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From Nanoscale Wetting Towards Enhanced Oil Recovery

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Abstract

In oil reservoirs, a significant amount of oil resides in small pores where nanoscale phenomena dominate wettability and drive the mobility of oil. Nanoscale phenomena hence control the quantity of oil to be recovered on the reservoir scale. However, there are significant scientific challenges in both experimental and computational quantification of wetting phenomena on the nanoscale. Experimentally, the challenge is controlling and characterizing extremely small amounts of liquids on sub-micron length scales. New measurement methods need to be developed in order to obtain high-quality data to be compared with simulation results. Computationally, the challenge is in the determination of adequate inter-molecular force fields, and accounting for multi-body effects requires molecular-level simulations including multiple fluids as well as surfaces. Such simulations strain computational resources. Nevertheless, an improved understanding of nanoscale phenomena to unlock trapped oil reserves demands combined experimental and computational investigation across multiple length scales. By investigating sub-micron oil droplets at an amorphous surface both theoretically and experimentally, we quantify local wetting properties at the nanoscale and probe the intrinsic wettability of the surface. The numerical simulations at the molecular level based on Classical Molecular Dynamics and Coarse-Grained Molecular Dynamics are compared with results obtained by means of high resolution microscopy. Our results demonstrate how the interactions between fluids and solids on the nanoscale determine the wetting behavior of the surface. The quantification of surface heterogeneities and chemical contaminants will enable the investigation of the effects of chemical additives such as polymers and nanoparticles on surface wettability. Ultimately, the results will be linked to mesoscale and macroscale enhanced oil recovery models.

Introduction

It is widely recognized that surface wettability plays a crucial role in any strategy adopted for Oil Recovery. A classic example is the well-known experiment of a pore doublet [Chatzis and Dullen 1983]: When a wetting fluid displaces a non-wetting fluid, a thinner channel branch shows a faster displacement than does a thicker branch, but both channels show similar displacement. The situation is different when a non-wetting fluid is forced into the pore doublet to displace the resident wetting fluid. In that case, the non-wetting fluid does not invade the thinner branch, displacing only the wetting fluid that was in the thicker branch. Porous media wettability strongly influences the immiscible displacement of a resident phase by an invading phase [Anderson 1987; Cuiec 1991]. In this experiment, the diameters of both channels are in the millimeter range. The role of surface wettability becomes even more important at the scales of micrometers or nanometers, i.e. the scales of rock pores.

Interactions between the solid media and liquids that determine the wettability of a surface are not well understood. The solid-liquid interactions are typically quantified by the measurement of contact angle, which is the angle where a liquid/vapor interface meets a solid surface. The contact angle is usually derived from the macroscopic sessile droplet profile, which is affected by many factors, such as roughness, surface heterogeneity, presence of chemical contaminants, and the effect of line tension. To isolate and quantify these effects, one needs an investigation of droplet profiles at the nanometer scale, where molecular liquid-solid interactions display the characteristics of the local chemical environment.

We have recently reported a measurement platform [Steiner 2015] for characterizing droplet profiles of spatially isolated, nanometer scale oil droplets. The experimental platform allows to perform Confocal Laser Scanning Microscopy (CLSM) from the underside of the sample and Atomic Force Microscopy (AFM) from the top. As schematically shown in Figure 1, by performing AFM and CLSM on the same droplet it is possible to determine the droplet topography (height resolution ~ 1nm) and contact area of the oil droplet at the surface (diameter resolution ~ 300nm) and establish the shape and volume of a sessile nanoscale droplet.

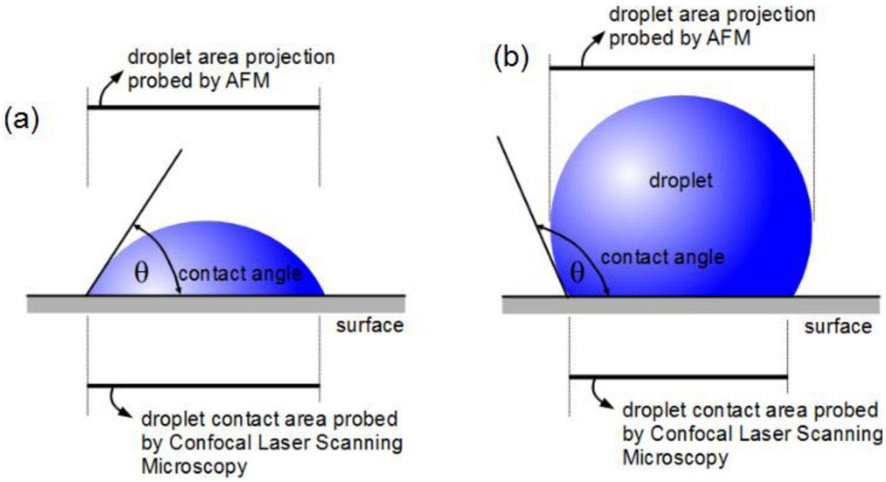

Figure 1—Schematic representation of droplet shape and the droplet area projection probed by atomic Force microscopy (AFM) and confocal laser scanning microscopy. (a) Contact angle smaller than 90 degrees, (b) contact angle larger than 90 degrees.

In the following, we perform numerical simulation of oil droplet shapes at the molecular level, based on Classical Molecular Dynamics (CMD) and Coarse-Grained Molecular Dynamics (CGMD), and we compare the simulation results with experimental droplet topographies. The molecular-level simulations provide a method to analyze how line tension and surface roughness affect the droplet profiles, and the experimental results are used to validate that the molecular interactions are correctly described in simulation.

Having the combined computational and experimental approach established, the platform can be used to quantify the wettability of various surfaces and to analyze how wettability is affected by chemical additives such as polymers and nanoparticles considered as agents for Enhanced Oil Recovery (EOR). Importantly, the approach enables the extraction and validation of critical parameters for computational propagation to larger length scales by means of appropriate multi-scale model linkage.

Presentation of Data and Results

We simulated in three dimensions the behavior of a decane droplet surrounded by nitrogen gas over a glass surface at the molecular scale by using CMD. The glass surface was implemented by using the

Amourphous Silicon Dioxide builder from the VMD package [Humphrey 1996], which creates a bulk glass. To obtain a suitable computational representation of a glass surface, a slab with thickness of about 4.2 nm was cut from the bulk. The dangling bonds from Silicon and Oxygen atoms were passivated with hydroxyl (OH) and hydrogen, respectively, resulting in a hydroxylated glass surface. In the next step, a cubic box (9 nm edges) containing 2257 decane molecules surrounded by 316 nitrogen molecules was placed onto the passivated glass slab. The molecules were distributed randomly in defined regions of the simulation box, see Figure 2 (a), and packaged by using the Packmol package [Matínez, 2009]. The dimension of the simulation box for the system consisting of glass, decane and nitrogen, is Lx = Ly = 28.5 nm, and Lz = 30 nm. These L dimensions were used in order to isolate the interactions between periodic images, and periodic boundary conditions were used in all directions. The number of decane and nitrogen molecules and the volume of the simulation box were chosen for reproducing the equilibrated density of pure nitrogen and pure decane, obtained by following the protocol for a specific temperature and pressure: a 1 picosecond run was performed for the NVE ensemble (micro canonical ensemble - constant Number of atoms, Volume and Energy), followed by 10 picoseconds for the NVT ensemble (canonical ensemble - constant Number of atoms, Volume and Temperature), and finally 2 nanoseconds for the NPT ensemble (isothermal-isobaric or grand canonical ensemble - constant Number of atoms, Pressure and Temperature). The protocols were performed for a cubic box (10 nm edge) containing 3089 decane molecules, and for a cubic box (20 nm edge) containing 160 nitrogen molecules. In both cases periodic boundary conditions were used in all three dimensions. The preliminary CMD simulations were performed first for decane and the isolated nitrogen systems, because the density of the glass/decane/nitrogen system cannot be equilibrated using the NPT ensemble. The reason is that the NPT ensemble does not contain enough nitrogen molecules to transfer energy from collisions (equivalent to pressure) to the glass surface. As a consequence, in the case of the glass/decane/nitrogen system we performed CMD simulations with the NVT ensemble only.

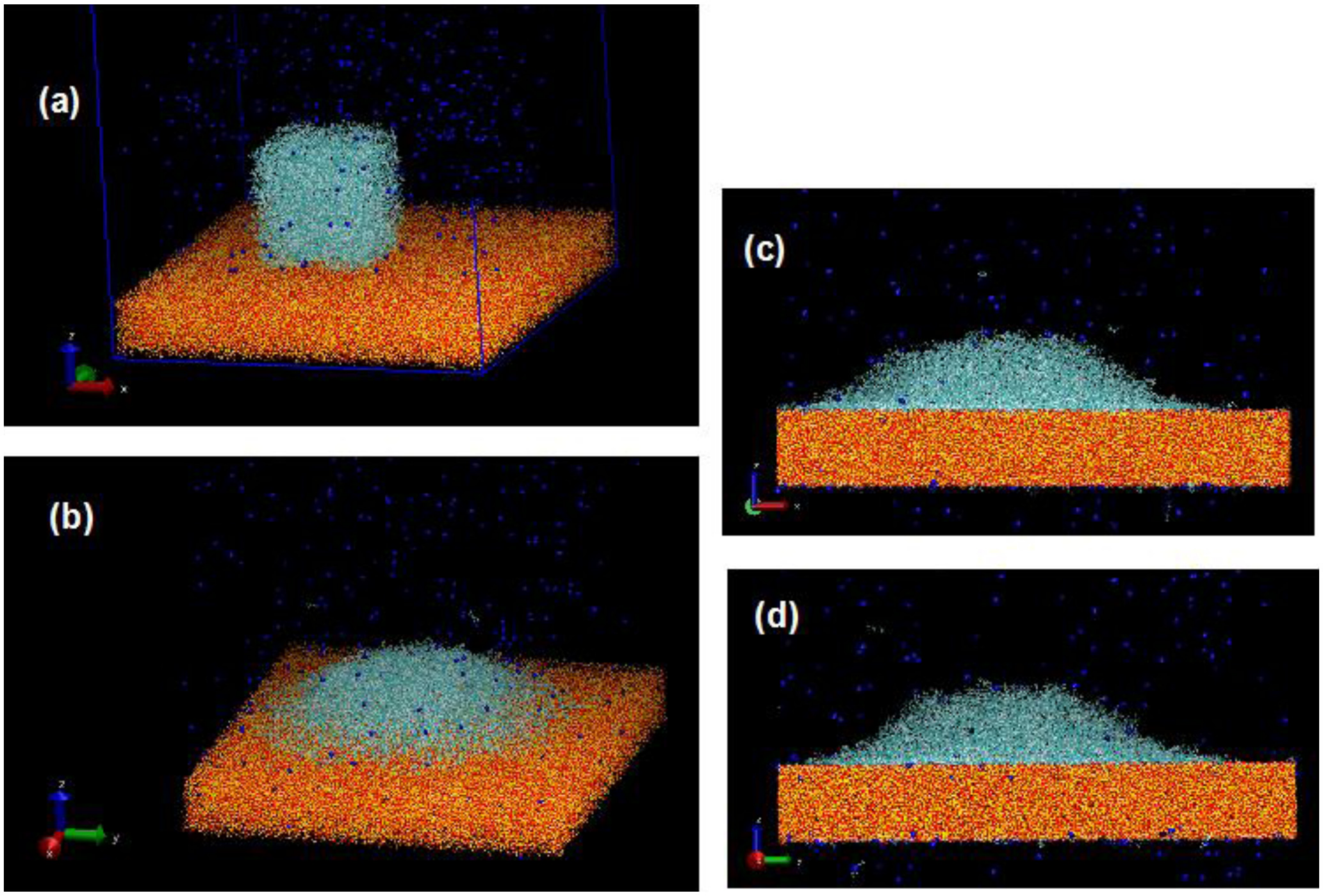

Figure 2—(a) Initial condition of Classical Molecular Dynamics Simulation (CMD). The modeled cube contains decane molecules (light blue), nitrogen molecules (dark blue), and Silicon (yellow) and Oxygen atoms (red) forming the glass substrate, respectively. (b), (c), (d) Side views of the steady-state geometry of a decane droplet on glass in nitrogen gas reached after 4 nanoseconds.

In the CMD simulations the interactions between atoms were modeled using a classical force field. For decane, CHARMM-based force field [Brooks 2009] parameters were used. For nitrogen the Lennard-Jones potential plus point of charge models [Potoff 2001, Hansen 2007] were used. For the simulation of the hydroxylated quartz slab we used the CHARMM Water Contact Angle (CWCA) force field [Cruz-Chu 2006]. In order to account for long-range electrostatic interactions, the reciprocal space particle particle particle-mesh (PPPM) method [Hockney 1989] was adopted. For all calculations we used a time step of 0.5 femtoseconds, a cutoff radius of 1 nanometer for van der Waals interactions, a temperature of 300 Kelvin and a pressure of 1 atmosphere. Note that temperature and pressure were chosen in order to compare the simulations with experimental results, which are conducted at ambient conditions. To control temperature and pressure, Nose-Hoover thermostats and barostats were used with a relaxation time of 0.1 picosecond and 1 picosecond, respectively. All CMD simulations were performed with the LAMMPS package [Plimpton 1995].

In Figure 2 we show the results of the CMD simulations for a decane droplet located at a glass surface and surrounded by nitrogen gas. After 2 nanoseconds the system reached a steady state and we continued the simulation for an additional 2 nanoseconds with the NVT ensemble. The simulated decane droplet shows a complex shape that apparently deviates from spherical curvature. Interestingly, in the three phase region (decane/glass/nitrogen) the formation of a decane precursor film occurs [Popescu 2012]. The presence of the precursor film and the lack of symmetry in the decane droplet, see Fig. 2 (c) and (d), poses a challenge for deriving a contact angle. To compare simulations with experimental results, we will refer in the following to droplet profile shape and to the ratio between droplet height and base diameter as suitable figures of merit.

Comparing droplet aspect ratios based on CMD simulations and AFM measurement across length scales differing by one order of magnitude, we obtain agreement: for an experimental droplet (height 60 nm, diameter 250 nm) the ratio of height to diameter is about 0.24 while for a much smaller decane droplet from our CMD simulations (height of 4 nm, 17.3 nm) the ratio is about 0.23. In order to perform and validate the comparison of experimental and simulation result on the same length scale we have performed CGMD [Fritsch 2013].

CMD simulations treat the system of interest with atomistic details, representing all atoms of the system as a point particle. The computational resources needed for evaluating the interactions in a simulation increases with the number of atoms, which limits both simulated length scale and time scale. CGMD is based on an effective description of the system with fewer degrees of freedom. Such a reduced model can be simulated using significantly less computational resources and thus extend achievable length scales and time scales. The typical approach is to represent a set of atoms with a single “superatom,” which we will refer to as CG bead in the following. This is accomplished through a mapping scheme which is a set of geometric rules that defines how CG beads are constructed from the all-atom simulation. An intuitive way to define these rules is to use the center of mass of a set of atoms to be represented as a CG bead. Figure 3 shows how we represent the atoms with CG beads in the cases of decane, nitrogen, and glass. For glass we define two types of beads: surface beads and bulk beads. A bulk bead represents 3 Silicon and 6 Oxygen atoms while a surface bead represents 3 Silicon, 6 Oxygen, and 2 Hydrogen atoms. The interaction potentials of CG beads are a priori unknown and must be determined by using a numerical routine based on all-atom CMD simulations. In the present case, the systematic, iterative Boltzmann inversion (IBI) numerical scheme from [Fukuda 2013] was adapted. In this method, effective pair potentials between CG beads are determined from all-atom CMD with an iterative refinement procedure. For the interaction between decane beads, the MARTINI coarse-grained force field was used [Marrink 2007].

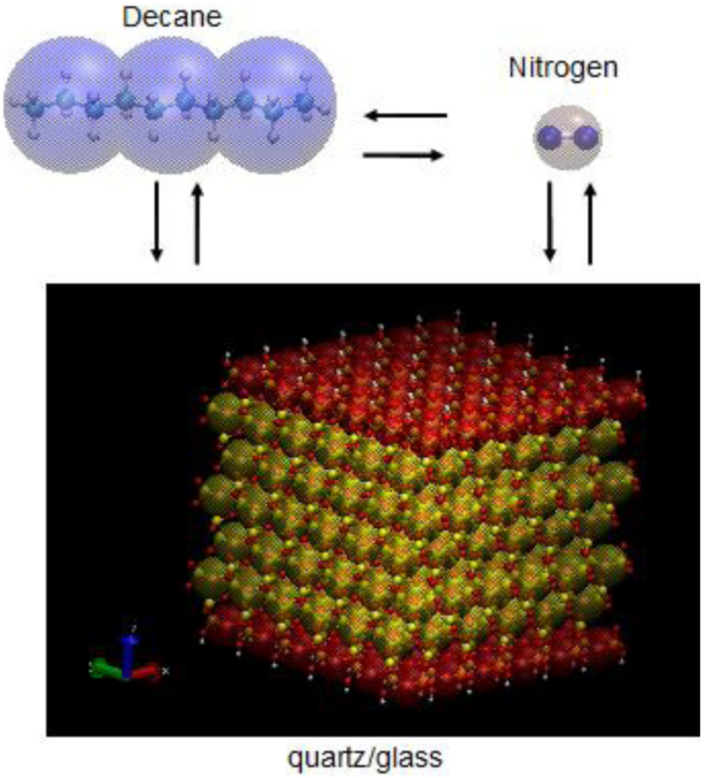

Figure 3—Schematic representation of coarse-grained (CG) mapping from an all-atom representation of the model system which is shown in Figure 2. The CG beads are visualized as transparent spheres.

In Figure 4, we show the results of CGMD simulations with the NVT ensemble at a temperature of 300 K. The dimensions of the simulation box are $L_x = L_y = 150$ nm and $L_z = 100$ nm. As the initial condition, Fig. 4 (a), a cube (57 nm edges) containing 591,657 packaged decane molecules (corresponding to 1,774,971 decane beads) is located on top of a glass surface containing 170,136 surface beads and 255,204 bulk beads, surrounded by 50,365 nitrogen beads. Fig. 4 (b),(c) show the steady state of a decane droplet on glass, which was reached after 9 nanoseconds. As a key result, the decane droplet topography obtained by the CGMD simulation is similar to the topography obtained by both CMD simulations and AFM measurements. The similarity to the CMD results indicates that the upscaling/linkage parameters from all-atom to coarse-grained methods are capturing well the dominant physical interactions. Moreover, the decane droplet profile in Fig. 4 (c) shows the presence of the precursor film [Popescu 2012] which is consistently observed in CMD simulations and the AFM measurements. The scale independent ratio of height to diameter (droplet height 32 nm, droplet diameter 140 nm) for CGMD is 0.23, as it is for the CMD result and close to the AFM result of 0.24.

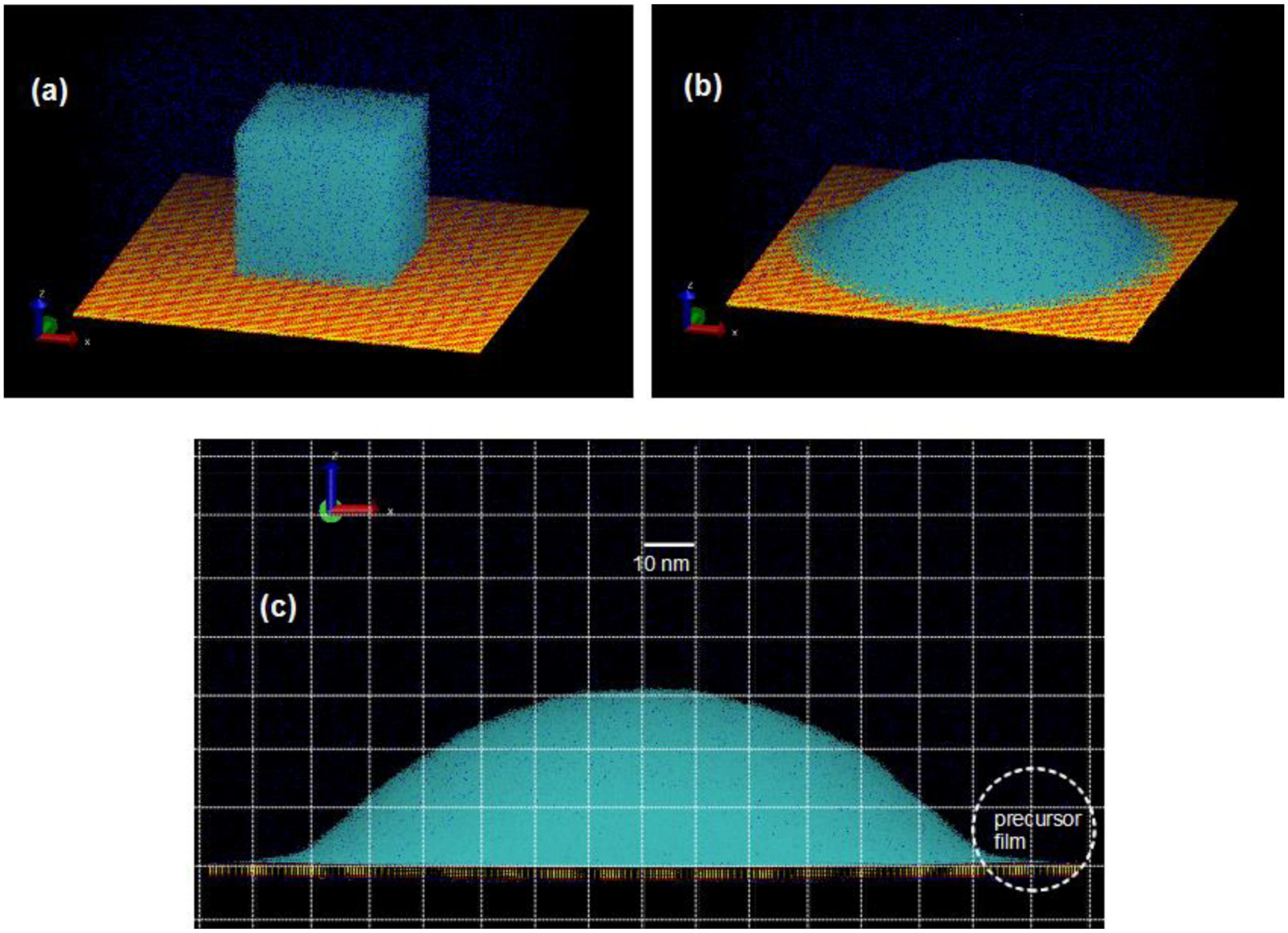

Figure 4—Coarse-Grained (CG) beads representation. Decane (light blue), Nitrogen (dark blue), and surface (red) and bulk (yellow) glass beads, respectively. (a) Initial simulation condition. (b) 3D view of decane droplet after 9 ns of Coarse-Grained Molecular Dynamics (CGMD) simulations based on NVT ensemble. (c) Side view of (b).

The droplet's aspect ratio provides a straightforward metric for comparison of droplets across multiple scales. To compare the shapes of the droplets it is, however, necessary to evaluate further their profiles. In order to quantify the droplet shape we fit model functions to both simulated droplet shapes and to the measured topography. We chose a model function that consists of an expansion in Bessel functions of the first kind, with the radial coordinate scaled by an ellipse. The fit results are shown in Fig. 5. For three droplets studied here, a sum over the first five Bessel functions results in a reasonable agreement with the data, with maximum fit residuals varying between 10% and 5% of the droplet height, and the majority of residuals less than 5% of the droplet height. The droplet shape can thus be represented by five expansion coefficients, c_0 through c_4, which can be compared across scales by normalizing to the droplet's peak height, which is equal to c_0. Figure 5(d) plots the normalized expansion coefficients for the three droplets studied here. The relative contributions of the five Bessel modes is fairly consistent among the three droplets, and based on our model, the measured droplet, which has a base radius of approximately 150 nm, is closer in shape to the larger simulated droplet of base radius 70 nm than it is to the smaller simulated droplet of base radius 8.65 nm. While the variation of droplet shapes across various length scales is subject to further investigation, our results demonstrate that nanoscale physics and chemistry need to be included in order to satisfactorily describe surface wetting phenomena on the nanoscale.

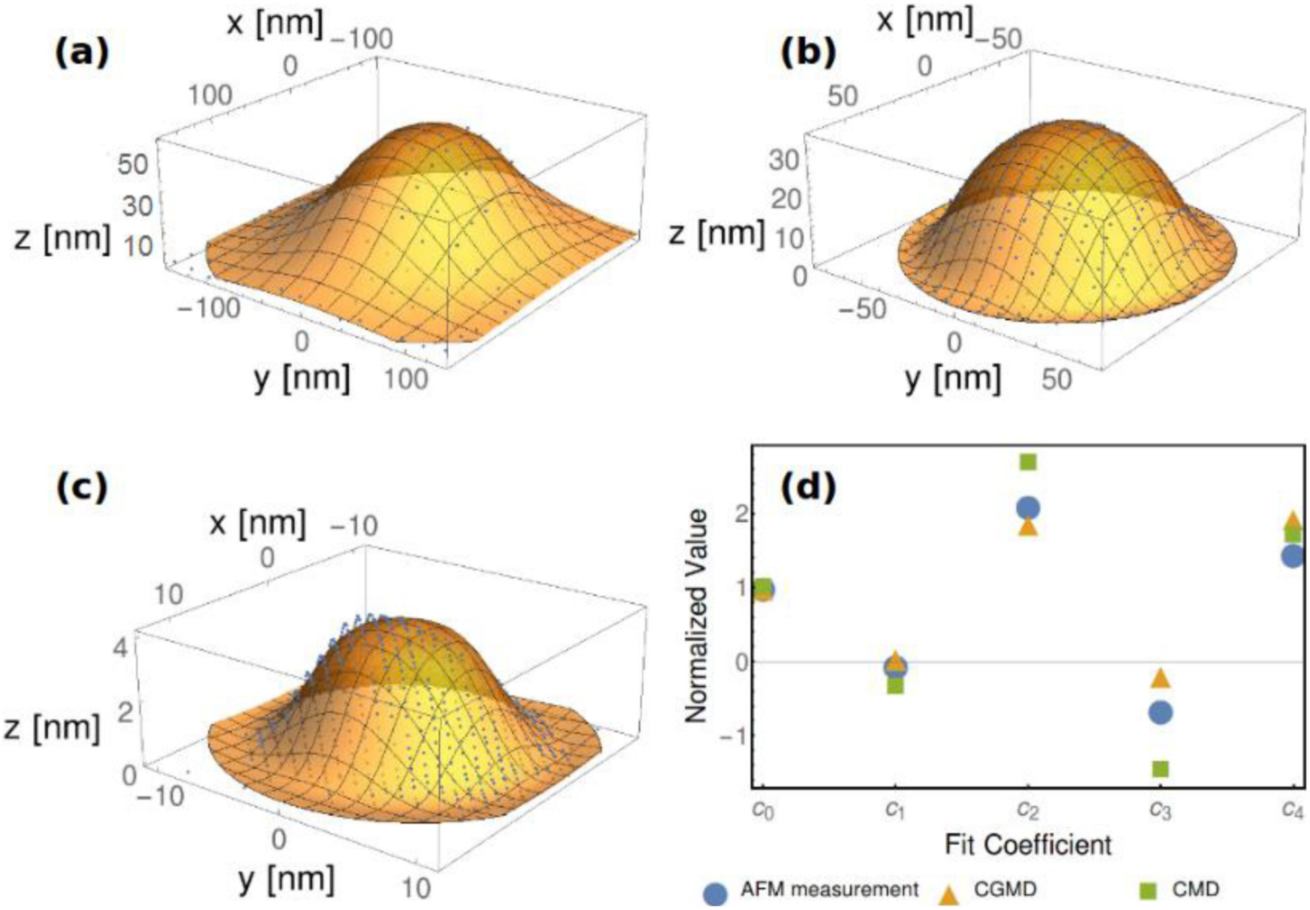

Figure 5—(a), (b) and (c) Model fits to the surfaces of decane droplets taken from AFM measurements, CGMD, and CMD simulations, respectively. Points are obtained from experimental measurements and numerical simulations, while the surfaces represent the expansion in Bessel functions. (d) Comparison of expansion coefficients for model fits to experimental data (blue dot), Coarse-Grained Molecular Dynamics data (dark yellow triangle), and Classical Molecular Dynamics Simulations data (green square).

Conclusions

In summary, a comparison between computational simulations and atomic force microscopy measurements of oil droplet profiles reveals that it is possible to isolate and quantify the effects of surface heterogeneity, chemical contaminants, line tension, and roughness at the nanometer scale. Moreover, the comparison shows that the Classical Force Fields used for performing the molecular dynamics simulations capture the interactions between oil molecules and the glass surface. Based on the agreement between the aspect ratios (height divided by the base droplet diameter) and model fits to the droplet surface topography we can conclude that: (i) the Force Fields from Classical Molecular Dynamics describe well the non-bonded (dispersion) interactions between decane/nitrogen and the glass surface; (ii) the upscaling parameters linking all-atom Classical Molecular Dynamics to the coarse-grained system capture the main interactions; (iii) for droplets with base diameters larger than 10 nm line tension phenomena are negligible; and (iv) relatively small surface features do not significantly influence the droplet shape. In conclusion, the combination of experiment, data analysis, and computational simulation is a powerful approach for quantifying wetting properties at the nanometer scale and will benefit the design, synthesis, and test of novel enhanced recovery agents for enhanced oil recovery.

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