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Micro-nano Processing Using Molecular Simulation for Modeling of Nanobubble and Nanofilm and Its Application

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Abstract

Molecular Simulation is a method to simulate the structure and behavior of molecules by using computer models at the atomic level, and then to simulate the various physical and chemical properties of the Molecular system. It is based on the experiment, through the basic principles, to build a set of models and algorithms, so as to calculate the reasonable molecular structure and molecular behavior. Molecular simulation can not only simulate the static structure of molecules, but also simulate the dynamic behavior of molecular systems. In this study, molecular simulation for modeling of nano-bubble and nanofilm was proposed and its application was introduced. It can be used for molecular sieve catalyst structure characterization, synthesis design, adsorption and diffusion. It can construct and characterize the structure of polymer chains and crystalline or amorphous bulk polymers, including blending behavior, mechanical properties, diffusion, cohesion and wetting, surface bonding and other important properties.

Keywords

Molecular Modeling; Nano Scale; Film.

1. Introduction

In recent years, molecular simulation technology has developed rapidly and been widely used in many fields. In the field of drug design, it can be used to study the mechanism of action of viruses and drugs. In the field of biological science, it can be used to characterize the multi-level structure and properties of proteins. In the field of material science, it can be used to study the structure and mechanical properties, the optimal design of materials. In the field of chemistry, it can be used to study surface catalysis and mechanism.

Aqueous interfaces and related phenomena [1,2] are ubiquitous in nature, which can affect various biochemical, atmospheric, pharmaceutical, and industrial processes. These processes are dependent on the molecular-level interaction of aqueous systems. To construct models of these phenomena, it is necessary to investigate the nano-scale properties of aqueous interfaces and films. As an example, flotation is a process to separate valuable minerals from worthless material or other valuable minerals, by modifying the surface properties of bubbles that carry these minerals to a froth layer. Bubble coalescence [3], is an essential aspect of the flotation process. This in turn is comprised of several phenomena, which need to be understood to model bubble coalescence: ion specific effect [4], thin film drainage [5] and rupture [6,7]. The molecular level view of the phenomena involved is incomplete, and it is proposed that molecular modeling can provide critical insight to improve our understanding.

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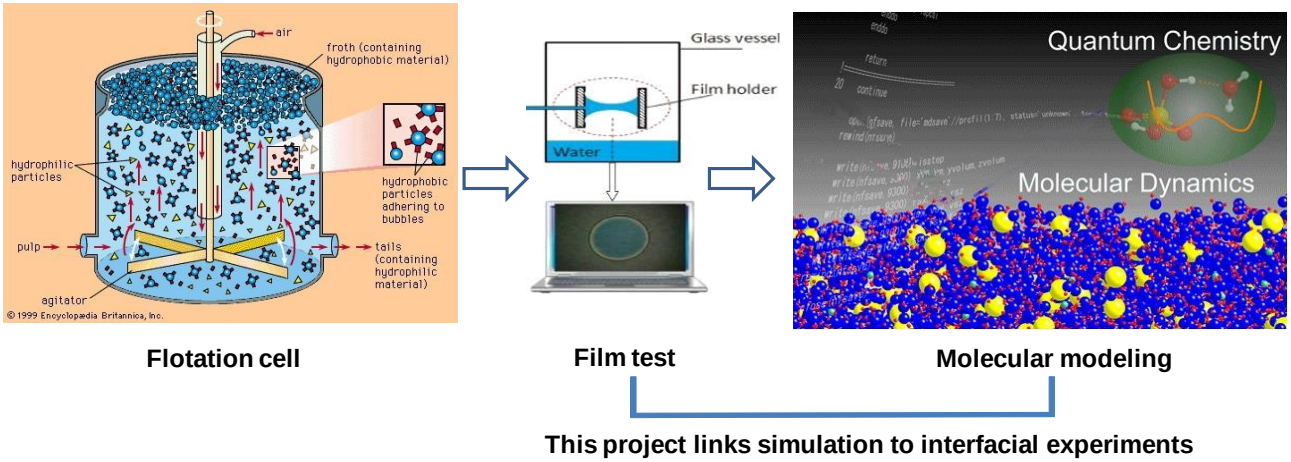

Figure 1. Examples of the scales of interfacial phenomena and research [6,8]

Figure 1 shows the different scales of research commonly conducted in this field. An example of macro scale research (and application) is a flotation cell. The efficiency and yield of the flotation cell depend greatly on the coalescence of bubbles within the cell [9]. The coalescence depends, partially, on the behavior of the thin film that is created when two bubbles approach each other. The behavior of thin films can be experimentally studied at the micro to nano-scale using a film test, e.g., thin film balance (TFB). This test can determine if a film is unstable, meta-stable, or stable under a range of conditions. The stability of the films under various conditions can be correlated with the coalescence behavior [10,11] within the cell and hence the cell's performance. Whilst the film test can correlate several factors with film stability, it cannot, by itself, reveal the molecular mechanisms that contribute to, or hinder, film stability. Thin films can be used to model the bubble coalescence when two bubble approaches, molecular modeling method can be applied to simulate the thin films.

As for the research scales, the first stage is a flotation experiment. At this stage, the flotation recovery rate and other macroscopic quantities can be obtained. The second stage is the medium scale stage, in which the film stability, the film rupture time, attachment time, and bubble coalescence can be studied. Finally comes molecular modeling, which is fundamental and also the major part. This work aims at developing some aspect of these techniques and theoretical advancement, and will focus on linking the latter two stages.

Molecular simulation techniques usually use Monte Carlo (MC) [12] and/or Molecular Dynamics (MD) simulations [13,14]. MD simulation uses classical Newton mechanics and statistical mechanics, and applies them to molecules. The force field can be pair-additive or polarizable [15,16]. Classical mechanics with force calculations are used to describe the motion of atoms. This is acceptable for most molecules at moderate temperatures.

The different ensembles [17], e.g., *NVT* (canonical ensemble), *NPT* (isothermal-isobaric) and *NVE* (micro-canonical ensemble), will be used for different purposes. By performing the simulation, we can obtain various properties that are of interest. The advantage of MD is that it can provide detailed information at the molecular level, that, in some circumstances, are impossible to obtain by experimental measurement due to the conditions or the scale required.

MD can be used to describe dynamic [18,19] as well as equilibrium properties. From the equilibrium state, various properties can be obtained such as the radial distribution function [20] (RDF), dipole moment, enthalpy of vaporization, isothermal compressibility, angle distribution, velocity autocorrelation function (VAF) [21], diffusion coefficient [22], binding energy, mean residence time (MRT) [23], surface potential [24], surface tension [25] and potential of mean force [26,27] (PMF). From these calculations, the relationship between the phenomenon and the physical mechanism can be investigated, so MD can be used as an

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important tool to enhance understanding and interpretation. There are many MD software packages available, e.g., GROMACS [28], AMBER [29], and LAMMPS [30,31]. Sometimes, GROMACS can be applied as it is fast and free, and AMBER for its incorporation of polarizable potential. Also, sometimes, in order to fit a special purpose, one may need to change codes, e.g., for the calculation of PMF.

2. Modeling of Nano-bubble and Film Rupture

Many experiments have been undertaken to investigate the film rupture process [32-36]. At the first stage of liquid film drainage when a relatively thick liquid phase exists between air bubbles, gravity plays an important role. When the thickness decreases to ~100 nm, the gravity effect becomes negligible, and interfacial interactions including electrostatic, dispersion, and hydration forces begin to be major factors in film drainage and rupture.

The experiment is accumulative result of many environmental effects [37-43]: random motion of microscopic particles, collisions of surrounding gas molecules, atmospheric humidity and so on. Experiments [40] using micro interferometry showed that foam films of ultrapure de-ionized (DI) water can last up to 10 s, and the contact time between two gas bubble surfaces at close proximity significantly influences the film drainage, rupture, and lifetime. Also using micro interferometry, Karakashev *et al*. [37] reported the effects of ions on film rupture and the lifetime of aqueous foam films formed from sodium chloride (NaCl), lithium chloride (LiCl), sodium acetate (NaAc), and sodium chlorate ($NaClO_3$). They found that relatively long-lasting and non-draining films prepared from salt solutions above 0.1 M could be observed. The film lifetime was significantly longer by 1 to 2 orders-of-magnitude (i.e., from 10 to 100 s). Also, both the film lifetime and the (average) thickness of the non-draining films increased with increasing salt concentration. This effect has not been observed with foam films stabilized by surfactants. The film lifetime and thickness also increased with increasing film radius. From all these experiments, the thickness order was usually ~100 nm, which is a very different value from the thicknesses obtained using computer simulations.

Computer simulations and experimental measurements have been used widely in attempts to understand chemical phenomena in bulk liquids, liquid/air, liquid/liquid and liquid-solid interfaces [44-49]. Understanding liquid film systems are important in understanding industrial processes such as phase separation, flotation separation of particle using gas bubbles, water desalination, etc. Aqueous film systems could be classified mainly as water films containing ions or liquid films containing surfactants. From the perspective of MD simulations, and given the experimental complications associated with the studies of thin films, it makes sense to combine experimental approaches with computational studies to discover new insights that can be used to interpret the fundamental aspect of the phenomena.

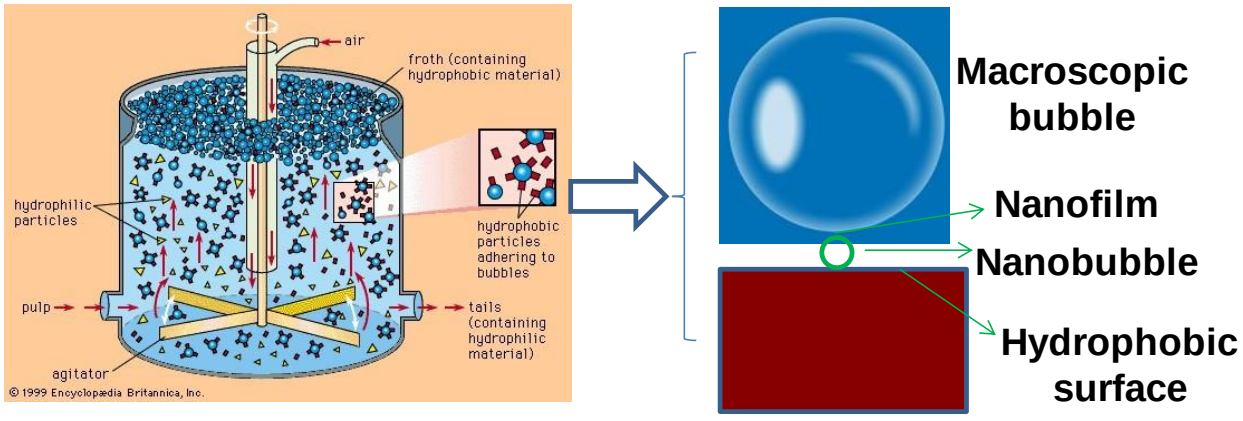

Figure 2. The illustration of liquid nano-film and macroscopic bubble

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Recent experiments [50,51] suggested that nano-bubbles can stably form at a hydrophobic surface and in an aqueous solution, and can be used to explain the liquid film rupture through a number of stages [52,53]. For example, during the film drainage between a big air bubble and a hydrophobic surface, the macroscopic bubble (in Figure 2) first approaches the apex of the largest surface nano-bubbles. An aqueous foam film in nano-meter size is effectively formed between the macroscopic bubble and the nano-bubble, where the van der Waals attraction is strong. The attractive van der Waals force can destabilize the film locally as traditionally proposed [54]. The local film destabilization can be further increased by the increase in the local capillary pressure due to the concave surface of the nano-bubble, causing the disappearance of the entire macroscopic film. Understanding the rupture of the nano-films is critical to the nano-bubble theory on the rupture of macroscopic films. Unfortunately, the nano-films cannot be directly visualized and examined due to the limit of optical resolution available. Therefore, studies of nano-film rupture by MD simulation would be extremely useful in this regard.

3. Modeling and Discussion

3.1. Interfacial structure of vapor-liquid surface using polarizable model

For the enhancement of ion at air-water interface [55,56] shown in Figure 3, non-polarizable model cannot observe this distribution profile, but polarizable potential can capture this phenomena.

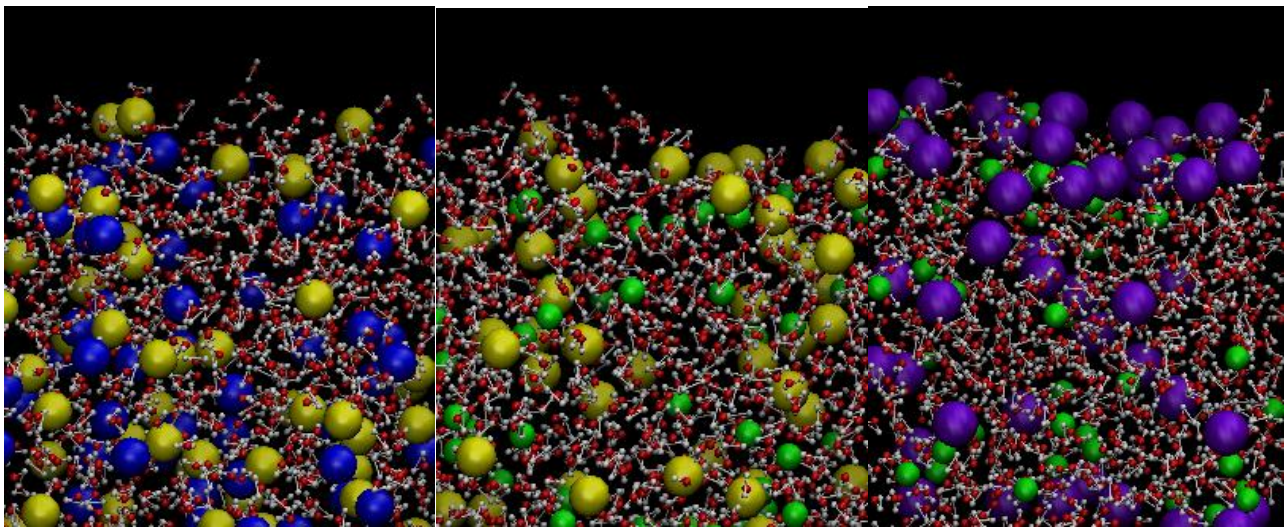

Figure 3. Ion distribution for CsCl, NaCl and NaI. Water Oxygen = Red, Water Hydrogen = White, Na = Green, Cl = Yellow, I = Violet, Cs = Blue

Table 1. Potential parameters for DC water and ions in the simulation.

Molecule	Atom type	$r_m/2$ (Å)	ε (kcal/mol)	q (e)	α (Å^3)
	H	0	0	0.519	0
H_2O	O	1.8150	0.1825	0	0
	M	0	0	-1.038	1.444
Cs^+	Cs	2.098	0.10	1	2.440
Na^+	Na	1.275	0.10	1	0.24
Cl^-	Cl	2.435	0.10	-1	3.690
I^-	I	2.876	0.10	-1	6.920

$r_m = \sigma * 2^{1/6}$, σ and ε are the Lennard-Jones parameters, q is the atomic charge, α is the atomic polarizability

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Water model of Dang-Chang was used, which can give reasonable structure and thermodynamic of the bulk and the air/liquid interface of water. The detailed parameters for DC water and ions employed were listed in Table 1, the MD simulations were performed on the system of 900 water and 50 cation halide (e.g., 50 Na^+, 50 I^-). The concentrate was 3 M for CsCl, NaCl, NaI. Ewald summation techniques were used, L-J cutoff was 11 Å, time step was 2 fs. During the simulation, SHAKE algorithm was applied to fix the water OH and HH bond lengths.

3.2. Experimental measurements and classical extended-DLVO theory

Usually in experiments [57], there are external factors that can affect the results, among which the approach speed, evaporation condition and impurity could be significant. To be more specific, at high approach speed, the films become unstable due to dynamic/hydrodynamic disturbances. At low speeds, the disturbances are insignificant, and the attractive van der Waals (sometimes VDW + hydrophobic force) and repulsive component (i.e., electrical double-layer, sometimes steric force) surface forces determine the film stability: if the total (net) force is repulsive and greater than the capillary pressure (at the film periphery, about 72 Pa) the films are stable; otherwise the films are not stable.

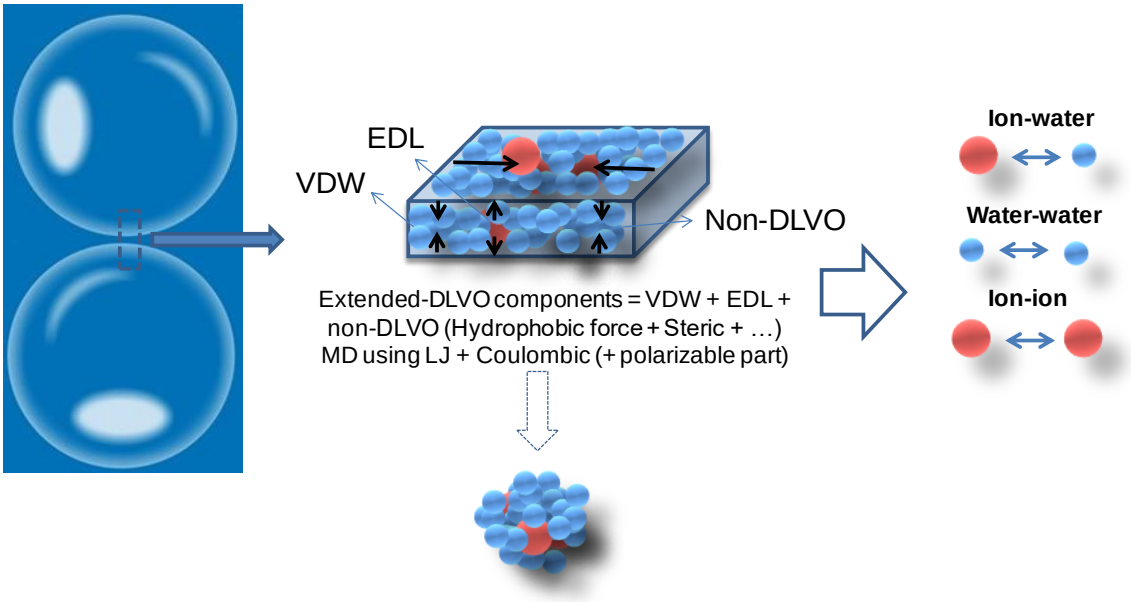

Figure 4. The relationship between surface forces within films and molecular modeling

At low concentrations, it was assumed that the ion was surrounded by water molecules. However, when the situation changed to concentrated salt films, the ion-water and ion-ion interactions became complicated, such that the combining rule (LJ, Lorentz-Bertelot) in MD may not be applicable to represent the real system. It was noted that the film needs to be able to form a stable film, and then the stability (evaluated by life time and the ability to withstand pressure) can be discussed. MD represents the total interaction among molecules within a film (Figure 4), and experiment is the net sum of total surface forces.

It should be noted that MD is in nanoscale below 5 nm, however, experimental tests for surfactant-free liquid films were usually above 30 nm. So it is actually difficult to compare them together, and in fact they cannot be compared.

4. Conclusions

Compared with their macroscopic counterparts, nano-bubbles exhibit many different properties and play an important role in the fields of surface physics, chemistry, biology and chemical

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industry. For example, interfacial nanobubbles can reduce the flow resistance of nanofluids, increase the recovery of mineral flotation, remove surface contaminants, and it could be applied in ultrasonic radiation technology for tumor imaging. In the experiment, the nanobubbles were prepared by solvent exchange and electrolysis. However, the formation of bubbles will be affected by many factors, such as the supersaturation of gas in the solvent exchange process, the solvent exchange rate, the shear rate of fluid and so on. It is difficult to control the formation and nucleation of nanobubbles. In this work, the relationship among liquid film rupture, nano-bubble and nano-film rupture was investigated, and MD simulations were performed to study the aqueous film and ion distributions. And surface forces by molecular simulations were compared with classical DLVO theory.

Acknowledgments

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