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Recent advances in estimating contact angles using molecular simulations and enhanced sampling methods

Hao Jiang and Amish J Patel



The contact angle between a solid surface and the interface between two coexisting fluids, which characterizes the relative preference of the surface for one fluid over another, plays an important role in many areas of science and technology. In recent years, significant progress has been made in both our understanding of contact angles estimated using molecular simulations, and our ability to perform such estimation with greater accuracy and efficiency. In this review, we highlight recent advances in these areas with a focus on two simulation approaches, which employ droplet geometries and free energies, respectively, for estimating contact angles.

Address

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

Corresponding author: Patel, Amish J. (amish.patel@seas.upenn.edu)

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Introduction

Wetting of solid surfaces by fluids is a ubiquitous phenomenon that is of interest across many disciplines, including but not limited to surface science, materials characterization, oil and gas recovery [1]. Molecular simulations offer a promising route to characterize surface wetting, and have long been used for this purpose. However, with the proliferation of high-performance computing and the development of force fields that afford quantitative agreement with experiments, the last decade has seen a resurgence in the modeling and simulation of wetting phenomena. Molecular simulations are also capable of providing valuable insights into the relationship between the microscopic characteristics of a surface and its wetting properties; such insights can, in turn, facilitate the design of novel materials, such as superhydrophobic surfaces, membranes for oil-water separation, and polymer separators for batteries. In this review, we focus on classical molecular simulations of wetting properties, and for the sake of concreteness, we further focus on solidliquid-vapor systems, wherein the preferential wetting of a solid by a liquid relative to its coexisting vapor is of interest. The wettability of the solid by the liquid can then be quantified using the interfacial tensions (γ) between the solid (S), liquid (L) and vapor (V) phases, and in particular using the wetting coefficient, $k \equiv (\gamma_{SV} - \gamma_{SL})/\gamma_{VL}$. For macroscopic droplets, k can be related to the angle, θ_{Y} , formed by a liquid droplet in contact with the solid surface, through the Young's equation as: $k = \cos \theta_{Y}$; a detailed discussion of Young's equation can be found in ref. [2].

Broadly speaking, there are two categories of simulation methods that are typically used to calculate $\theta_{\rm Y}$. In the first group of methods, a sessile droplet is simulated on a solid surface, and the contact angle is extracted from the average droplet shape [3,4]. The second group of methods employ enhanced sampling techniques to estimate a free energy that depends on the wetting coefficient, k [5]. In this review, we focus on these two groups of simulation methods for estimating $\theta_{\rm Y}$, and in particular on methodological developments in the last five years. The rest of the paper is structured as the following: in section 2, we review recent advances in our understanding of contact angles estimated from droplet geometries, and highlight the finite size effects that must be considered when using such approaches. In section 3, we discuss and compare different methods that use free energy calculations to estimate $\theta_{\rm Y}$. We conclude with a summary of the methods discussed here.

Estimating contact angles from droplet geometries

The sessile droplet method, commonly used for the experimental determination of contact angles, can also be used in molecular simulations. In this method, a liquid droplet is placed on a surface, and allowed to equilibrate until it attains a well-defined shape. Although the droplet shape undergoes substantial fluctuations in the simulations, the contact angle is obtained by averaging over these fluctuations, and estimating the angle, θ_D , between the surface and the tangent to the average droplet shape at three phase contact. In practice, either a spherical (Figure 1-I) or a cylindrical droplet (Figure 1-II) can be used to estimate θ_D . Since it is straightforward to simulate a liquid droplet on a solid surface, and to characterize its geometry, the sessile droplet method is particularly easy to use, making it a popular approach for estimating contact angles [6-11]. However, care must be exercised to equilibrate the droplet shape [12^{••}], and to account for



The contact angle (θ) can be estimated using the shape of either a (I) spherical or a (II) cylindrical droplet simulated on solid surface. The radius of the 3-phase contact line (blue dashed line) is denoted by *a*, and the droplet base radius by r_b . For the cylindrical droplet, the length of the contact line is independent of the droplet shape. (III) Schematic illustrating how the contact angle estimate (θ_D) depends on a somewhat arbitrary choice of the contact plane; θ_D changes from θ_1 to θ_2 as the location of the contact plane is moved up by δh ; the droplet radius is denoted by r_d . (IV) Schematic illustrating linear fits (dashed lines) to $\cos \theta$ versus 1/a; adapted from ref. [15**] with permission from AIP Publishing. Finite size effects tend to be more pronounced for systems with stronger surface-fluid interactions [15**].

finite size effects [13,14] and systematic errors [15^{••}] that are unavoidable when using this approach. Although the droplet shape tends to a spherical (or cylindrical) cap at equilibrium, it has been shown that the corresponding relaxation time can be quite long (on the order of 100 ns) [16[•]]. To circumvent this challenge, a number of recent studies have introduced ways to estimate contact angles from instantaneous droplet geometries. Santiso et al. proposed a surface meshing technique to estimate the local contact angle at all points along the three-phase contact line [17]. Khalkhali *et al.* employed a convex hull algorithm to represent the droplet surface using triangles, and the angles between vectors normal to the triangles and solid surface were used to obtain a distribution of θ_D values [18[•]]. Finally, Ravipati et al. used a smeared droplet density to identify instantaneous droplet interfaces, and estimate the corresponding θ_D -values [16[•]].

Finite size effects

For the nanoscale droplets that must be employed in molecular simulations, the balance of forces isn't determined by the interfacial tensions alone, but can also be influenced by the line tension, τ , which is defined as the excess free energy per unit length of the three-phase contact line. Thus, contact angles obtained from droplet geometry, θ_D , can differ from θ_Y , and for spherical [19], where a is the radius of the contact line. Indeed, a number of simulation studies have found $\theta_{\rm D}$ to depend on droplet size [13,14]. However, the magnitude of such finite size effects arising from line tension are not well characterized; in particular, both the value and the sign of τ , as well as its dependence on the surface or the fluids in question remain poorly understood. Simulations have reported τ -values differing by orders of magnitude [7,20]. Moreover, the vapor-liquid surface tension of a nanoscopic spherical droplet deviates from that of a macroscopic droplet (γ_{VL}^{∞}) , varying with the droplet radius, r_d , as, $\gamma_{VL}(r_d) = \gamma_{VL}^{\infty}(1 - 2\delta/r_d)$, where δ is the Tolman length [21]. Along these lines, the line tension, τ , ought to also depend on the contact line radius (a); the notion of a line tension stiffness has been introduced to admit such a dependence. Thus, $\theta_{\rm D}$ ought to depend not only on the line tension, but also on the Tolman length and the line tension stiffness; alternatively, τ in the modified Young's equation can be viewed as an effective line tension rather than the pure line tension representing a free energy per unit length of the contact line [22,23]. The effective line tension then includes the contribution from the pure line tension, the Tolman length, and the line tension stiffness.

droplets in particular, the Young's equation modified to account for line tension is given by: $\cos \theta_{\rm D} = k - \tau / (\gamma_{VI} a)$

Important insights into some of these contributions have been provided by recent studies that investigate how $\theta_{\rm D}$ varies with size. Zhang et al. [15^{••}] studied spherical water droplets on Lennard-Jones (LJ) substrates with varying LJ-water attractions, and found that $\theta_{\rm D}$ has a stronger dependence on contact line radius (a) for hydrophilic surfaces than for hydrophobic surfaces; see Figure 1-IV. Kanduc estimated $\theta_{\rm D}$ using both spherical and cylindrical water droplets (that are infinitely long due to periodic boundaries) on self-assembled monolayer surfaces with varying polarities [12**,24]. Similar to the findings in Ref. [15^{••}], estimates of θ_D were found to depend on droplet size, with the dependence being more pronounced for hydrophilic surfaces with higher polarities. Interestingly, despite the fact that cylindrical droplets have an infinitely long contact line radius (1/a=0), estimates of θ_D were found to depend on the droplet base radius (r_b in Figure 1 - II); the dependence was nevertheless found to be weaker than that for spherical droplets.

Systematic errors in θ_{D}

Although it is easy to extract contact angles from droplet shapes, doing so requires that a contact plane be specified, where the tangent to the droplet surface is drawn to estimate $\theta_{\rm D}$ [25]. However, the location of the solid-liquid interface can't be defined unambiguously on molecular length scales. The choice of the contact plane thus becomes somewhat arbitrary, and as shown in Figure 1-III, estimates of $\theta_{\rm D}$ depend on this choice. Interestingly, Zhang *et al.* found that the different estimates of $\theta_{\rm D}$ obtained using different three-phase contact planes, all converge to the same macroscopic contact angle (θ_Y) upon extrapolating to infinite contact line radius (1/a = 0)[15^{••}]. This observation can be rationalized by recognizing that the uncertainty in $\cos \theta_{\rm D}$ arising from a corresponding uncertainty of δh in the contact plane is proportional to $\delta h/r_d$, where r_d is the radius of the droplet [22]. Thus, the lack of a unique prescription for choosing the contact plane introduces an inherent uncertainty in estimates of $\theta_{\rm D}$, with the uncertainty being particularly significant for small droplets. Moreover, for liquid droplets consisting of a given number of molecules, the ambiguity in the determination of $\theta_{\rm D}$ is expected to be more pronounced for hydrophobic surfaces, which support droplets with smaller radii, than for hydrophilic surfaces.

Although contact angles can be readily estimated from droplet geometries, it is important to recognize that such estimates, θ_D , can differ from the equilibrium macroscopic contact angle, θ_Y , and that such differences can be substantial especially if small droplets are employed. Compared with spherical droplets, θ_D obtained using cylindrical droplets tends to display smaller finite size corrections, likely due to a smaller contribution from line tension effects. Systematically varying droplet size, and extrapolating the θ_D -values thus obtained to infinitely large droplets, provides a way to obtain accurate estimates of $\theta_{\rm Y}$.

Estimating contact angles using free energy calculations

In this approach, molecular simulations are combined with enhanced sampling techniques to characterize a wetting process and calculate the corresponding free energy change, which is related to the wetting coefficient $k \equiv \cos \theta_{\rm Y}$). Although different simulation algorithms (molecular dynamics or Monte Carlo), enhanced sampling schemes, and processes can be employed towards this end, some may be more judicious than others, depending on the properties of the surface and the fluids of interest as well as the interactions between them. Below we describe recent methods for obtaining contact angle estimates ($\theta_{\rm F}$) from free energy calculations, as well as the processes and algorithms they employ; we also discuss the conditions under which it is suitable to employ these methods. Although free energy calculations are more involved than simulations of droplets [5,26-28,29°,30,31°, we elaborate on why they also tend to provide contact angle estimates that are more accurate.

Characterizing interface potentials using Monte Carlo simulations

Enhanced sampling methods have been used to calculate interface potentials, which quantify the excess free energy of a fluid film in contact with a solid surface [32]. Originally designed for grand canonical Monte Carlo (GCMC) simulations, the interface potential method has two variants; namely, the drying potential and the spreading potential [5,33]. In the drying potential method, the solid surface of interest is placed in contact with a liquid film; the surface is then systematically (reversibly) dried, so that it is eventually in contact with a film of vapor (Figure 2-I). To carry out this process, the fluid is sandwiched between the surface of interest and a "sticky" wall that has a strong, favorable interactions with the fluid. By decreasing the chemical potential of the fluid in a GCMC simulation (and through the corresponding deletion of fluid molecules), the surface is systematically dried, and a vapor film forms near the surface; the corresponding surface excess free energy is obtained as a function of the vapor film thickness (or overall fluid density) using the transition matrix MC or similar sampling algorithms [34]. For partially wetting surfaces, the surface excess free energy exhibits a minimum at a small film thickness (corresponding to the wetted surface), and a plateau at large film thicknesses (corresponding to a macroscopic vapor film). Because the surface-liquid interface is replaced by a surface-vapor interface and a vapor-liquid interface in the drying potential method, the free energy difference per unit surface area between the plateau and the minimum is given by: $\Delta F_{dry} = \gamma_{VL} + \gamma_{SV} - \gamma_{SL} = \gamma_{VL}(1 + k) = \gamma_{VL}$ $(1 + \cos \theta)$. For the surface of interest to undergo drying,



Figure 2

Schematic representation of the (I) drying and (II) spreading interface potentials obtained using GCMC simulations. Adapted from ref. [5] with permission from AIP Publishing. (III) Schematic illustrating the dry-surface method, wherein surface-fluid interactions are turned off reversibly to allow estimation of ΔF_{vac} using MD simulations. Reprinted with permission from ref. [40]; copyright (2015) American Chemical Society. (IV) Schematic illustrating of the method introduced by Netz and co-workers for estimating the spreading potential using MD simulations [29**,44]. Reprinted from ref. [29**] with permission from AIP Publishing.

it must have weaker interactions with fluid than the "sticky" wall employed; the drying potential is thus well suited for studying the wetting properties of solvophobic surfaces, i.e., systems with weak surface-liquid interactions.

In contrast, the spreading potential method is better suited for studying solvophilic surfaces. In this method, a vapor film is placed between the solid surface of interest and a "hard" repulsive wall, and the surface is systematically wetted, so that a liquid film forms near the surface (Figure 2-II). The surface excess free energy as a function of the liquid film thickness displays a minimum at a small film thickness, and a plateau at large film thicknesses, with the corresponding free energy difference per unit surface area between the plateau and the minimum being given by: $\Delta F_{wet} = \gamma_{SL} + \gamma_{VL} - \gamma_{SV} = \gamma_{VL}(1 - k)$ $= \gamma_{VL}(1 - \cos \theta)$. Thus, if the fluid vapor-liquid interfacial tension, γ_{VL} , is known, θ can be readily estimated from the values of either ΔF_{dry} or ΔF_{wet} , obtained from the drying and spreading potential methods, respectively.

Importantly, in the interface potential method (for both the drying and spreading potential variants), neither the initial state nor the final state feature three-phase contact lines or curved interfaces (Figure 2-I,II). Thus, the corresponding free energy differences (ΔF_{dry} and ΔF_{wet}), are unaffected by line tension or curvature effects. Moreover, in contrast with approaches based on droplet geometry, which require a somewhat arbitrarily chosen contact plane location, the free energy differences extracted using the interface potential method are unambiguous, and so are the contact angles estimates thus obtained. Finally, the interface potential can also shed light on whether the interfacial system undergoes a first- or second-order wetting transition [5]. Due to these advantages, the drying and spreading potential methods have been used to study the wetting properties of a wide variety of systems, ranging from water on non-polar surfaces [35] and ionic liquids on non-ionic substrates [36], to liquid-liquid-solid systems, such as octane and water on silica surfaces [37^{••}].

Interface potential estimation using molecular dynamics simulations

Due to their ability to sample configurations with systematically varying fluid densities (and thereby film thicknesses), simulations that are performed in the grand canonical ensemble (e.g., GCMC simulations) are particularly well suited for estimating interface potentials. Although MD simulations can be more computationally efficient than MC simulations for large or complex fluid molecules, running MD simulations in the grand canonical ensemble is not straightforward, making it challenging to estimate interface potentials using MD simulations. To address this challenge, a number of free energy methods have recently been developed to facilitate characterization of wetting properties using MD simulations.

In the phantom-wall method of Muller-Plathe and coworkers, a repulsive wall that interacts only with the fluid molecules (but not the solid) is reversibly moved away from the surface, transforming the solid-liquid interface into a solid-vacuum interface [28]. The corresponding free energetic cost of the process per unit surface area is $\Delta F_{vac} = \gamma_{S,}$ $V_{ac} + \gamma_{VL} - \gamma_{SL} = \Delta F_{dry} + (\gamma_{S,Vac} - \gamma_{SV}) [28,38,39^{\bullet\bullet}].$ The dry-surface method of Leroy and Muller-Plathe employs a closely related process, wherein surface-fluid attractions are turned off (Figure 2-III), and the resulting free energy change, ΔF_{vac} , is estimated using MD simulations [40,41^{••}]. Due to the ease with which the dry-surface method can be implemented in different MD simulation packages (without modification of their source codes), it has been widely used to characterize the wetting properties of solid surfaces, and to develop force fields parameters for such surfaces [41^{••},42,43]. We note that the both phantomwall and dry-surface methods estimate $\Delta F_{\rm vac}$, which approximates ΔF_{dry} well only when $\gamma_{S,Vac} \approx \gamma_{SV}$. Such an assumption is true for surfaces that have weak interactions with the fluid, e.g., water near hydrophobic surfaces. In contrast, when the solid surface has strong, favorable interactions with the fluid, there is substantial adsorption of fluid molecules from the vapor onto the solid surface, and γ_{SV} is expected to be smaller than $\gamma_{S,Vac}$.

In contrast with the phantom-wall and dry-surface methods, which seek to estimate ΔF_{dry} , and are well suited to the study of hydrophobic surfaces, methods that attempt to estimate ΔF_{wet} are expected to be better suited for characterizing the wetting behavior of strongly hydrophilic surfaces. To this end, Kanduc and Netz proposed a scheme for estimating the spreading potential using MD simulations, and used it to study water on selfassembled monolavers of alkane chains terminated with polar head groups [29^{••},44]. In this scheme, water is confined between the surface of interest and a repulsive "hard wall" as was done in the MC simulations [5] (Figure 2-II). However, to estimate the excess surface free energy as a function of water film thickness (or equivalently, water density) using MD simulations in the canonical ensemble (with a constant water density), the authors perform independent free energy calculations for every water density; i.e., every symbol in Figure 2-IV represents a separate free energy calculation, requiring more than 40 biased simulations. Although computationally demanding, the method provides access to the spreading potential using MD simulations, and is able to capture the transition from partial to complete wetting as surface polarity is increased.

Surface wetting and interfacial properties using enhanced sampling (SWIPES)

Independent of whether GCMC or MD simulations are used, a characteristic feature of the process employed by methods based on the interface potential is the creation of vapor-liquid (or vacuum-liquid) interfaces. Although such interfaces are planar at the end of the process, their formation tends to proceed through different interfacial structures that display in-plane inhomogeneity (Figure 3-I) [45–50]. Transitions between such inhomogeneous structures can give rise to hysteresis, and care needs to be taken to minimize its impact on the estimation of free energy, e.g., by using temperature expanded ensembles [47] or by increasing the number of biased simulations used [29^{••}].

To circumvent the hysteresis associated with the formation of vapor-liquid interfaces, we recently introduced an enhanced sampling method called "SWIPES" [31^{••}]. As shown in Figure 3-II, SWIPES employs a process in which the solid surface is systematically wetted by moving (or "swiping") a vapor-liquid interface along the surface (no new interface is created). In particular, a biasing potential is used to increase the number of fluid molecules, N_v , in an observation volume, v (dashed line in Figure 3-II), in order to wet surface [27]. Although the system setup features both a curved vapor-liquid interface and three-phase contact lines, neither the curvature of the interface, nor the length of the contact line changes during the process; thus, the free energy of the process is unaffected by Tolman length or line tension effects. The free energy per unit surface area wetted is thus simply equal to $-\gamma_{\rm VL} \cos \theta$. Estimating the wetted surface area, which is proportional to the distance the vapor-liquid interface moves along the solid surface, ΔH , and the





(I) Simulation snapshots highlighting the various inhomogeneous structures that form when the fluid (green) dewets the solid (black). Reprinted with permission from ref. [45]; Copyright (2008) American Chemical Society. Transitions between different dewetted morphologies can result in hysteresis and complicate estimation of the corresponding free energy. (II) Schematic representation of the SWIPES method, which circumvents such hysteresis effects by employing a process that translates a vapor-liquid interface along the solid surface. Reproduced from ref. [31**] with permission from The Royal Society of Chemistry. By biasing the number of fluid molecules, N_v , in an observation volume, v (dashed lines), and estimating the corresponding free energy, ΔF , and surface area wetted by the fluid, which is proportional to the distance, ΔH , that the interface moves, SWIPES enables estimation of $\gamma_{VL} \cos \theta$ [31**].

corresponding free energy, ΔF , then enables estimation of the surface wetting properties. The SWIPES method can be used in conjunction with both MC and MD simulations, as well as to characterize the wetting properties of systems with a wide range of surface-fluid interactions, from fully dewetting and partially wetting to fully wetting surfaces. Moreover, by using a purely repulsive (fully dewetting) surface, the fluid vapor-liquid interface tension, γ_{VL} , can also be estimated using SWIPES. Finally, SWIPES is relatively straightforward to implement and also computationally efficient, providing reasonable estimates of $\cos \theta$ in roughly 5 nanoseconds of simulation time (Figure 6 of Ref. [31^{••}]).

Conclusions

In this review, we discuss different approaches for calculating contact angles using classical Monte Carlo or molecular dynamics simulations. We focus the discussion on two types of approaches, which rely on a characterization of droplet geometries and free energies, respectively. In first approach, equilibrium simulations of liquid droplets are performed, and contact angles are obtained from a characterization of droplet shapes. Although these approaches are straightforward to implement, care must be exercised to account for finite size effects that may arise from line tension, interfacial curvature, or a somewhat arbitrary choice of the solid-fluid contact plane; errors arising from such effects can be mitigated by using large, cylindrical droplets or by systematically varying droplet sizes and extrapolating to infinitely large droplets.

Methods based on free energy calculations are not as straightforward as the droplet simulations, but tend to provide more accurate contact angle estimates. A prominent approach in this category involves estimation of interface potentials or surface excess free energies; the drying and wetting potential methods variants of the interface potential method are well suited for studying systems with weak and strong surface-fluid interactions, respectively [5,33]. Although interface potentials can be readily estimated using Monte Carlo simulations in the grand canonical ensemble, it is challenging to estimate the pertinent free energies using molecular dynamics simulations in the canonical ensemble; we discuss a number of recent methods (e.g., dry-surface, phantom-wall) that have been developed to address this challenge [28,29^{••},40]. We also discuss a recent free energy method, SWIPES, that differs from methods based on the interface potential in its use of a process, which involves moving a vapor-liquid interface along the surface of interest to systematically wet the solid surface [31^{••}].

Disclosure

The authors declare no conflict of interest.

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