Mechanism of Oil Detachment from a Silica Surface in Aqueous Surfactant Solutions: Molecular Dynamics Simulations

Qian Liu,[†] Shiling Yuan,*,[‡] Hui Yan,[‡] and Xian Zhao*,[†]

[†]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China
[‡]Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan 250100, China

ABSTRACT: The mechanism of oil detachment from solid surfaces in aqueous surfactant solutions is studied by molecular dynamics simulations. At the initial simulation, the hydrophilic silica surface changes into a hydrophobic one due to the adsorption of the alkane molecules. Two-dimensional ordered arrangement of alkane molecules on the first layer is the key to the oil detachment from the silica surface. Upon addition of cetyltrimethylammonium bromide (CTAB) solution, the alkane molecules on the solid surface can be detached from a hydrophilic silica surface. Ultimately, the silica surface becomes hydrophilic, and the oil molecules are solubilized in the surfactant micelles. During the process of oil detachment, it is demonstrated that the formation of a water channel in the oil phase between the surfactant solution and the silica surface is vital for the oil detachment. Meanwhile, water molecules can penetrate the oil–water interface by diffusion and form the gel layer at the water–silica interface under the hydrogen-bonding and electrostatic interaction, in the close vicinity of the contact line. Both of these will accelerate the removal of the oil molecules from the silica surface under the surfactant solution. According to the energy and configurations with time evolution, one three-stage model of oil detachment from the silica surface is developed at the molecular level. The simulation results agree with the experimental phenomenon.
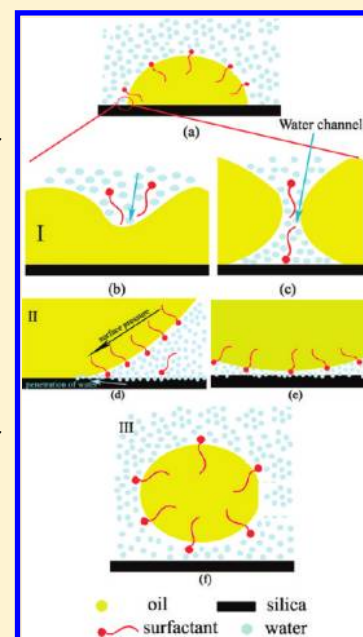
1. INTRODUCTION

The mechanism of a surfactant to aid in the removal of oil drops from solid surfaces is crucial for many applications in enhanced oil recovery, ore flotation, detergency, and printing. Technologically oriented experiments on detachment of oil drops from solid substrates were carried out, and several mechanisms of a surfactant to aid in oil removal have been identified.[1–10] Recent papers[11] have reported that there are three stages of the detachment process of an oil drop, situated above a horizontal substrate. They correspond to three different driving factors: (i) the interfacial tension decreases because of surfactant adsorption, (ii) the three-phase solid–oil–water contact line spontaneously shrinks owing to the penetration of water between the oil and solid phases, and (iii) at sufficiently small contact radius, the shape of the oil–water interface becomes unstable, and the drop detaches under the action of buoyancy. The latter experiments[6,12–14] show that "roll-up" is related to shrinking of the three-phase solid–oil–water contact line, which, in turn, is due to the molecular penetration (diffusion) of water molecules between the oil drop and the solid phase. This process was termed the diffusion mechanism of oil detachment.

There are also many experimental indications that water may dissolve or diffuse into and swell the glass (and silica) surface,

forming a surface gel layer.[15–23] This effect has been detected by surface-force measurements[19,21,23] and on the adsorption process of macromolecules.[22] The authors considered that the water molecules may break silicon–oxygen bonds and form a hydroxylated surface as a part of the dissolution process,[23] and the formation of a gel layer may include an ion exchange process, in which sodium ions at the glass surface are replaced by protons.[16,18,22] Swelling of the surface layers has been directly observed in some glasses in humid atmospheres by analytical methods. They found that the surface area increased at least 10 times, and some water clusters are formed on the interface.[20]

In addition, many studies are focused on the cases where the motion of the contact line on a solid surface is strained by some external force or potential gradient, including the processes of liquid deposition on a moving or porous substrate.[24–30] They hypothesized that water molecules, from the gel layer at the water–glass interface, can penetrate the oil–water interface by diffusion, at least in the close vicinity of the contact line. Wasan et al.[6] directly observed the dynamics of water-film penetration
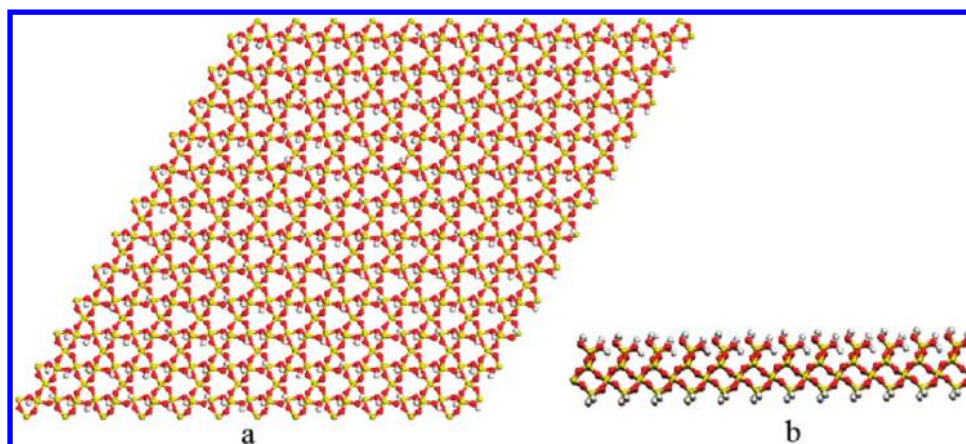
Figure 1. Snapshots of silica surface used in the simulations: (a) top view and (b) side view. Color for the united atom scheme: O - red, Si - yellow, and CH_2 - gray.

between the oil phase and the solid. Once such a disjoining aqueous film has been formed, even a weak shear flow is able to detach the oil drop from the solid surface. Kralchevsky et al.[31] also found indications that water molecules can propagate through lateral diffusion in a thin layer on the solid surface. The driving force of the detachment process, viz., the imbalance of the interfacial tensions at the contact line, is engendered by the water penetration, while the line friction force compensates this imbalance and determines the stationary speed. Chatterjee[32,33] investigated the critical conditions for buoyancy-induced detachment of oil drops from a substrate due to instability in the shape of the oil−water interface. Although the mechanism of the oil detachment has been studied by many experimental methods, the important details of the detachment is still difficult to be obtained by experiment technology at the molecular level. Thus, we demonstrate the mechanism of penetration of the oil−silica interface at a molecular level, which is the cause of the continuing detachment process.

Over the past few years, computer simulation has become a powerful method for the study of such complex interfacial systems.[34−39] From these computer experiments, it is possible to extract information about the dynamical, thermodynamical, and structural properties of interfacial systems at the molecular level, which sometimes are not easy to obtain from some experiments. For instance, molecular dynamics (MD) simulations can be used to study the spreading of a partially wetting aqueous drop in air on a hydrophobic surface, which can be facilitated by the adsorption of surfactants from the drop phase onto the air/aqueous and aqueous/hydrophobic solid interfaces of the drop.[40,41] Large-scale MD simulations can be used to study droplet spreading. Coninck[41] described a method to calculate the average frequency of displacements of atoms in the vicinity of the solid/liquid interface. Tomassone[40] examined the surfactant structure at the spreading periphery. In particular, they have demonstrated that T-structured surfactants can form bilayers at the spreading front, while linear chain surfactant molecules retain separate air/liquid and solid/liquid monolayers, which cojoin at the contact line using MD simulations. These computer simulations are considered complements for experimental methods, and provide molecular-level insight into the effect and conformation of surfactants on a solid substrate.

In this paper, MD simulations are used to investigate the dynamic process of the detachment of oil drop from silica surface immersed in a surfactant solution. Our attention is focused on the diffusion of water molecules, the effect of cetyltrimethylammonium bromide (CTAB) at different stages, and microscopic conformational changes of oil molecules. On the basis of the simulation results, we demonstrate the mechanism of a surfactant to aid in the removal of oil drops from solid surfaces at a molecular level.

2. SIMULATION DETAILS

The GROMACS free software package (version 4.0.5) including Lennard-Jones and Coulombic site−site interactions in addition to bond stretching, angular bending, and improper and proper dihedral interactions with the united atom parametrization was employed for the MD simulations. In this work, the dodecane (C12) was used as the model oil molecule. The silica surface, which has an amorphous structure, is held fixed throughout the simulations (as shown in Figure 1). The force field parameters for amorphous SiO_2 are taken from the work of Warne et al.[42] and are given in Table 1.

Table 1. Parameters for the LJ Potential Used to Model Interactions between Surfactant Head Groups and SiO_2

atom	charges/e
Si of SiO_2	0.31
H of SiO_2	0.40
O of SiO_2	−0.71
N of CTA^+	1.220
CH_3 of CTA^+	−0.074

These parameters were empirically derived. $C_{12}TAB$ (n-dodecyltrimethyl ammonium bromide) surfactant is examined in MD simulations in an aqueous medium in the presence of a negatively charged silica surface, which was covered by the model oil. The parameters and charges for tetramethylammonium ions are taken from the work of Jorgensen and Gao.[43] These parameters were derived by fitting to experimental thermodynamic and structural data on pure liquids and dilute solutions. The parameters for bromide ions are taken from the work of Lybrand et al.[44] The potential used to model the water molecules is a simple point charge (SPC) model.[45]

The following strategy was implemented. In preparing the configuration of the simulations, a rectangular basic box of 60 × 60 × 60 Å³ was used, with the z-axis being perpendicular to the
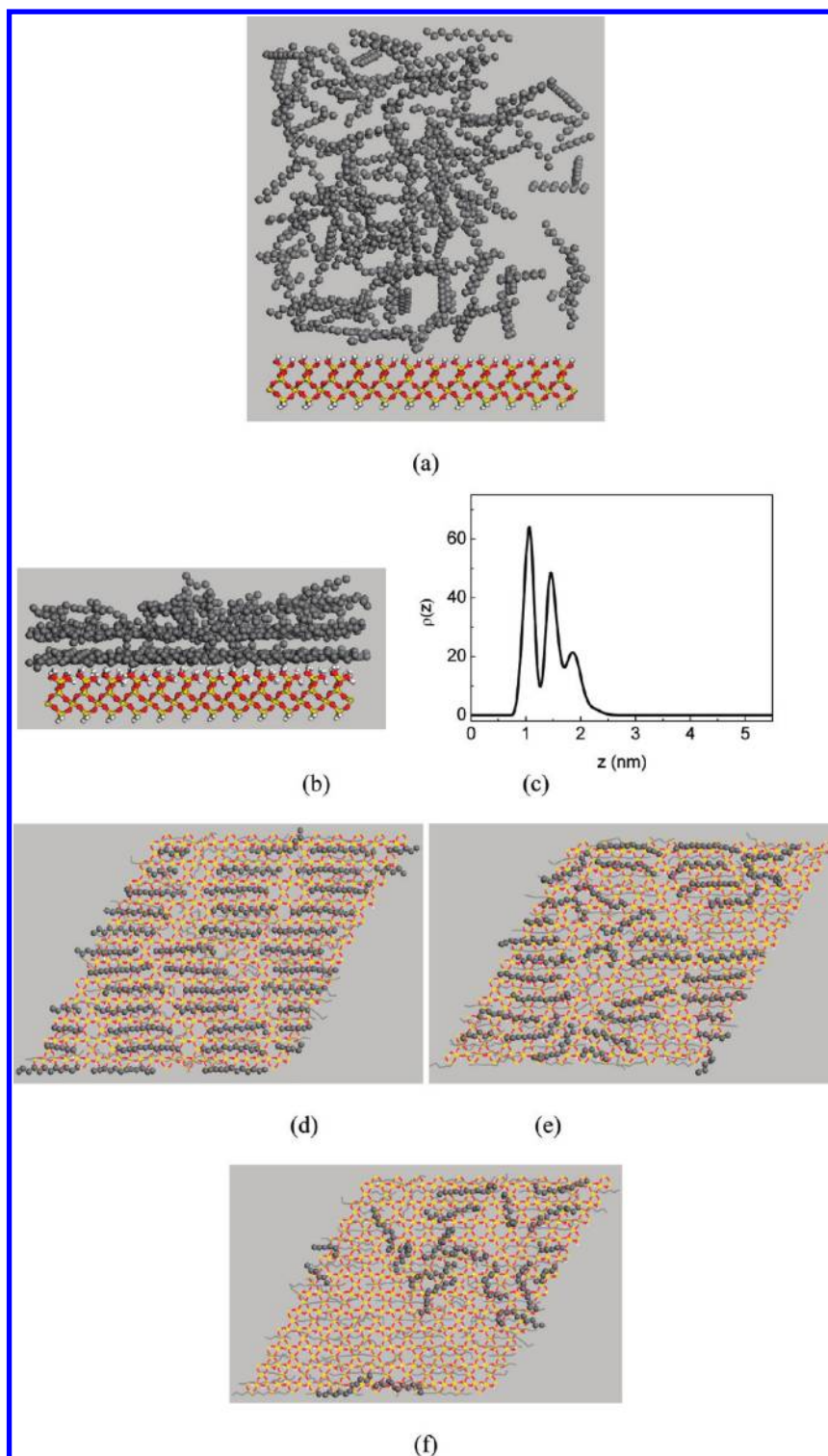
Figure 2. Snapshots of the configurations of the system at the beginning (a) and the end (b) of the simulation run. Top view of the C12 first layer (d), second layer (e), and third layer (f) displayed in CPK mode on the silica surface. Colors for the atom scheme are O - red, Si - yellow, H - white, and CH_2 - gray, respectively.

silica surface. Periodic boundary conditions were applied in all directions. At the beginning, in order to obtain the hydrophobic surface, we first study the behavior of C12 molecules on the silica surface. Ninety-three C12 molecules were placed in the simulation box without water. The simulations were initialized by minimizing the energies of the initial configurations with the steepest descent method. After the initialization, all the MD

simulations were carried out under canonical ensemble (NVT) with a time step of 1 fs according to previous studies. After approximately 10 ns, one hydrophobic silica surface covering 93 C12 molecules was obtained. Second, the effect of surfactant on the detachment of oil molecules on the surface was evaluated. The simulated system containing 12 CTAB molecules, 12 bromide ions, and 3897 water molecules was added into the
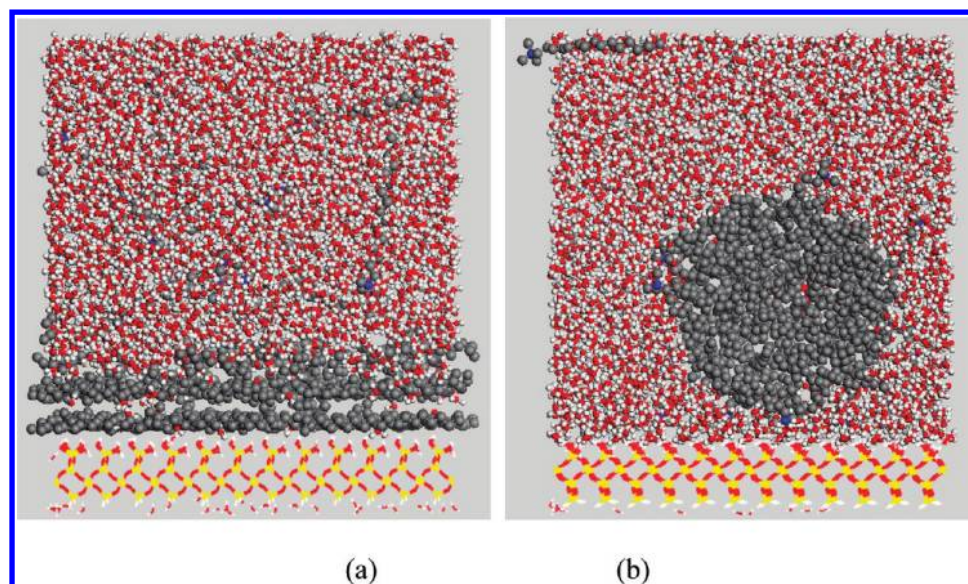
Figure 3. Snapshots of the configurations of the system at the beginning (a) and the end (b) of the simulation run. Colors for the atom scheme are O - red, Si - yellow, H - white, CH_2 - gray, and N - blue.
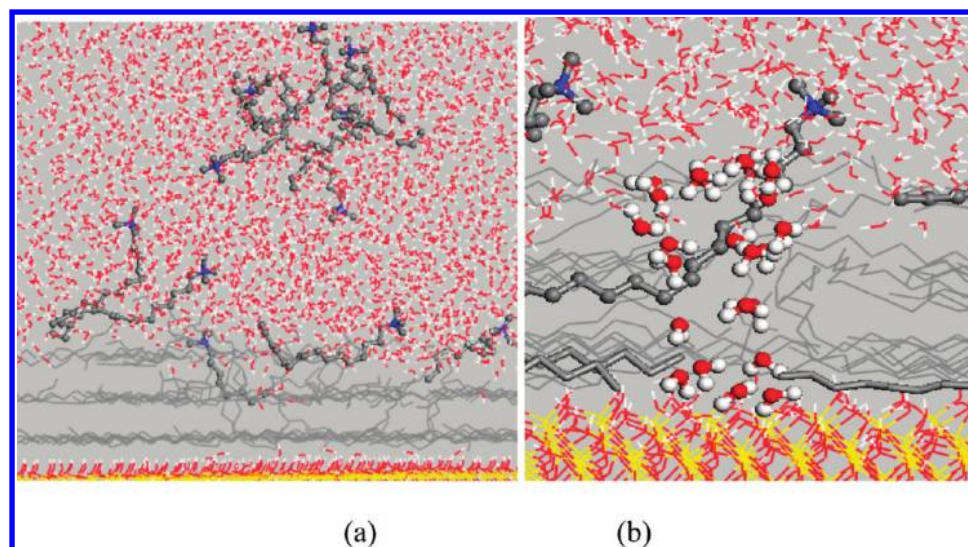

Figure 4. The adsorption of CTA^+ ion on the water–oil interface at 100 ps. CTAB and the water molecules around the surfactants are displayed in CPK mode, and the C12 molecules in the first layer are shown in Stick mode. Color details are identical to those in Figure 3.

rectangular basic box. Another long time of MD simulation was continued extending to 10 ns. In all simulations, the temperature of the systems was kept constant at 298 K by the Berendsen thermostat algorithm with a coupling constant of 0.1 ps, and the trajectories were collected in an interval of 1 ps for further analysis.

3. RESULTS AND DISCUSSION

3.1. Construct of Hydrophobic Silica Surface. In the natural world, the silica surface is inherently hydrophilic. When in contact with crude oil, the silica surface will change into a hydrophobic one due to the adsorption of alkanes. Thus, the hydrophobic surface should be constructed first before the simulations are run in order to simulate the detachment of oil from the hydrophobic surface. In the system, 93 C12 molecules are initially placed above the silica surface (Figure 2a). Due to the interaction of the CH_2 group with silica surface, the C12 molecules migrate to the surface quickly. After 10 ns,

The alkane molecular density forms three clear peaks near the hydrophilic surface, which are located at $z = 1$ nm, $z = 1.5$ nm, and $z = 1.9$ nm, respectively (Figure 2c). These mean that three layers of alkane are formed on the hydrophilic silica surface. Finally, due to the adsorption of the alkanes, the silica surface changes from a hydrophilic surface to a hydrophobic surface. From the profiles in Figure 2c, it is found that the C12 molecules are adsorbed on the silica surface and are arrayed in three layers, parallel to the surface. At $z = 1$ nm, a sharp peak indicated the formation of the first layer (Figure 2d). The alkyl chains remain flat and extended on the silica surface, and the alkane molecules result in well-organized aggregates on the surface. Especially for the first layer (Figure 2d), it has fulfilled and ordered arrangement. However, the number density of the second and third layer decreases, and the arrangement of alkyl molecules is out of order (Figure 2e,f). There are more vacancies in the second and third layer compared with those in the first layer. During the detachment of alkane molecules on

the silica surface, we think that two-dimensional ordered arrangement of alkane molecules on the first layer is the key to changing the silica surface from a hydrophobic surface to a hydrophilic one.

3.2. Detachment Process of Oil Drops from Solid Substrates in CTAB Solution. The hydrophilic silica surface becomes a hydrophobic surface due to the adsorption of alkanes (Figure 3a), and there is about 2.5 nm thickness of the alkyl layers on the surface and no water in the vicinity of the silica surface at the initial model of simulations. In the presence of aqueous solution, the hydrophilic silica surface covered by alkane molecules is unstable thermodynamically. Theoretically, the alkanes can ultimately be detached from a hydrophilic silica surface in the CTAB solution (Figure 3b). When the aqueous solution with CTAB surfactant was put on the alkane molecules in the simulation model, the surfactant molecules can be adsorbed on to the oil/water interface through hydrophobic interaction of alkyl chains with the alkane molecules (Figure 4a). We think that the hydrophobic interaction is important for the surfactant molecules at the beginning of simulations. In the solution, these amphiphilic molecules can aggregate to form one micelle or premicelle (Figure 4a), and around the oil/water interface, some molecules can absorb the alkyane molecules (i.e., oil phase).

After some surfactant molecules contact the alkyl molecules on the silica surface, the electrostatic interaction may be another important driving force for the detachment of alkane molecules. It is known that electrostatic interaction belongs to the long-range interactions, which begins in the range of several nanometers. However, the van der Waals interaction is a short-range one, which is around 1 nm. In the model of simulation, the 2.5 nm oil layer of alkane molecules was constructed on the hydrophilic surface. It is just in the range of the electrostatic interaction. In the simulation, the silica surface has an amorphous structure and a net negative charge. The charge of O atoms, H atoms, and Si atoms on the silica surface is −0.71e, 0.40e, and 0.31e, respectively. Additionally, the N atom of the headgroup in the CTAB surfactant molecule is +1.22e. Especially for the water molecules, in the simulation, we selected the SPC model, in which the oxygen atom is −0.82e and the hydrogen atom is +0.41e. Although the alkyl chains of surfactant molecules are hydrophobic, we note that there are several water molecules around the headgroup or the alkyl chain of surfactant molecules (Figure 4a). These phenomena are attributed to the attractive results of electrostatic interaction due to the opposite charge on the methyl group of the alkyl chain, water molecules, and silica atoms.

In fact, the long chain of surfactant molecules with several water molecules will disturb the aggregates of alkane molecules under the hydrophobic interaction on the silica surface, especially the alkanes in the third layers. The less ordered molecules in the upper layers (Figure 2f) on the silica surface will be destroyed by the surfactant molecules first, and then under the perturbation of alkyl chains of CTAB molecules, several water molecules will enter into the next alkane layers under the strong long-range electrostatic interaction with the silica surface. Under the disturbance, the water molecules will continuously destruct the ordered layers of alkane molecules. Eventually a few water molecules will enter into the gap between the ordered alkane molecules in the first layer and the hydroxyl group on the silica surface (Figure 5a). Thus, a small water-channel is formed between the aqueous solution and the silica surface through the oil phase. During the process, the
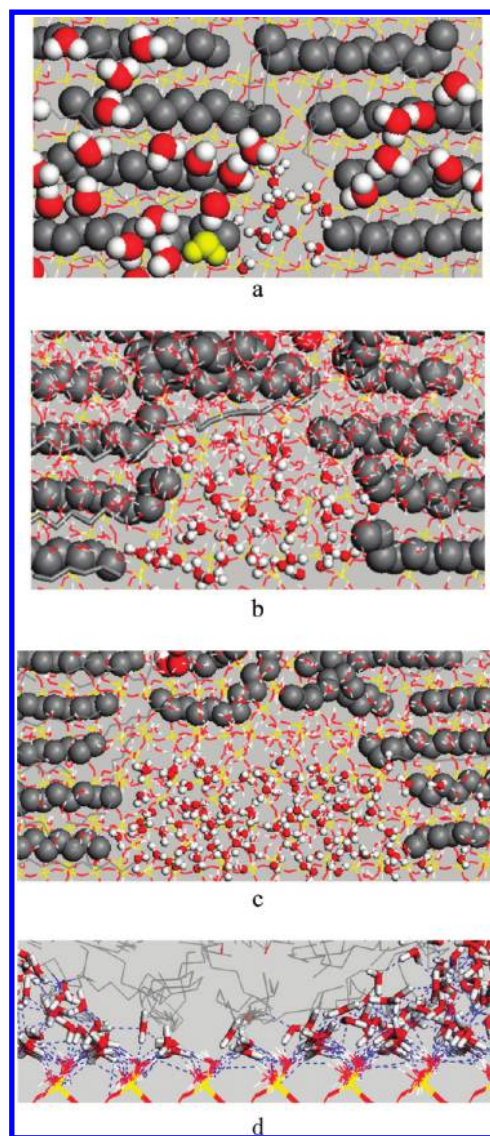

Figure 5. Consecutive snapshots of the formation of the "water-channel": (a) 150 ps, (b) 700 ps, (c) 1500 ps. The water molecules in the water channel are displayed in ball-and-stick mode, and the C12 molecules are shown in CPK mode. (d) The H-bonding structure among water molecules and the hydroxyl group on the silica surface at 4 ns. Color details are identical to those in Figure 3.

long-range electrostatic interactions between water molecules and the silica surface promote the movement of water molecules toward the silica surface.

Once the water channel has formed between the oil layers and the surface, the H-bonding interaction will become the third driving force for the detachment of an oil drop from the solid surface. The types of H-bonding include the ones between the water molecules and the hydroxyl group on the silica surface, and the ones among the water molecules in the water channel. The former H-bonding is helpful for the adsorption of water molecules on the silica, and the latter can ensure that more water molecules enter into the solid surface through the water channel. Finally, the water channel becomes wider with time evolution (Figure 5a,b,c). When the oil drop is left on the silica surface, one water layer is formed on the surface, and the water molecules form the strong H-bonding interaction with the silica surface. Figure 5d shows the H-bonding structure
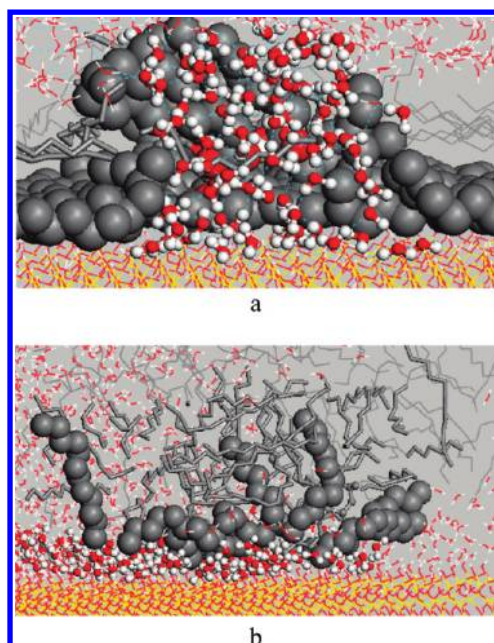
Figure 6. Microscopic conformational changes for the alkyl chain of oil molecules. The water molecules in the water channel (a) and in the vicinity of the silica surface (b) are displayed in ball-and-stick mode, and the C12 molecules in the first layer are shown in CPK mode for clarity. Color details are identical to those in Figure 3.
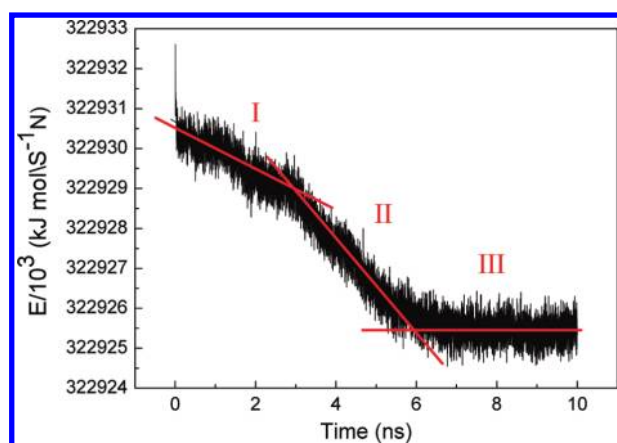

Figure 7. The total energy of the system decreases as a function of time.

Figure 8. Time evolution of the number density profiles of different components in the direction (z) normal to the interface: (a) H_2O; (b) C12.

Figure 9. Bonding patterns between (a) one adsorbed alkane molecule and the hydrophilic surface, and (b) one adsorbed H_2O molecule and the hydrophilic surface.

among water molecules and the hydroxyl group on the silica surface. There is a gel layer formed in the vicinity of the hydrophilic silica surface.

In fact we focus on the structure of alkane molecules in the first layer on the silica surface when the water channel is formed. We note that the structure of alkane molecules around the water channel become vertical to the silica surface from initially being parallel to the surface under the spatial exclusion (Figure 6a). Additionally, the H-bonding interaction between the water molecules and the hydroxyl group of the silica surface makes the water molecules move along the silica surface, thus more ordered alkane molecules will be stripped from the surface. Finally, the water layer on the silica promotes the formation of an oil drop (Figure 6b).

3.3. Mechanisms. As stated in the discussion above, the adsorption of alkane molecules on a hydrophilic surface is unstable thermodynamically. Therefore, the oil drops can be
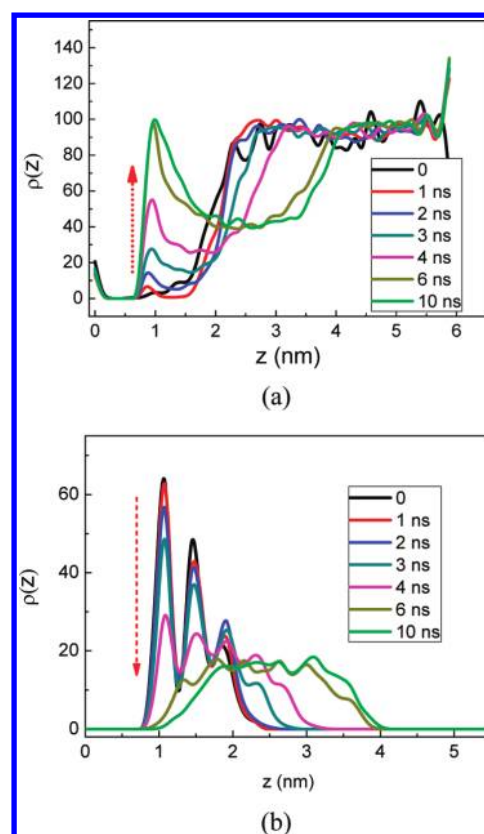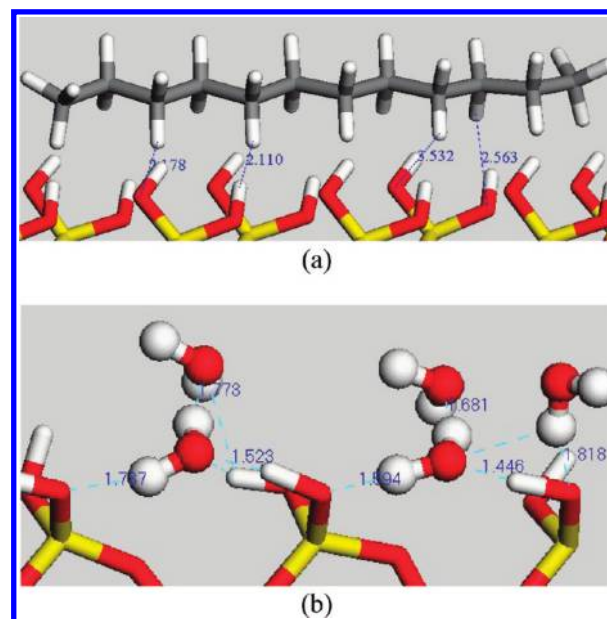
detached from a glass substrate even in pure water (without any surfactant), but the process will be very slow under natural geological conditions. Hence, the presence of surfactant is not a precondition for the penetration of water molecules between glass and oil. However, when present, the surfactant will
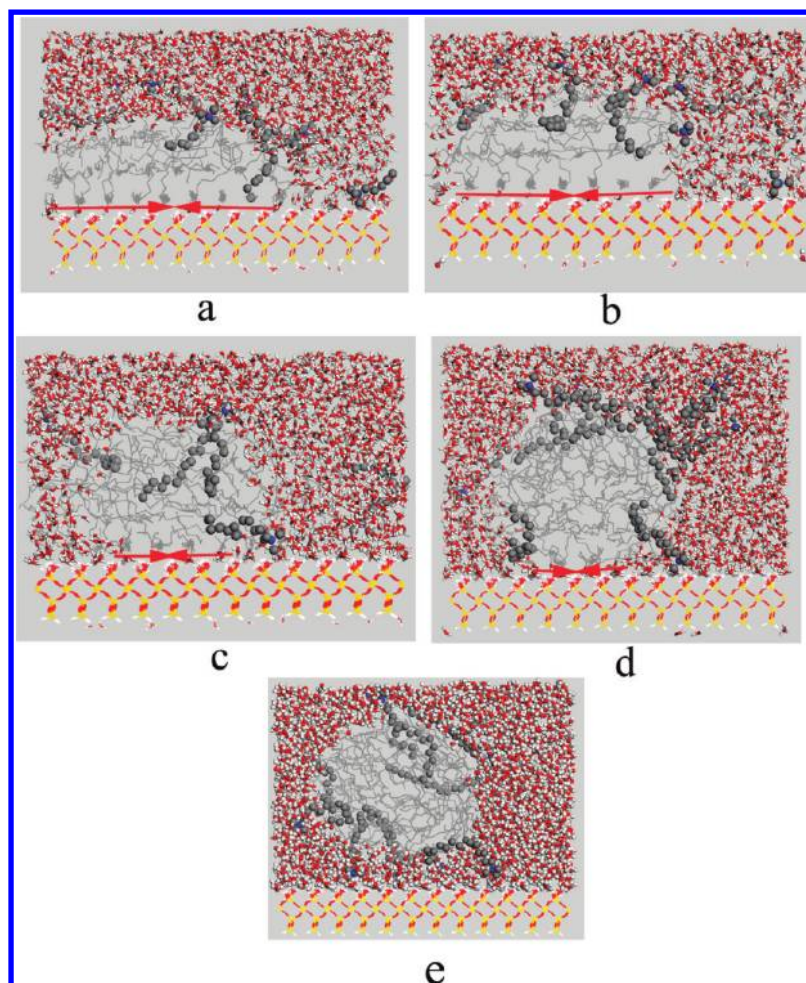
Figure 10. Snapshots of the shrinking of the three-phase contact line: (a) 2.5 ns, (b) 3 ns, (c) 4 ns, (d) 5 ns, and (e) 10 ns. The water molecules and CTAB are displayed in ball-and-stick mode, and the C12 molecules and the silica surface are shown in line mode. Color details are identical to those in Figure 3.

accelerate the detachment of oil drops. On the other hand, if the substrate is essentially hydrophobic and there is no development of a water layer, the presence of surfactant in the water phase, and its carryover ahead of the contact line, could be a necessary condition for the occurrence of spontaneous drop detachment.

Figure 7 shows that the total energy of the system decreases with time evolution and it can be approximately divided into three stages. During the first 3 ns (Stage I), the total energy of the system decreases slowly due to the adsorption of surfactant molecules from the aqueous solution to the oil layer, including the destruction of alkanes layers, the formation of the initial water channel, and the expansion of the water channel under the H-bonding. In the second stage (Stage II), the oil drop detachment from the silica surface is fast, including the water diffusion along the silica surface through H-bonding between water molecules and the hydroxyl group of the silica. The total energy of the system quickly decreases from 3 ns to 6 ns. Stage III reflects the detached equilibrium of the oil drop in the system, mainly focusing on the aggregates of the surfactant and alkane molecules in the aqueous solution. The energy profile of the system is flat, indicating that the system is at steady-state. A three-stage model based on the total energy change of the system adequately explains the mechanism of oil detachment from solid surfaces in aqueous surfactant solutions. Figure 8 shows the time evolution of the number density profiles of

different components of the system in the direction normal to the interface for the three stages. The surfactant molecule has different roles in the three stages of the oil detachment process. The surfactant aggregation and the detailed explanation for three stages are as follows.

In Stage I, at the beginning of the simulation, oil molecules lay on the silica surface layer by layer, and three peaks of C12 density profiles can be seen as shown in Figure 8b. The number densities of the water molecules (Figure 8a) were zero below the oil layer ($z < 2.5$ nm). A water−oil interface at about 2.5 nm was observed. In the first 100 ps, some surfactants adsorbed to the oil/water interface immediately and formed a monolayer through hydrophobic interaction of their tails with the oil molecules that are adsorbed on the silica surface. The perturbation of alkyl chain of CTAB disturbs the arrangement of the upper oil layer. The less ordered layer is destroyed first, and the water molecules will enter into the next alkane layer. Due to the strong electrostatic interaction, the water molecules continuously move toward the silica surface. Thus, the density profile peaks of water molecules are shifted toward a smaller z value from 0 to 4 ns (Figure 8a). As the water-channel is formed, the alkane molecules that lay on the silica surface turn to become vertical to the surface. The number density of alkane at 1 and 1.5 nm is decreased gradually as a function of time (Figure 8b). During Stage I the hydrophobic interaction between the oil and CTAB and the

electrostatic interaction between the water molecules and silica surface are the driving forces of the formation of the water-channel.

In Stage II, the water molecules destroy the first oil layer, which is in the vicinity of the solid surface (Figure 6a). For the C12 molecule, the distances between the H atom in the methyl group of C12 molecules and the O atom on the silica surface is lager than 2.5 Å, (shown in Figure 9a), indicating that no hydrogen bond formed between the silica surface and the C12 molecules. The interaction of the C12 molecule and the silica surface is very weak, in contrast with that of the water molecule. For the water molecules, the O−H-type hydrogen bond is formed between the water molecule and the silica surface, as the distances are 1.446 Å for the O (H_2O) and H (SiO_2) and 1.592 Å for H (H_2O) and O (SiO_2) (shown in Figure 9b). So, the water molecules must displace the C12 molecules. This could be used to explain the diffusion of water molecules along the oil−solid boundary in the zone of the three-phase contact.

Under the strong hydrogen bonding between the water molecule and the silica surface, the density of water molecules at the silica surface increased with time evolution, and the density profile peak of H_2O at 1 nm became much sharper (Figure 8a). The water molecules can diffuse along the boundary, swell the silica surface, and form a surface gel layer. During the water−oil−solid contact-line motion (Figure 10), oil molecules are taken out of potential wells at the solid surface and replaced by water molecules. The alkyl chain of C12 molecules rolled up under the repulsion between water and oil molecules, so that the density profile peak of C12 at 1 nm decreased quickly with time evolution and disappeared around 6 ns (Figure 8b), when the water molecules completely disjoin the oil from the solid (Figure 10).

In addition, the CTAB molecules in the aqueous solution will facilitate the penetration of water on the silica surface. First, some of the CTAB molecules are adsorbed at the oil/water interface. The interfacial tension of the oil−water interface quickly decreases, which affects the force balance at the three-phase contact line. The contact line shrinks to reach an equilibrium position. Second, other CTAB molecules move toward the silica surface through the water-channel. The positively charged CTA^+ headgroup can be attracted to the oppositely charged sites on the silica surface (Figure 10b), and they will cover the newly formed oil−water interface and decrease the surface energy. Consequently, the surfactant molecules facilitate the detachment of the oil from the silica surface. During Stage II, the total energy of the system decreased much faster than that of the first stage. The O−H-type hydrogen bond between the water molecules and the silica surface, and the adsorption of CTAB at the water/oil interface and the solid/oil interface are the driving force of the detachment of oil molecules from the silica surface.

In Stage III, at the final stage of the process (Figure 10d), the contact-line becomes so small that the shape of the pendant oil drop becomes unstable. The buoyancy force tends to detach the drop from the substrate. The number density of the C12 molecules is zero in the vicinity of the silica surface (at about 0.8 nm). The silica surface becomes hydrophilic, and the oil is solubilized in the surfactant micelles. In the vicinity of the hydrophilic silica substrate, the water molecules align themselves such that one or both of the hydrogen atoms in the molecules are oriented toward the oxygen atoms on the silica surface, and the headgroups of CTAB are attracted to the
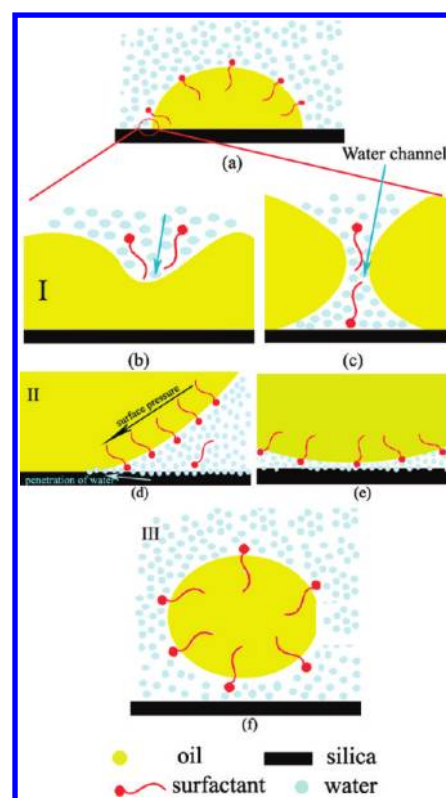

Figure 11. Schematic diagram of the detachment of an oil drop from a silica substrate in a surfactant solution.

oppositely charged sites on the silica surface. There is consequently a greater density of water molecules at the silica surface than in the surroundings. A sharp peak of the H_2O density profile can be observed at 1 nm in Figure 8. For about 6 ns, the total energy of this stage is the lowest and is allowed to equilibrate by which time the system is fully equilibrated, as shown in Figure 7.

4. CONCLUSIONS

The detachment of oil drops from a solid surface is of considerable interest to many industrial areas. In general, an oil drop is situated above a horizontal solid plate immersed in a water phase (Figure 11a). In this paper, we are focused on the simulation of solid−oil−water boundary conditions at the nanometer level (Figure 11b,c,d,f) and give the schematic model of the detachment of an oil drop from a silica substrate in a surfactant solution. We have demonstrated that the formation of a water-channel is vital for oil detachment. Moreover, water molecules can penetrate the oil−water interface by diffusion and form a gel layer at the water−silica interface, in the close vicinity of the contact line. This will accelerate the removal of the oil molecules from the silica surface.

One can identify the following stages of detachment of a drop situated above a horizontal substrate. In Stage I, the surfactants are adsorbed at the water−oil interface, through hydrophobic interaction of their tails with the oil molecules (Figure 11a). Due to the electrostatic interaction between water molecules, the CTA^+, and the silica surface, the CTA^+ solution moves toward the silica surface and disturbs the order-organized oil layer. Thus, the water-channel is formed, which is vital to the oil detachment from the silica surface (Figure 11b,c).

In Stage II, due to the hydrogen bond between the water molecules and the silica surface and the adsorption of CTAB at the solid-oil interface, the water molecules can disjoin the oil from the solid surface and penetrate the surface layer of the silica. As a result, the water−oil−solid contact line shrinks. A surface gel layer is formed at the silica surface. (Figure 11d). In Stage III, the contact line becomes so small (Figure 11f) that the shape of the oil−water interfaces becomes unstable. The buoyancy force tends to detach the oil drop from the substrate, and the oil molecules completely disjoin from the solid surface (Figure 11e). This three-stage model is developed in detail at a molecular level. The main factors that control the oil detachment have been pointed out and can be used for optimization in enhanced oil recovery, ore flotation, detergency, and printing.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shilingyuan@sdu.edu.cn (S.Y.); zhaoxian@sdu.edu.cn (X.Z.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Cutler, W. G., Davis, R. C., Eds. *Detergency: Theory and Test Methods, Parts I−III*; Dekker, New York, 1981.

(2) Cutler, W. G., Kissa, E., Eds. *Detergency: Theory and Technology*; Dekker: New York, 1987.

(3) Dillan, K. W.; Goddard, E. D.; McKenzie, D. A. *J. Am. Oil. Chem. Soc.* **1979**, *56*, 59.

(4) Gum, M. C.; Goddard, E. D. *J. Am. Oil. Chem. Soc.* **1982**, *59*, 142.

(5) Mahé, M.; Vignes-Adler, M.; Rosseau, A.; Jacquin, C. G.; Adler, P. M. *J. Colloid Interface Sci.* **1988**, *126*, 314.

(6) Kao, R. L.; Wasan, D. T.; Nikolov, A. D.; Edwards, D. A. *Colloids Surf.* **1988/1989**, *34*, 389.

(7) Carroll, B. *Colloids Surf. A* **1993**, *74*, 131.

(8) Miller, C. A.; Raney, K. H. *Colloids Surf.* **1993**, *74*, 169.

(9) Thompson, L. *J. Colloid Interface Sci.* **1994**, *163*, 61.

(10) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Interfaces and Membranes*; Elsevier: Amsterdam, 2001; p 268.

(11) Kolev, V. L.; Kochijashky, I. I.; Danov, K. D.; Kralchevsky, P. A.; Broze, G.; Mehreteab, A. *J. Colloid Interface Sci.* **2003**, *257*, 357.

(12) Powney, J. *J. Text. Inst. Trans.* **1949**, *40*, 549.

(13) Stevenson, D. G. *J. Text. Inst. Trans.* **1951**, *42*, 194.

(14) Stevenson, D. G. *J. Text. Inst. Trans.* **1953**, *44*, 548.

(15) Tadros, Th.F.; Lyklema, J. *J. Electroanal. Chem.* **1968**, *17*, 267.

(16) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*; Wiley: New York, 1979.

(17) Hunter, R. *Foundation of Colloid Science*; Clarendon: Oxford, 1987.

(18) Doremus, R. H. *Glass Science*, 2nd ed.; Wiley: New York, 1994.

(19) Vigil, G.; Xu, Z.; Steinberg, S.; Israelachvili, J.N. *J. Colloid Interface Sci.* **1994**, *165*, 367.

(20) Trens, P.; Denoyel, R.; Guilloteau, E. *Langmuir* **1996**, *12*, 1245.

(21) Yaminsky, V. V.; Ninham, B. W.; Pashley, R. M. *Langmuir* **1998**, *14*, 3223.

(22) van Duijvenbode, R. C.; Koper, G. J. M.; Böhmer, M. R. *Langmuir* **2000**, *16*, 7713.

(23) Adler, J. J.; Rabinovich, Y. I.; Moudgil, B. M. *J. Colloid Interface Sci.* **2001**, *237*, 249.

(24) Petrov, J. G.; Ralston, J.; Hayes, R. A. *Langmuir* **1999**, *15*, 3365.

(25) Blake, T. D.; de Coninck, J. *Adv. Colloid Interface Sci.* **2002**, *96*, 21.

(26) Starov, V. M.; Kostvintsev, S. R.; Sobolev, V. D.; Velarde, M. G.; Zhdanov, S. A. *J. Colloid Interface Sci.* **2002**, *252*, 397.

(27) Blake, T. D.; Shikhmurzaev, Y. D. *J. Colloid Interface Sci.* **2002**, *253*, 196.

(28) Chi, M. P.; Anh, N. V.; Evans, G. M. *Langmuir* **2003**, *19*, 6796.

(29) Christov, N. C.; Ganchev, D. N.; Vassileva, N. D.; Denkov, N. D.; Danov, K. D.; Kralchevsky, P. *Colloids Surf. A* **2002**, *209*, 83.

(30) Rowe, A. W.; Counce, R. M.; Morton, S. A. III; Hu, M. Z.-C; DePaoli, D. W. *Ind. Eng. Chem. Res.* **2002**, *41*, 1787.

(31) Kralchevsky, P. A.; Danov, K. D.; Kolev, V. L.; Gurkov, T. D.; Temelska, M. I.; Brenn, G. *Ind. Eng. Chem. Res.* **2005**, *44*, 1309.

(32) Chatterjee, J.; Eotvos, C. *Adv. Colloid Interface Sci.* **2002**, *98*, 265.

(33) Chatterjee, J. *Adv. Colloid Interface Sci.* **2002**, *99*, 163.

(34) Grant, L. M.; Tiberg, F.; Ducker, W. A. *J. Phys. Chem. B* **1998**, *102*, 4288.

(35) Ducker, W. A.; Wanless, E. J. *Langmuir* **1999**, *15*, 160.

(36) Wanless, E. J.; Ducker, W. A. *Langmuir* **1997**, *13*, 1463.

(37) Ducker, W. A.; Grant, L. M. *J. Phys. Chem. B* **1996**, *100*, 11507.

(38) Manne, S.; Cleveland, J. P.; Gaub, H. E.; Stucky, G. D.; Hansma, P. K. *Langmuir* **1994**, *10*, 4409.

(39) Jaschke, M.; Butt, H.-J.; Gaub, H. E.; Manne, S. *Langmuir* **1997**, *13*, 1381.

(40) Shen, Y.; Couzis, A.; Koplik, J.; Maldarelli, C.; Tomassone, M. S. *Langmuir* **2005**, *21*, 12160.

(41) de Ruijter, M. J.; Blake, T. D.; De Coninck, J. *Langmuir* **1999**, *15*, 7836.

(42) Warne, M. R.; Allan, N. L.; Cosgrove, T. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3663.

(43) Jorgensen, W. L.; Gao, J. *J. Phys. Chem.* **1986**, *90*, 2174.

(44) Lybrand, T. P.; Ghosh, I.; McCammon, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 7793.

(45) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.