]) [96].

In previous work, the particle, the wall of the channel, and the fluid were all treated as atomic systems interacting via Lennard-Jones (LJ) potentials, $V_{ij}(r) = 4\epsilon [(\frac{\sigma}{r_{ij}})^{12} - A_{ij}(\frac{\sigma}{r_{ij}})^6]$, where A is an interaction parameter which controls the attraction between the various atomic species. A higher value of A between particle and fluids atom presents a more wetting fluid.



Figure 3.1 Snapshots of the solid particle adsorbed to the wall for the case motionless of the particle (left) and translating along the tube (right). [96]

Drazer et al. also found that the adsorption transition of the particle, which depends on the wetting properties of fluids, is independent of particle shape [97]. Moreover, they found a clear transition between adsorption and non-adsorption depending on the value of the dimensionless attraction coefficient A. In highly wetting suspending fluid, the particle moves along the center of the channel and the average velocity of the particle agrees with the solution by continuum Stokes equation. For the case that particle in less wetting fluids, particle follows the continuum dynamics only in the early time. The particle is eventually adsorbed to the solid walls and executes an intermittent stick-slip motion subsequently. Also, the particle which initially gets adsorbed in the less wetting fluid is found to detach from the wall as switching the less wetting to a highly wetting fluid.

In this chapter, we will investigate the adsorption phenomena of a particle to the liquid/solid interface and liquid/liquid interfaces in a static system using MD simulations. The wetting properties of the liquid were modeled by varying the attractions between solid and liquid phase using simple LJ potentials. We will first study the properties of a spherical particle, such as the particle structures and the interactions energies, with different densities in the bulk, and then extend the simulation to a fluid-filled channel system. For particles at the liquid/liquid interfaces, we will measure the contact angles and the interaction energy and compare them to theoretical values. These provide us with a basic understanding of particles in static systems under equilibrium condition when no force is added to the fluid.

3.2 Particle in bulk solvent

For a planar solid surface, we have shown previously that the adsorbed fluid layer on the solid becomes denser with larger values of the solid/liquid attraction. Therefore, it is important to evaluate the fluid structure around a spherical particle with different wettability. In order to reveal the transport of particles with different wettability, we will present the molecular structure of the fluid surrounding these nanoparticles. The solid and liquid atoms are interacting via Lennard-Jones potential using eq. (2.8). For interactions between same material, the attraction coefficient is set to be 1. The particle is constructed from atoms in an FCC lattice inside a spherical region of radius 6σ . The atoms are fixed at the lattice sites. The particle follows rigid body dynamics, and the total force and torque on the rigid body are computed as the sum of the forces and torques on all the atoms. In addition, the wettability is controlled by the attraction between solid and liquid atoms. Figure 3.2 and Table 3.1 present the details of the simulated rigid particles. The temperature

of the system is $1.0\epsilon/k_B$ maintained in the fluid by a Nosé–Hoover thermostat. The particle is initially placed in the center of the simulation domain and the surrounding bulk solvent has a density of $0.8\sigma^{-3}$.



Figure 3.2 Illustration of the particle for density $\rho = 1.0\sigma^{-3}$ and $\rho = 4.0\sigma^{-3}$ with a radius of 6σ .

R [σ]	$ ho_p ~[\sigma^{-3}]$	Ν	I $[m\sigma^2]$
6.0	1.0	935	2.06×10^{4}
6.0	4.0	3586	$7.7 imes 10^{4}$

Table 3.1 Properties of particle studies in this thesis. N is the total number of atoms in particle and I is the mass moment of inertia of particle: $I = m(1/N) \sum_{i} r_i^2$.

Figure 3.3 shows the liquid radial distribution function g(r) around nanoparticles of different densities $(1.0\sigma^{-3} \text{ and } 4.0\sigma^{-3})$. The radial distribution function describes how the fluid density varies as a function of distance from the particle. For both densities of particles, the surrounding liquid is highly structured with oscillations and a spacing around 1σ between peaks. The effect of solid-liquid interaction is weak on the fluid structure for $\rho_p = 1.0\sigma^{-3}$. In contrast, for the denser particle, on increasing the solid-liquid attraction the fluid structure becomes stronger, in that the layering of fluid become pronounced and the peak position is closer to the surface of the particle.



Figure 3.3 Radial distribution function of surrounding fluids for two different densities as a function of the distance from nanoparticles in the bulk: a) $\rho_p = 1.0\sigma^{-3}$ b) $\rho_p = 4.0\sigma^{-3}$. The radius of the particle is R = 6.0\sigma and density of the liquid is $0.8\sigma^{-3}$.

3.3 Particle at liquid/liquid interface

As a solid particle is at a gas/liquid or liquid/liquid interface, at equilibrium state, the surface tensions acting at the three-phase contact line, determine the contact angle of the particle, and can be calculated by Young's equation. The particle contact angle θ_p shown in Figure 1.5 can also be calculated form its equilibrium geometry. For a spherical particle, the contact angle θ_p is related to the height h that the particle goes into the less wetting phase and the particle radius R, and can be written as,

$$\cos\theta_p = 1 - h/R. \tag{3.1}$$

We performed simulations on a nanoparticle surrounded by two immiscible LJ fluids in a rectangular simulation domain with size $160\sigma \times 40\sigma \times 20\sigma$ as shown in Figure 3.4. When $A_{1s} = A_{2s}$, the particle is at the fluid/fluid interface with half of the volume in liquid 1 and the other semi-sphere in liquid 2 since the attraction to both liquids is the same. In this case, the particle contact angle is $\theta_p = 90^\circ$. The density of both liquids is $\rho_L = 0.8\sigma^{-3}$ and particle density is either $\rho_p = 1.0\sigma^{-3}$ or $\rho_p = 4.0\sigma^{-3}$. The fluid/fluid interaction is set as $A_{12} = 0.2$, corresponding to a surface tension $\gamma_{12} \approx 2.0\epsilon \sigma^{-2}$ as shown in Figure 2.7. The liquid 1 interacts with the particle atoms with $A_{1s} = 0.5$ and the interaction of liquid 2 with the particle A_{2s} varies from 0.1 to 0.9. All simulations are maintained at a constant reduced temperature $k_b/T = 1.0$ calculated by a Nose-Hoover thermostat.



Figure 3.4 Snapshot of simulation setup for a nanoparticle at the liquid/liquid interface. Same interaction parameter is used here for liquid 1-particle and liquid 2-particle, and particle contact angle θ_p is equal to 90°. We use equation (3.1) to measure the contact angle of the particle for different wettabilities. The location of the fluid/fluid interface is chosen as the intersection point of the two fluids density profiles of the two fluids and the center of mass of the particle is tracked after the system reaches its equilibrium state. As the attraction between liquid 2 and particle becomes stronger, the particle tends to move deeper into liquid 2 until it is totally immersed in liquid 2, giving a contact angle of 0 degrees or complete wetting. In Figure 3.5, we present the wall contact angle obtained from direct measurements method as discussed in the previous chapter compared to the particle contact angle calculated by equation (3.1). We find a good agreement on the contact angle for the particle and the wall, for both densities. The contact angles for wall and particle both decrease with an increasing A_{2s} . When $A_{2s} < 0.5$, the contact angle is larger than 90° and the denser solid shows bigger contact angle compared to less dense solid. In contrast, for $A_{2s} > 0.5$ the contact angle for denser solid is smaller and both are under 90°. We also observed that the solid shows complete wetting for $A_{2s} \ge 0.8$ for $\rho = 4.0\sigma^{-3}$.



Figure 3.5 Wall (θ) and particle contact angles (θ_p) as a function of the solid/liuiqd interaction parameter A_{2s} with $A_{1s} = 0.5$ and $A_{12} = 0.2$ for solid density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$ respectively. Wall CA is measured by direct measurement method and particle CA is calculated from eq. (3.1).

3.4 Particle at liquid/solid interface

3.4.1 Particle adsorption to at liquid/solid interface

We used molecular dynamics stimulation applied to the system shown in Figure 3.6, a colloidal particle immersed in one fluid confined between two parallel plates. The fluid, particle and wall atoms interact via Lennard-Jones potential, $V_{\alpha\beta}(r_{ij}) = 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - A_{\alpha\beta} \left(\sigma/r_{ij} \right)^{6} \right]$. Similar to previous studies, the interaction parameter A is 1 for atoms of the

same type and we also assume that the particle and wall are made of the same material. Therefore, the interaction between the wall and particle corresponds to A=1. The fluid atoms are initialized in an FCC lattice with a number density of $0.8\sigma^{-3}$ and the temperature is maintained at $1.0k_B/T$, corresponds to the liquid phase in LJ system. Using Nose-Hoover thermostat, we allow the fluid lattice to melt for 10000τ to reach an equilibrated state. The parallel walls have a density of $1.0\sigma^{-3}$ with three layers of FCC lattice. The wetting properties of the fluid-solid is specified by the attraction parameter A from LJ potential. In our simulation. we vary the interactions A_{ls} between fluid and solid.

In the simulation, a solid particle is released from the center of the channel as shown in Figure 3.6. The solid particle is constructed by a sphere of radius R=6 σ with number density of $1.0\sigma^{-3}$ (or $4.0\sigma^{-3}$) using an FCC lattice with atoms fixed to their relative positions. Periodic boundary conditions are imposed in all directions.



Figure 3.6 Schematic and explicit views of a colloidal spherical particle moving in parallel plates. The radius of the particle is $R=6\sigma$ and the separation of the wall is Ly=40 σ .

To investigate the effect of the wettability conditions on particle adsorption to a solid surface, we simulated the motion of a particle in a single fluid confined by two parallel walls at various values of attraction parameters A_{2s} .

The required diffusive time for a particle to reach the wall is around 20000 τ , which can be estimated as $(\frac{L_y}{2} - R)^2/2D$, where L_y is the height of the channel as 40 σ , and D is the diffusion coefficient given by Stoke-Einstein equation,

$$D = k_B T / 6\pi \mu R. \tag{3.2}$$

In our case, the viscosity of the LJ fluid for assigned density and temperature is $\mu \cong 2.0m\sigma^{-1}\tau^{-1}$ [98], $k_BT = 1.0$, and the diffusion coefficient is approximately $D \cong 0.0044\sigma^2/\tau$. Therefore, in order to observe the interaction between the particle and wall, the simulation should be much longer than the estimated diffusion time. To ensure the particle has enough time to approach the wall surface, the time scale of the simulations is set to 80000 τ .

Figure 3.7 shows the particle trajectory in the y-direction as a function of time for five independent realizations, from the less wetting to the more wetting fluid, corresponding to $A_{ls} = 0.5 - 0.9$. We present results for two different particle densities. We find that the adsorption occurs in the less wetting fluid when $A_{ls} < 0.7$ for $\rho_p = 4.0\sigma^{-3}$ and particle with density $1.0\sigma^{-3}$ are all adsorbed. For most of the adsorption cases, particle rapidly move to the upper or the lower wall and the center of the particle is located at its nominal maximum value $L_y - R$. However, for $\rho_p = 1.0\sigma^{-3}$ and $A_{ls} = 0.9$, there exists a 1σ

thickness of liquid between the particle and the wall instead of adhesive directly to the wall surface. We have run multiple independent simulations and all the tests are found to follow similar phenomena.

When the particle is adsorbed to the surface, there is no movement in x and z directions, which are the directions parallel to the wall. We also observe the tendency of shorter adsorption time for particles released in a less wetting fluid. In conclusion, the adsorption of particles on solid walls is found to have a dependence on the fluid wetting properties, namely a competition of interactions between particle/liquid and particle/wall.





Figure 3.7 The vertical position of the particle vs. time for a single realization at different values of A_{ls} (0.5~0.9) for particle density: a) $1.0\sigma^{-3}$ and b) $4.0\sigma^{-3}$. The jump to position in y ~14 for σ for lower values of A_{ls} corresponds to adsorption at the surface of the wall. (The height of the channel is $L_y = 40\sigma$ and the particle radius is $R = 6\sigma$).

In order to understand the adsorption phenomena from an energetic perspective, we measured the interaction energy of a particle in the bulk solvent and the energy when it is attached to the surface of the wall. The energy difference can be calculated as

$$\Delta E = E_{p-wall} + E_{p-liquid} - E_{p-bulk}, \qquad (3.3)$$

where E_{p-wall} , $E_{p-liquid}$ are the interaction energy between particle/wall and particle/liquid when the particle is adsorbed, and E_{p-bulk} is the interaction energy between the particle and the bulk solvent when the particle is suspended. The energy difference is investigated for a particle with density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$ on a density $1.0\sigma^{-3}$ wall surface with different fluid-solid attraction coefficients. For those cases in which the particle cannot be spontaneously adsorbed to the wall in a high wetting fluid, we first use a small value of A_{ls} to adsorb the particle and then switch this A_{ls} to the required value. After the system get to equilibrium, we find the adsorption process is irreversible and we measure the interaction energy E_{p-wall} , $E_{p-liquid}$ for a particle in the more wetting fluids.

Figure 3.8-Figure 3.10 present the interaction energies E_{p-bulk} , $E_{p-liquid}$ and E_{p-wall} respectively as a function of the attraction coefficient A_{ls} for particle density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$ adsorbed to a wall with density $1.0\sigma^{-3}$. We observe that the interaction energy for particle/bulk and particle/liquid both decrease with an increasing A_{ls} . When the particle is attached to the wall, the energy between particle and wall is measured for various A_{ls} . E_{p-wall} is found to have a constant value in less wetting fluid and increase to a higher value as $A_{ls} > 0.7$. Since E_{p-wall} is related to the particle position corresponding to the wall and the number of atoms in the particle, we plot the probability distribution function of particle position in y direction when it is adsorbed to the upper wall as shown in Figure 3.11. The denser particle is found to be more adjacent to the wall because it experiences stronger attraction between particle and wall due a larger number of atoms in the particle. When the density of the particle is $4.0\sigma^{-3}$, we observe that the peaks of the probability distribution function for the particle position in y increases with a decreasing A_{ls} , which shows that the particle tends to adsorb closer to the wall with a smaller A_{ls} where the attraction between liquid and particle is weaker. However, this trend can only be found at $A_{ls} < 0.7$ for $\rho_p =$ $1.0\sigma^{-3}$, in which the adsorption position is determined by the location of the peak value of probability p(y), leading to the nonmonotonic interaction E_{p-wall} . Moreover, for $A_{ls} <$

0.9, the existence of 1σ thickness of liquid between particle and wall in Figure 3.7a is not found in the probability distribution function. This is because the simulations for measuring p(y) is done by switching the attraction parameters from a low value to all the other tested values, where the particle has already been attached to the wall. At this low value, no formation of the liquid layer is found as a suspended particle get adsorbed.

For a particle with density of $1.0\sigma^{-3}$, the energy difference calculated from equation (3.3)) is found to increase with $A_{ls} < 0.7$ and drops afterwards. Also, the values of energy difference for all tested A_{ls} is found to be negative, which indicates that the particle experiences a lower energy when being attached to the wall instead of suspended in the bulk. This adsorption of the suspended particle to the wall surface is observed for A_{ls} = 0.5~0.9, which is shown in Figure 3.7b. For a particle with density $4.0\sigma^{-3}$, the energy difference monotonically increases with A_{ls} , and it is negative when $A_{ls} < 0.8$ but positive for attraction coefficients larger than 0.8. This is mostly in agreement with the findings of particle adsorption observed in Figure 3.7a that the transition from less wetting to more wetting occurs at $A_{ls} = 0.8$ for a particle adsorbed to the wall. However, there is one exception for $A_{ls} = 0.8$ that the energy difference is negative, but no adsorption is observed. This may be caused by an energy barrier that prevent the particle to get adsorbed to the wall or the mismatch between lattices. After adsorption occurred, we switched A_{ls} to a value between 0.7 and 1.0 for $\rho_p = 4.0\sigma^{-3}$, particle still retained on the solid/liquid surface instead of detachment, which might be due to the energy barrier so that the particle is hard to be released from the wall to the bulk.



Figure 3.8 Interaction energy between a suspended particle and the bulk as a function of the solid-liquid interaction parameter A_{ls} for particle density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$.



Figure 3.9 Interaction energy between an absorbed particle and the liquid as a function of the solid-liquid interaction parameter A_{ls} for particle density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$.



Figure 3.10 Interaction energy between an absorbed particle and the wall as a function of the solid-liquid interaction parameter A_{ls} for particle density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$.



Figure 3.11 Probability distribution function for the position particle adsorbed to liquid/solid interface in the vertical direction with various interactions ($A_{ls} = 0.1 \sim 1.0$) for particle densities $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$. (The first layer wall lattice is located at y=20.7 σ in contact with fluid atoms for both cases and the particle radius is $R = 6\sigma$.)



Figure 3.12 The difference in interaction energy ΔE from equation (3.3) as a function of sthe olid-liquid interaction parameter A_{ls} for particle density $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$. Negative value in ΔE indicates particle experience lower energy when it is adsorbed, and a positive value indicates lower energy when the particle is in the bulk solvent.

3.4.2 Particle friction force and adhesion force

As discussed in section 1.2.3, the remobilization of a particle deposited on a solid surface by a moving interface is theoretically determined by the force balance, which is related to the surface tension force, the particle friction force and the adhesion force between the particle and the wall. To better understand how these forces influenced the transport processes of the particle, the friction force and the adhesion force are measured by MD simulations.

As shown in Figure 1.11, when forces are exerted on the particle, the particle is partly interacting with fluid 1 and partly with fluid 2 due to the position of the interface. In our simulations, however, the forces are measured when the particle is in the bulk liquid instead of at an interface, since we want to eliminate the effect of other forces acting on the particle,

such as the surface tension force. In the simulation, we will add a linearly increasing force on all the atoms contained in the particle in horizontal and vertical directions separately, and the trajectory of the particle is tracked to determine the entrainment moment.

In order to investigate the detachment of particles from a wall in a single fluid, we apply an external force on the attached colloid particles and observe their behavior in order to determine the moment it is displaced from the initial position. If the force is in the horizontal direction and is slowly increased with time, there exists a certain value that particle starts to move along the wall instead of pinning, and this external force can be considered as equivalent to the particle dynamics friction force $(\tilde{F}_{ext}^{\parallel} = \tilde{F}_F)$. As shown in Figure 3.14, we measured the particle trajectory in the x-direction as a function of the horizontal external force and the friction force for different particle densities at various solid-liquid attraction coefficients. All the forces are normalized using the characteristic magnitude of surface tension forces, $2\pi R\gamma$, where γ is the liquid/liquid surface tension used in our desorption simulations discussed in the next chapter, which is $\gamma = 2.0 \epsilon \sigma^{-2}$ for $A_{12} = 0.2$. We slowly increase the force $\tilde{F}_{ext}^{\parallel}$ adding horizontally on the particle from 0 to 1.0. When X=0 as shown in the figure, it indicates there is no movement on the particle until the force is reached to a certain value do we obverse particle starts to slide along the wall.



Figure 3.13 The particle trajectory in the x direction as a function of the increasing horizontal external force $\tilde{F}_{\text{ext}}^{\parallel}$ for different A_{ls} : a) particle density is $1.0\sigma^{-3}$. b) particle density is $4.0\sigma^{-3}$.



Figure 3.14 Particle friction force (\tilde{F}_F) as a function of particle-fluid attraction coefficient. To estimate the value of \tilde{F}_F for two different particle densities: $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$, an increasing external force is added to the particle in the parallel direction along the wall.

Similarly, as the growing external force is added in the direction normal to the wall, the point at which particle detached from the wall can be regarded as the particle pull-off force,

which is equivalent the particle-wall adhesion force $(\tilde{F}_{ext}^{\perp} = \tilde{F}_A)$. Even though particle and wall are of same material, the particles immersed in the liquid experience a liquid/solid interaction, leading to the different adhesion force as various interactions are applied. In Figure 3.15, we plot the particle trajectory in the y-direction as a function of the vertical external force. We observed that there is a sudden jump for particle released from the upper wall (y=14 σ) to the lower wall (y=-14 σ) as the force is increased to a certain value. This force is equivalent to the adhesion force between particle and wall, and is plotted as a function of A_{ls} shown in Figure 3.16.



Figure 3.15 The particle trajectory in the y-direction as a function of the increasing vertical external force $\tilde{F}_{\text{ext}}^{\perp}$ for different A_{ls} : a) particle density is $1.0\sigma^{-3}$. b) particle density is $4.0\sigma^{-3}$.



Figure 3.16 Required detachment force (\tilde{F}_p) to pull off a particle from the solid interface as a function of particle-fluid attraction coefficient. To estimate the value of \tilde{F}_p for two different particle densities: $1.0\sigma^{-3}$ and $4.0\sigma^{-3}$, an increasing external force is added to the particle in the direction normal to the wall.

We find that the particle friction force is independent with solid-liquid interactions, and the minimum force leading to translational motion of the particle along the wall is $\tilde{F}_F \approx 0.6$ for $\rho_p = 1.0\sigma^{-3}$ and $\tilde{F}_F \approx 0.45$ for $\rho_p = 4.0\sigma^{-3}$ averaged from all measured A_{ls} . The normal force required to detach the particle from the solid surface, referring as \tilde{F}_A shown in Figure 3.16, decreases from 4.5 to 2.0 as solid-liquid attraction increases $\rho_p = 4.0\sigma^{-3}$. However, when the particle density is $1.0\sigma^{-3}$, the effect of solid-liquid interaction on the pull-off force is very small, and the adhesion force is more or less the same, which is around 2.5 as A_{ls} increases from 0.5 to 0.9. This may be caused by irregulate adsorption position presented in Figure 3.11b, and there is not much difference on the energy difference between particle at adsorption and in the bulk.

Chapter 4 Particle in Dynamics Systems

4.1 Introduction

The transport and fate of colloidal particles in porous media affects a broad range of phenomena, from the fouling of membranes used in water treatment and the effective permeability of oil and gas reservoirs, to the spreading of contaminants in the subsurface and possible remediation strategies [1], [99], [100]. Continuous progress has been made in our understanding and modeling since the introduction of colloid filtration theory in saturated systems [101], but predicting the behavior of nanoparticles remains challenging [102], [103]. Unsaturated and multiphase flows in geological porous media present additional difficulties to predict nanoparticle transport, due to the dynamic interaction of the colloids with moving interfaces in multiphase flows [104]. A critical aspect that this works aims to understand is the remobilization of deposited colloidal particles by dynamic liquid-liquid interfaces and the moving (three-phase) contact line. This phenomenon plays a key role in various natural and industrial processes, such as groundwater transport in the vadose zone [53] and enhanced oil recovery operations [105]. Most of the available experimental work provides qualitative descriptions of the particle behavior, characterized by the average remobilization rate or removal efficiency [106], [107]. Only a small number

of experimental studies have investigated the remobilization of individual particles by moving fluid interfaces in modeled porous media [108]-[110]. Moreover, these experimental studies were performed at a mesoscopic level (i.e., pore-level) and thus lack details of the physics at play for individual particles during remobilization events. It is necessary to investigate the different forces acting at the single-particle level to understand how dynamic processes affect colloidal detachment and remobilization [104]. In this work, we consider the motion of liquid-liquid interfaces past a single nanoparticle deposited on a flat wall and document the presence of different dynamic regimes, including interface pinning, stick-slip motion, and particle rolling and detachment, depending on the magnitude of the driving force and the contact angle that the interface forms with the particle. Moreover, we elucidate the dominant role of the surface tension forces acting on the studied nanoparticles and how such forces determine the emergence of different dynamic regimes. We also find that particle detachment cannot be accurately predicted by a static balance of surface tension and adhesion forces as it is in most cases preceded by particle rolling.

4.2 Simulation setup

In previous work, using molecular dynamics (MD) simulations we showed that lowwettability liquids can induce the spontaneous adsorption of a nanoparticle to a solid wall [96], [97], [111]. In this work, we investigate the fate of a nanoparticle, initially deposited on a solid wall, as a three-phase contact line moves past it, depending on the wettability of the two liquids. This problem has the essential components of the remobilization phenomenon encountered in multiphase-flows in porous media. The MD simulations were

performed using the open-source package LAMMPS [112]. To model interactions between any pair of atoms i and j in the system, corresponding to any given species α and β , we employ a generalized Lennard-Jones (LJ) potential, $V_{\alpha\beta}(r_{ij}) = 4\epsilon \left[\left(\sigma/r_{ij} \right)^{12} - A_{\alpha\beta}(\sigma/r_{ij})^{12} \right]$ $(r_{ij})^6$]. Here, r_{ij} is the interatomic separation, σ is roughly the size of the repulsive hard core, and will be used as a characteristic length scale, and ϵ is the depth of the potential well, which will be adopted as the characteristic energy scale. To reduce the computational cost, the LJ potential is truncated at a distance $r_{ij} \approx 2.5\sigma$. The dimensionless attraction parameter $A_{\alpha\beta}$ modulates the attractive van der Waals interactions between the various atomic species in the system and, as a result, determines the wetting of the solid, as well as the interfacial tension between the immiscible liquids [56], [96], [113]. We consider two immiscible liquids, a high-wettability ($\alpha = H$) and a low-wettability ($\alpha = L$) one, with $A_{\rm HL} = 0.2$, corresponding to a surface tension $\gamma = 2.0 \epsilon \sigma^{-2}$. We consider a single type of solid atoms composing both the walls as well as the nanoparticle ($\alpha = S$). The lowwettability liquid interacts with the solid atoms with $A_{LS} = 0.5$ and the interaction of the high-wettability liquid with the solid $A_{\rm HS}$ ranges from 0.5 to 0.9. This results in contact angles $\theta \leq 90^\circ$, where θ is the contact angle of the liquid-liquid interface with the solid wall measured on the side of the high-wettability liquid, as indicated in Figure 4.1. The attraction parameter between atoms of the same species is always $A_{\alpha\alpha} = 1$. Table 4.1 summarized the values used for the attraction parameter $A_{\alpha\beta}$ in the simulations.

Attraction parameter $A_{\alpha\beta}$	Nanoparticle Atoms $(\alpha = S)$	Wall Atoms $(\alpha = S)$	High-wettability liquid ($\alpha = H$)	Low-wettability liquid ($\alpha = L$)
Nanoparticle Atoms $(\alpha = S)$	$A_{SS} = 1$	$A_{SS} = 1$	$A_{HS} = 0.5 - 0.9$	$A_{LS} = 0.5$
Wall Atoms $(\alpha = S)$	-	$A_{SS} = 1$	$A_{HS} = 0.5 - 0.9$	$A_{LS} = 0.5$
High-wettability liquid ($\alpha = H$)	-	-	$A_{HH} = 1$	$A_{HS}=0.2$
Low-wettability liquid ($\alpha = L$)	-	-	-	$A_{LL} = 1$

Table 4.1 The values of the attraction parameter $A_{\alpha\beta}$ used in the simulations. Four types of atoms are used, which include nanoparticle atoms (S), wall atoms (S), high-wettability liquid (H) and low-wettability liquid (L).

The number density of both liquids is $\rho_{\rm L} = 0.8 \sigma^{-3}$, the wall density is $\rho_{\rm W} = 1.0 \sigma^{-3}$ and that of the nanoparticle is $\rho_{\rm P} = 1.0 \sigma^{-3}$ or $4.0 \sigma^{-3}$. As in previous work, both walls and nanoparticle have a rigid fcc lattice structure [101]. When the wall and particle are of the same density $1.0 \sigma^{-3}$, the nanoparticle contact angle θ_p is similar with the wall contact angle θ , and both angles are smaller than 90° as $\theta_p = \theta \le 90^\circ$. However, it is important to note that when the particle density is $4.0 \sigma^{-3}$, since $\rho_{\rm P} > \rho_W$, the nanoparticle contact angle $\theta_p \le \theta \le 90^\circ$ is smaller than that for the wall. In fact, the nanoparticle shows perfect wetting for $A_{\rm HS} \ge 0.8$, with the nanoparticle leaving the interface and staying inside the high-wettability liquid. The temperature of the system is maintained at T = $1.0 \epsilon/k_B$, where k_B is the Boltzmann constant, using a Nose-Hoover thermostat [114].



Receding interface

Advancing interface

Figure 4.1 (Color online) Snapshot of two immiscible fluids moving past a nanoparticle deposited in a flat wall from a molecular simulation. The high-wettability liquid (H) is represented by the darker atoms and the lighter one corresponds to the low-wettability (L) liquid. The attraction parameters in the simulation are $A_{\rm HS} = 0.7$ ($A_{\rm LS} = 0.5$).

A snapshot from one of the MD simulations is presented in Figure 4.1, showing the two immiscible liquids confined between two parallel plates and moving past a nanoparticle deposited on one of the flat walls. The radius of the nanoparticle is $R = 6\sigma$, the separation between the two flat walls is $L_y = 40\sigma$, the length of the channel along the forcing direction is $L_x = 160\sigma$ and $L_z = 20\sigma$. Periodic boundary conditions are applied in all three directions. We also indicate in the figure the advancing interface, corresponding to the high-wettability liquid displacing the low-wettability one. Analogously, the receding interface displacement shown in Figure 4.1 corresponds to the opposite case of a lowwettability liquid displacing a high-wettability one. Initially, we let the system equilibrate, starting with the particle in the low-wettability fluid, which results in its spontaneous adsorption onto the solid wall [96]. Then, a constant force f_x oriented along the channel is applied to each of the atoms on both liquids, which produces a total driving force F_{MD} . In what follows, we use non-dimensional units, based on the characteristic time $\tau =$ $\sqrt{m\sigma^2/\epsilon}$, where m is the mass of the atoms, together with the characteristic length scale σ and energy scale ϵ of the modeled pairwise interactions between atoms.

4.3 Results and discussion

Figure 1.11 shows the schematic of the forces acting on a nanoparticle deposited on a solid substrate and interacting with an advancing (Fig. 1.11a) and a receding (Fig. 1.11b) interface. Three distinct type of forces act on the deposited particle and determine its behavior, possibly leading to mobilization and detachment. First, the adhesive and friction forces, F_A and F_F , which prevent normal detachment and horizontal sliding, respectively, originate from the particle-substrate interaction. In addition, when the liquid is moving, there would be a hydrodynamic-drag force, F_D , acting on the particle. Finally, capillary forces acting on the particle have two components, the surface tension force, F_{γ} , acting on the three-phase contact line as the liquid-liquid interface moves past the nanoparticle, and the capillary pressure force, F_{Pc} , originating on the Laplace pressure difference between the two liquids due to the (net) curvature of the liquid-liquid interface. The position of the contact line on the particle is determined by the filling angle ϕ , which for an advancing interface goes from 180° at initial contact with the high-wettability liquid to 0° when the particle is fully immersed in it. The filling angle goes from 0° to 180° as a receding interface moves past a particle. We note that the supplementary angle $\pi - \phi$ is sometimes used as the filling angle. The (red) dashed line in the figure indicates the equilibrium position $F_{\gamma} = 0$, which corresponds to $\phi = \theta_p$ and a flat interface in the absence of any geometric confinement. Therefore, when the filling angle is $\phi < \theta_p$ (or $\phi > \theta_p$), the

surface tension force tends to increase (or decrease) the filling angle, as shown in Fig. 1.11. For a flat interface, the surface tension force is given by

$$F_{\gamma} = 2\pi R \gamma \sin \phi \sin(\theta_p - \phi), \qquad (4.1)$$

which reaches its maximum value for $\phi = \theta_p/2$ (for $\phi < \theta_p$) or $\phi = (\theta_p + \pi)/2$ (for $\phi > \theta_p$) [31]. In the absence of confinement, there is no Laplace contribution to the capillary forces. On the other hand, in a channel of height H we can estimate the curvature (away from the particle) as $r_c = H/(2\cos\theta)$ and the capillary pressure force can be estimated as $F_{P_c} = \pi R^2 \sin^2 \phi \Delta p = \pi R^2 \sin^2 \phi \gamma 2 \cos \theta / H$, where we have used the Laplace equation $\Delta p = \gamma/r_c$ [104]. Comparing the two forces, we find that the capillary force is negligible in our system ($F_{P_c} \ll F_{\gamma}$) and should only be considered in highly confined situations where $H \cong R$ and $F_{P_c} \sim F_{\gamma}$. Therefore, in what follows we normalize all the forces in the system using the characteristic magnitude of surface tension forces, $|F_{\gamma}| \sim 2\pi R\gamma$; for example, the normalized surface tension force is $\tilde{F}_{\gamma} = F_{\gamma}/2\pi R\gamma$. Finally, ignoring the local curvature of the interface, and considering that both advancing and receding interfaces are driven in the same direction along the channel, the axial and normal components are obtained by projecting the force using the contact angle θ [21].

$$\begin{bmatrix} \tilde{F}_{\gamma}^{\parallel} & \tilde{F}_{\gamma}^{\perp} \end{bmatrix} = \begin{cases} \sin^2 \left(\frac{\theta_p}{2}\right) [\sin \theta & \cos \theta] & \text{if } \phi < \theta_p \\ \cos^2 \left(\frac{\theta_p}{2}\right) [\sin \theta & -\cos \theta] & \text{if } \phi > \theta_p. \end{cases}$$
(4.2)





Figure 4.2 (color online) Regime map for the dynamics of a liquid-liquid interface moving past a deposited nanoparticle: a) $\rho_W = \rho_p = 1.0 \sigma^{-3}$, b) $\rho_W = 1.0 \sigma^{-3}$ and $\rho_p = 4.0 \sigma^{-3}$, parametrized by the normalized force driving the interface, \tilde{F}_{MD} , and the contact angle θ . The solid (dot-dashed) line corresponds to the maximum surface tension force in the horizontal direction as given in Eq. (4.2) for a receding (advancing) interface, $\phi > \theta_p$ ($\phi < \theta_p$). Symbols indicate simulations results. Square symbols indicate interface pinning of the receding (solid squares) or the advancing (open squares) interface and pinned particle with both interfaces passing through (open-solid squares). Circles indicate stick-slip motion of the particle along the wall due to its interaction with a receding interface (solid circles) or with both interfaces intermittently (open-solid circles). Solid triangles indicate that after adsorption the particles leave the interface and move into the high-wettability liquid. The shading indicates the regions where different behaviors are observed.

Three distinguishable regimes were documented in our parametric study varying the driving force F_{MD} and contact angle θ : Interfacial pinning at small driving forces; Stickslip and Intermittent Stick-slip particle motion at larger forces and high contact angles and Rolling-induced detachment at larger forces and small contact angles. These results are summarized in the regime map presented in Figure 4.2b. In addition to these regimes, pinned particle is observed at large driving forces and small contact angles for the less dense particle, which is presented in Figure 4.2a. The snapshots for different regimes discussed are shown in Figure 4.3, which correspond to those indicated in Figure 4.2 as: SM1 corresponds to pinning by the receding interface; SM2 corresponds to particle pinning; SM3 corresponds to a stick-slip particle motion induced by the receding interface and the trajectory is presented in Figure 4.5a; and SM4 corresponds to an intermittent stick-slip particle motion along the wall; SM5 corresponds to a detachment case in which the particle remains at the interface and the trajectory is shown in Figure 4.5b; SM6 corresponds to particle detachment and, after detachment, the particle goes to the bulk of the highwettability fluid and the trajectory is plotted in Figure 4.5c;





SM3: Stick-slip particle



SM4: Intermittent Stick-slip





Figure 4.3 Snapshots of the dynamics of liquid/liquid interfaces moving past a deposited spherical particle. The particle is initially immersed in low-wettability liquid and interacts with the advancing interface first. The stripes on the particle help to observe the rotation motion of the particle.

Interfacial Pinning. For small driving forces, we observe the pinning of the liquid-liquid interface when the surface tension force acting on the three-phase contact line can balance the external driving force ($F_{\gamma}^{\parallel} = F_{\rm MD}$). Therefore, the pinning regime only occurs for $\phi < \theta_p$ for the advancing interface (dot-dashed line in Figure 4.2) and for $\phi > \theta_p$ for the receding interface (solid line in Figure 4.2). We observe good agreement between this prediction and simulation results, in that there is no pinning of the advancing interface for driving forces above the predicted critical values (indicated by the dot-dashed line in the figure), but we still observe pinning by the receding interface. To see more details on the different forces, we plot the interaction forces for particle/low-wettability liquid, particle/liquids and particle/wall in horizontal and vertical directions in Figure 4.4. The red lines indicate the displacement on particle trajectory in

both directions respectively. We overserved two sudden changes on the interaction force for the particle with each liquid, which indicates particle interacts with the advancing interface at $\sim 3000\tau$, and after this interface passed through the deposited particle, the particle interacts with the receding interface at $\sim 15000\tau$.



Figure 4.4 Interfacial pinning by receding interface: particle displacement (a) in the x-direction (left axis) and the component of interaction forces in the x-direction, (b) particle displacement in the y-direction (left

axis) and the component of interaction forces in the y-direction, for particle/high-wettability fluid, particle/low-wettability fluid, particle/fluids and particle/wall (right axis) are plotted as a function of time. Particle pinning. The pinning of particle with advancing and receding interfaces passing by can only be observed when the density of particle and wall are both 1.0 σ^{-3} . The particle stays at its initial attached position without interfacial pinning, which is mostly located in the region for $\theta < 67^{\circ}$ and above the critical values of receding interface pinning. The external driving force in this region is larger than the surface tension force for both advancing on receding interfaces, so that the surface tension force is not enough to pin the interfaces, leading to the movement in the fluid/fluid interface. However, there are a few cases that particle pinning is found to occur under the critical curve, where the driving force is around 0.5. This might be cause by the deformation of the receding interface, resulting in the change of Laplace pressure across the interface. The receding interface tries to remain partially pinned to the particle, and the interface under the particle squeezes out, leading to the interfacial depinning, as shown in Figure 4.3-SM2. For small contact angles, we find that the interface shape tends to break down from, both ends in contact with the walls to a 'bubble' shape in which the less wetting fluid is surrounded by high-wettability one without connecting to the wall at the particle side. This 'bubble' shape passage cannot be recovered for large driving force, since it interacts with another particle due to periodicity in a very short time.




Figure 4.5: a) Stick-slip motion along the channel, vertical position, and incipient rotation (around the z-axis) for a nanoparticle at the receding interface. Inset shows the motion of the nanoparticle as it initially interacts with the receding interface. b) Rotation-induced nanoparticle detachment by the receding interface (at interface). The plot shows $\Delta \alpha_z = \theta_p/2$, the rotation around the z-axis, the motion along the wall and the resulting separation normal to the wall (y-axis, amplified by a factor of 10 for clarity). c) Rotation-induced nanoparticle detachment by the receding interface (in bulk). Inset shows the initial interaction with the receding interface (All cases are indicated in Figure 4.2.)

Stick-slip motion. At larger driving forces, we see that the liquid-liquid interface induces the sliding of the particle along the wall, even for forces below the solid line corresponding to the maximum surface tension force for the receding interface and independent of the contact angle. In this case, the surface tension force acting on the particle (intermittently) exceeds the maximum friction force. To confirm that the surface tension force could overcome the friction force, we estimated the maximum friction force for a particle immersed in a single-phase liquid. We performed an independent set of simulations applying a force along the channel wall, F_{ext}^{\parallel} , on a deposited particle. The minimum force

leading to axial motion of the particle was $\tilde{F}_{\text{ext}}^{\parallel} = \tilde{F}_F \approx 0.45$, with a small decrease as the attraction parameter between the liquid and the wall increases. Although these measurements are performed in a single-phase fluid, the sliding behavior in the presence of the liquid-liquid interface is observed at values of the driving force similar to the singlephase friction force, $\tilde{F}_{MD} \gtrsim 0.4$. Interestingly, the motion is not a continuous sliding but rather analogous to the stick-slip motion previously observed in single-phase fluids (see Figure 4.5a [96]. Note that the particle remains at the liquid-liquid interface during the stick-slip motion, resulting in a pinning-sliding intermittent motion of the interface itself. We also examined the detailed dynamics of the nanoparticle and observed that rotation of the nanoparticle along the z-axis precedes the sliding motion, but no continuous rotation is observed as the particle moves with the interface, as shown in Figure 4.5a. As the particle is rotationally sliding with the receding interface, the force between particle and liquid is negative in the y direction from Figure 4.6b, indicating that the liquids are trying to pull the particle away from the wall. In addition, the particle/liquid force in the horizontal direction changes between 0 to 0.5 (Figure 4.6a), which explains the possibility of the stickslip motion of the particle. When this force increases and passes the value friction force, it could cause the change in the motion of a particle from 'stick' to 'slip'.



Figure 4.6 Stick-slip motion along the channel: particle displacement (a) in the x-direction (left axis) and the component of interaction forces in the x-direction, (b) particle displacement in the y-direction (left axis) and the component of interaction forces in the y-direction, for particle/high-wettability fluid, particle/low-wettability fluid, particle/fluids and particle/wall (right axis) are plotted as a function of time.

Intermittent Stick-Slip motion. Another regime change is observed for larger external forces, above the maximum of the static surface tension force for the receding interface given in Eq. (4.2). In this case, a different type of intermittent motion is observed (indicated by the half-solid half-empty symbols in Figure 4.2, the particle is alternatively carried by the advancing and receding interfaces It is also important to note a reverse motion that occurs as the receding interface makes contact with the particle. During this transient, when $\phi < \theta_p$ the surface tension force pulls the particle upstream in the horizontal direction and away from the wall. This is also shown in Figure 4.5a where we observe a (small) upstream translation along the wall. However, no significant displacement is observed in the normal direction. Figure 4.7 present the interactions forces for intermittent stick-slip motion, which is analogous with stick-slip motion shown in Figure 4.6, expect more consecutive interfaces interact with the particle.





Figure 4.7 Intermittent stick-slip motion along the channel: particle displacement (a) in the x-direction (left axis) and the component of interaction forces in the x-direction, (b) particle displacement in the y-direction (left axis) and the component of interaction forces in the y-direction, for particle/high-wettability fluid, particle/fluids and particle/wall (right axis) are plotted as a function of time.

Rolling-induced detachment. For large driving forces, $\tilde{F}_{MD} \gtrsim 1$, we observe some cases of nanoparticle detachment induced by the receding interface. Interestingly, in this case the equilibrium calculations presented in Eq. (4.1) show that the receding interface exerts a negative normal force ($\phi > \theta_p$). On the other hand, the external forcing in this case is comparable to the Laplace pressure for a curvature similar to the width of the channel, and the deformation of the interface cannot be neglected. In fact, we have observed the formation of drops of the low-wettability liquid immersed in the high-wettability liquid for forces $\tilde{F}_{MD} \approx 1$. As a result, the local orientation of the liquid-liquid interface can no longer be approximated by the contact angle with the wall, as assumed in Eq. (4.1). In order to

estimate the required detachment force, we measured the force normal to the substrate that is required to pull the particle off the surface of the solid (pull-off force) and obtained \tilde{F}_A^{max} increasing from 2 to 4 as the attraction parameter increases. Interestingly, this value is larger than \widetilde{F}_{γ} , independent of its orientation. In addition, and similar to the sliding case, we observe that detachment is always preceded by rotation of the nanoparticle along the zaxis. Figure 4.5b and c show both the rotation of the nanoparticle, together with its motion along the wall as well as its separation from the initial position normal to the wall. These results indicate that there is significant rotation preceding (and probably leading to) any separation from the wall, which renders the static calculations no longer valid and demonstrates the importance of interfacial dynamics in particle detachment. Detachment is commonly observed at intermediate contact angles, when there is significant contrast in the wetting behavior of the two liquids, and it occurs as the high-wettability liquid surrounding the particle is displaced by the less-wetting liquid. After detachment, the contact angle determines whether the particle remains at the interface ($\theta_p > 0^\circ$) or not $(\theta_p = 0^\circ)$, as indicated by the up- and down-pointing triangles, respectively, in Figure 4.2. Interestingly, the particle goes into the bulk after detachment is only observed when the particle is more wetting than the wall. Instead of lifting the particle when the particle is released from the wall at 5500τ , the particle experiences a force in the opposite direction of the wall from the liquids and the component of this force in the vertical direction is around 2.5 at its peak value, which can be found in Figure 4.8.



Figure 4.8 Rolling-induced detachment: particle displacement (a) in the x-direction (left axis) and the component of interaction forces in the x-direction, (b) particle displacement in the y-direction (left axis) and the component of interaction forces in the y-direction, for particle/high-wettability fluid, particle/low-wettability fluid, particle/fluids and particle/wall (right axis) are plotted as a function of time.

In the simulations presented in this chapter, the potential is truncated but not shifted. We have also run a number of independent simulations using a Force-Shifted Lennard-Jones potential (a Lennard-Jones potential with a linear term that ensures continuity in the force at the cutoff radius), and the results were analogous to those discussed in the chapter.

4.4 Conclusion

The results in this work document the role of dynamic effects in the mobilization of adsorbed nanoparticles by the forced displacement of a liquid-liquid interface and indicate that particle detachment could be significantly underestimated by static models. For sufficiently small values of the driving force, the nanoparticles pin the liquid-liquid interface and the observed behavior can be predicted by a static force balance. Above a critical force magnitude predicted by a static analysis, the nanoparticles undergo stick-slip motion with incipient rotation inducing the transition from stick to sliding motion. Rotation also plays a crucial role for larger forces, in this case the interaction of the particle with the receding interface results in particle detachment at moderate contact angles. Dynamic effects associated with particle rotation and the observed stick-slip and sliding motion can result in the remobilization and removal of nanoparticles for driving forces that are much smaller than the critical value predicted by conventional static models. Hence, static force balances can significantly overestimate the forces required for particle detachment and underestimate the corresponding remobilization rates employed in continuum models such as colloid filtration theory. Considering the dynamic effects and different regimes documented in this work it is possible to develop improved transport models to better

predict the fate of colloidal particles in multiphase flows under different wetting conditions and for physical dimensions ranging from nano to microscales.

Chapter 5 Conclusion

The objective of this thesis is to study the mobilization of a deposited particle by a dynamic interface and the moving contact line. This work revealed previously unknown aspects on the detachment of a colloidal particle by a moving interface and demonstrated that the rolling of may be a dominant detachment mechanism in the presence of a moving liquid/liquid interface. We first carried out studies on equilibrium state for particles interacting with a liquid/liquid interface. In the static model, the behavior of particle can be determined by the force balance, possibly leading to mobilization or detachment. The forces are the particle adhesion and friction force, the hydrodynamic drag force if the liquid is moving, and the surface tension force acting on the three-phase contact line. When vertical upward net force is positive, detachment of particle from solid substrate might occur, otherwise, the particle remains attached to the substrate or sliding along the substrate occurs based on the horizontal forces. However, the dynamic effects on a moving interface passed through a deposited particle is not discussed in this static force balance model. In the following part of this work, we investigated the fate of a nanoparticle deposited on a solid surface as a liquid-liquid interface moves past it by varying the wettability of the solid the magnitude of the force driving the displacement of the interface using molecular dynamics simulation.

In chapter 2, we started with studies on simple liquids model and discussed the interfacial properties of planar liquid/liquid and liquid/solid interface with a Lennard-Jones fluid. The solid/liquid interaction is characterized by an attraction coefficient, that large attraction between solid and liquid results in a high-wettability liquid, and weak attraction leads to a low-wettability liquid. The surface tension decreased with an increasing attraction coefficient. Moreover, we showed the contact angles for a planar surface, as well as the contact angle for a spherical particle, and both solid atoms are fixed on an FCC lattice site by rigid body dynamics. The contact angles for different shape but of same destiny showed good agreement for all simulated solid/liquid attraction coefficients.

In the third part, we investigated that the adsorption of the particle onto a solid surface depends on its wettability. We found that particle adsorption could be observed if the particle was initially suspended in a low-wettability liquid. There exists a critical value that no adsorption occurred when the attraction coefficient is above the critical due to the strong attraction between the liquid and the particle. Moreover, switch the high-wettability liquid to low-wettability liquid after particle gets adsorbed would not result in the detachment of the particle from the wall which may due to an emery barrier.

In the fourth part, we presented single particle mobilization by moving fluid/fluid receding and advancing fronts in parallel plates channel using molecular dynamic simulation and discussed how dynamics affect the transport of particles in the presence of moving liquid/liquid interfaces. The parameters studied in this work are the wettability of the solid the magnitude of the force driving the fluids. As expected, a receding interface, in which the low-wettability liquid displaces a high-wettability one, has a stronger effect on the deposited particles. These simulations exhibited cases in which the horizontal component of the force acting on the particle (and the corresponding torque) lead to rollinginduced desorption even in unfavorable cases, that is when the vertical component of the interfacial force pushes the particle towards the solid surface. In addition, Interfacial pinning is observed at small driving forces. At larger driving forces and large contact angles, we observe stick-slip motion, with intermittent interfacial pinning and particle sliding at the liquid-liquid interface. At smaller contact angles of the high-wettability liquid, we observed rolling-induced detachment of the deposited particle, in which particle rolling precedes particle separation from the solid surface and demonstrated the importance of dynamic effects. After detachment, the particle would remain at the interface or migrate to the high-wettability liquid depending on the contact angle. Moreover, compared to the static models, the interfacial pining cases can be predicted by this force balance model, in which the driving force is sufficiently small. Above a critical value of predicted by the static force analysis, the particle experiences the stick-slip motion, where the transient from stick to slip is induced a particle rotational motion. The driving forces that needed to detach the particle are found much smaller than the crucial value predicted by the static model as a result of the dynamic effects. We concluded that the static model is not able to accurately predict the behavior of the particle in the presence of a moving interface. It overestimated the forces require for particle detachment and underestimated the particle mobilization and removal efficiencies.

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