

Date: June 14, 2012

To: Prof. M. Scott Shell
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Subject: Dynamic Gas Enrichment at Liquid-Wall Interface

Abstract

The dynamic development of a gas enrichment layer along a hydrophobic interface was studied using a Molecular Dynamics (MD) simulation of a simple 3-component Lennard-Jones (LJ) fluid system. The simulation consisted of a wall modeled by a single sheet of explicit LJ atoms held fixed via a harmonic potential and maintained at constant temperature using an Andersen thermostat. A liquid film with gas dissolved in it was placed next to the wall, and the parameters were tuned initially such that the interface is hydrophilic (i.e. the interaction between the liquid and wall atoms is more favorable than the interaction between wall and gas atoms). After equilibration, the wall/particle interaction parameters were switched from being hydrophilic to hydrophobic, and the gas deposition process was observed until the enrichment layer became fully developed. A movie of one of the trajectories was rendered in Chimera, and an animation of the evolution of the liquid/gas density profiles in the system was prepared by averaging over 10 independent MD trajectories. The initial and final (equilibrium) states of this process show excellent agreement with literature [1].

Summary

There has been much interest in recent years on the subject of hydrophobicity and gas enrichment due to research in flows with slip along solid boundaries, and more recently, nucleation and persistence of various nanoscopic gaseous domains (e.g. surface nanobubbles) that form along hydrophobic interfaces [1]. Both experimental and computational studies have established the presence of a gas enrichment layer across hydrophobic surfaces when immersed in a liquid that has gas dissolved in it. A study by Dammer and Lohse [1] probed this phenomena using a simple LJ fluid model and established a set of density profiles for both hydrophilic and hydrophobic cases involving a number LJ gases with differing parameters. Their effort also investigated slip along the surface by tracking particle velocities near the liquid-wall interface when the fluid is sheared. The aim of this project is to reproduce their equilibrium results, as well as to investigate the transient process of gas deposition that establishes the gas enrichment layer.

The MD code developed for this project employs the velocity Verlet algorithm. For this particular study, a truncated and shifted LJ potential is used for intermolecular interactions, given by

$$U_{ij} = 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) - U_{cut} \quad (1)$$

where ϵ_{ij} and σ_{ij} are the particle energy and diameters of interaction for particles i and j , respectively, and r_{ij} is the distance between them. In its present form, the code can generate any desired number of different LJ fluid types within sub-regions of a rectangular box of arbitrary x-,y-, and z-direction lengths. If a wall is required, any of the atom types present can be tethered to some position in space using a harmonic potential, given by

$$U_i = \frac{1}{2}k(\bar{r}_i - \bar{r}_0) \quad (2)$$

where k is the spring constant, r_i is the position vector of the particle, and r_0 is a vector specifying the point of the harmonic potential energy minimum for each particle. Such walls can be readily translated by giving r_0 some velocity. The code currently only supports periodic boundary conditions (PBC).

This generalized code was used to develop a model similar to the one used by Dammer and Lohse in their MD study of hydrophobicity [1]. The global simulation box is rectangular, with a length that is three times longer in the z-direction than in the x- and y-directions. A single monolayer of LJ atoms are tethered to

their initial position with a harmonic potential (using $k = 1000$), establishing a wall surface (silver atoms, figure 1). Immediately to the left of this boundary, a thin region of atoms that corresponds to a liquid film is initialized (blue atoms). Further to the left of this film, there is a region of gas atoms (red atoms), followed by a

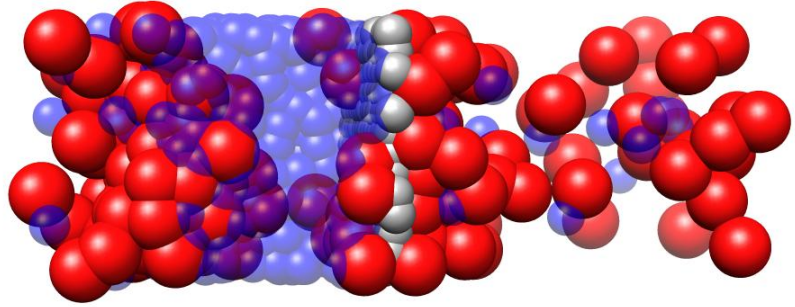


Figure 1 – A snapshot of the system generated using Chimera. The silver atoms correspond to the thermostatted wall. The blue atoms are the liquid and red atoms are the gas. This image was taken at a late point in a simulation with a hydrophobic wall. A monolayer of gas atoms can be observed near the liquid-gas interface.

vacuum region that is immediately filled by the gas upon system initialization. All data provided in the following discussion was generated with a total of 1354 atoms, with 144 wall atoms, 1037 liquid atoms, and 173 gas atoms. The system was energy minimized prior to equilibration in each case and a potential cutoff radius of $r_c = 5\sigma$ was used due to the presence of an interface. Hydrophobicity/hydrophilicity is achieved by adjusting the energies of interaction (ϵ_{ij}) between the liquid, gas, and wall atoms, as well as the radii of the three species (σ_{ij}). All data provided in this report utilizes ϵ_{ij} and σ_{ij} values suggested by Dammer and Lohse in their work [1]. The actual values are $\epsilon_{gg} = \epsilon_{gw} = 0.4$, $\epsilon_{gl} = 0.712$ and $\epsilon_{ll} = 1.2$. ϵ_{lw} was taken to be 0.7404 in the hydrophilic case and 0.3996 in the hydrophobic case. The values of σ_{ij} used are $\sigma_{ww} = \sigma_{lw} = \sigma_{ll} = 1.0$, $\sigma_{gw} = \sigma_{gl} = 1.31$, and $\sigma_{gg} = 1.62$.

The system is first initialized with wall interactions corresponding to the hydrophilic case. Wall atoms are maintained at constant temperature throughout the total simulation by being weakly coupled to a heat bath via an Andersen thermostat with a frequency of 0.02. A temperature of $T^* = 1.0$ (in LJ-reduced units) is used. After the system reaches equilibrium (after $\sim 1 \times 10^5$ time steps), the wall/particle interactions are changed from being hydrophilic to hydrophobic. With hydrophobicity switched on, the dynamic evolution of the system is tracked as it moves towards a new equilibrium and a gas enrichment layer develops along the liquid-wall interface. Graphs showcasing the transient evolution of the gas density profiles for this process are provided in the top plot in figure 2, and a video is available upon request. The rightmost peak that develops is the liquid-wall gas enrichment layer. These intermediate profiles for the dynamic system evolution were averaged over 10 independent MD trajectories, each generated with a different random seed. The standard deviation for the profiles at two of the times is shown in the second plot in figure 2.

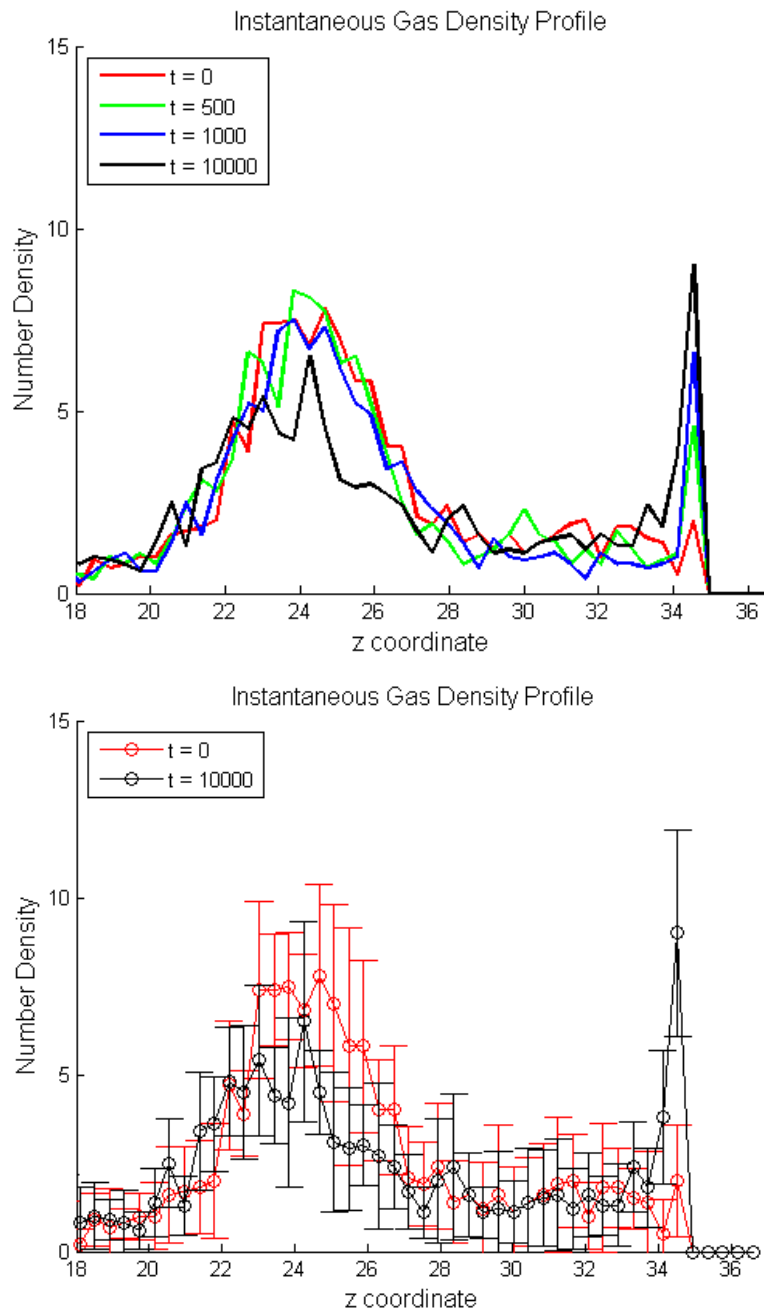


Figure 2 – Density profiles for the gas in the system near the wall at different times, with t in units of 50 time-steps. The increase in density around $z = 24$ corresponds to enrichment at the liquid-gas interface, and the increase around $z = 34$ corresponds to the gas enrichment layer at the liquid-wall interface. A video of the first plot is available upon request. The bottom plot shows the standard deviation in the profile measurements at times $t=0$ and $t = 10000$.

The profiles indicate that as the gas layer gradually develops, the liquid-gas interface enrichment layer is slowly depleted. Furthermore, in the hydrophilic equilibrium case and during the dynamic deposition process, there is a significant increase in the gas density right above the liquid film, which is

absent in the equilibrium density profiles for the hydrophobic interface. This is due to the molecules in the gas phase experiencing an attraction to the gas molecules at the liquid-gas interface, and this spike in density disappears as the liquid-gas enrichment layer is depleted. Eventually, a gas layer of approximately width σ develops (i.e., a monolayer, which is also visible in figure 1, previous page), again in good agreement with the findings of Dammer and Lohse [1].

After a sufficiently long time, the system approaches equilibrium, and the resulting profiles are provided in figure 3. The equilibrium graphs clearly indicate the presence of a gas enrichment layer near the wall-liquid interface in the hydrophobic case (near $z = 34$). In the hydrophilic case, this layer is altogether absent. In both scenarios, substantial gas enrichment near the gas-liquid interface is present. There is also substantial structuring in the liquid near the interface, which is diminished in the hydrophobic case. The hydrophobic density profile indicates that this gas enrichment layer forms beyond a monolayer of liquid atoms. Thus, some liquid appears to be trapped between the layer of gas and the hydrophobic interface.

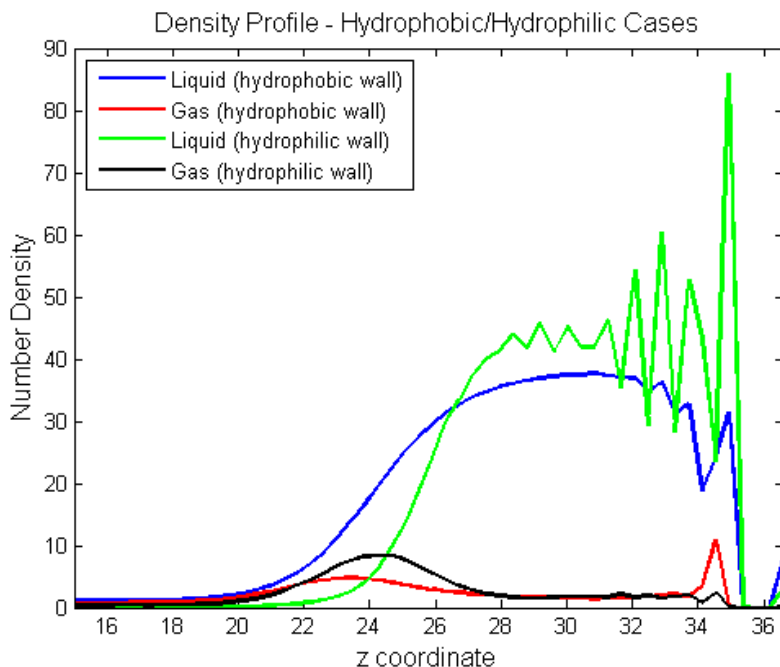


Figure 3 - Equilibrium density profiles for the hydrophobic/hydrophilic cases near the liquid-wall interface. The wall is located at $z = 37$. In the hydrophobic case, significant gas enrichment can be observed. Graphs were obtained by averaging over $\sim 1 \times 10^6 / 5 \times 10^6$ (hydrophilic/hydrophobic) time-steps and over 10 separate MD trajectories.

This can be explained by taking note of the σ_{ij} values (which establish the interaction potential minimum location) used to generate the provided results. More specifically, $\sigma_{lw} = 1.0$, while $\sigma_{gw} = 1.31$. The potential well for the gas-wall interactions is located slightly beyond the potential well for the liquid-wall interactions, which is what determines the location of the first liquid layer. Therefore, the most favorable location for gas atoms to aggregate near the wall lies between the first and second liquid layers, simply as a consequence of the model parameters chosen. Strongly pronounced structuring in the liquid is not entirely required for this to occur; similar equilibrium profiles were generated in LAMMPS using a LJ-93 potential, which removes much of the structure. In spite of the less-ordered film, there still is a substantial layer of liquid between the gas layer and wall. The nature of the enrichment density profile may also be affected by gas-gas interactions; for future studies, it is recommended that a thicker (bi- or tri-layer) wall be used to fully remove any interactions between gas molecules in the enrichment layer and gas molecules in the bulk beyond the wall. It is possible that such interactions might affect the gas layer properties, especially with the longer cutoff radius used in these simulations.

References

- [1] Dammer, S. M. and Lohse, D. "Gas Enrichment at Liquid-Wall Interfaces," *Phys. Rev. Lett.* **96**, 206101 (2006).