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Contact Angle Relaxation during Droplet Spreading: Comparison between Molecular Kinetic Theory and Molecular Dynamics

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The macroscopic behavior of the contact line during the spontaneous spreading of a droplet can be described in terms of microscopic quantities, specifically the substrate−liquid and liquid−liquid interactions. Here, for the first time, the results of molecular dynamics simulations of very large sessile drop systems are compared with the predictions of the molecular−kinetic theory of wetting. Good agreement is obtained, with both approaches yielding a consistent set of molecular parameters and macroscopic behavior which is consistent with experiments.

Introduction

When a liquid drop is placed in contact with a flat substrate, capillary forces drive the interface spontaneously toward equilibrium. As the drop spreads, the contact angle, θ, relaxes from its initial maximum of 180° at the moment of contact to its equilibrium angle, $\theta^0 > 0$ in the case of partial wetting or 0° if the liquid wets the solid completely. The dynamics of spontaneous spreading are usually described at the macroscopic level by an energy balance between a capillary driving force and the hydrodynamic resistance to spreading.[1−10] The results more or less fit master curves showing relationships between the radius of the base and time or between contact angle and time. The macroscopic parameters of these master curves are the surface tension and viscosity of the liquid and the volume of the drop. A similar relationship between the spreading rate and viscosity has been obtained[11] using a simplified treatment of the molecular−kinetic theory of viscous spreading given by Cherry and Holmes.[12]

In this article, we use the Blake and Haynes equation to describe the dependence of θ on contact line speed.[13] This equation is also based on molecular−kinetic theory but emphasizes surface effects rather than viscous flow. Although it neglects hydrodynamic aspects of flow and viscous dissipation near the wetting line, it links microscopic quantities such as the frequency and length of molecular displacements with the macroscopic behavior of the contact angle within the partial wetting regime. Good agreement is obtained with experiment,[13,14] but while the approach is fundamental and the resulting coefficients are reasonable, these coefficients can be obtained only by curve fitting and not a priori. Thus, we have no certain way of establishing their physical validity for a given system nor the conceptual validity of the molecular kinetic theory.

However, interactions on the molecular level are also the basis for molecular dynamics simulations. Starting from the well-known Lennard-Jones interaction between atoms and the dynamics given by Newton's equations, the position and velocity of every atom may be calculated. With the introduction of powerful computers, we are now able to simulate the spreading of a realistic droplet on top of a substrate.[15] Here we develop a method to extract contact angles from our simulations, thus leading to a direct microscopic description of the dynamics of contact angle relaxation. Starting from a spherical droplet placed in contact with a solid substrate, we simulate the droplet spreading toward its equilibrium configuration and contact angle. This approach allows us to verify the fundamental mechanism of wetting and provides us, for the first time, with an independent way to measure directly the microscopic parameters in the molecular−kinetic theory. This advance is what we would like to establish in this article.

Results and Discussion

Let us first review the molecular−kinetic theory.[13] According to this theory, the macroscopic behavior of the wetting line depends on the overall statistics of the individual molecular displacements which occur within the three-phase zone where the fluid−fluid interface meets the solid surface. The velocity of the wetting line is characterized by K, the frequency of molecular displacements, and λ, their average length. In simple cases, λ is the distance between two neighboring adsorption sites on the solid surface.[13] If K^+ is the frequency of molecular displacements in the direction of wetting and K^- is that in the reverse direction, then the net frequency is $K^{\text{net}} = K^+ - K^-$. The velocity of the wetting line is therefore given by $v = \lambda K^{\text{net}}$. At equilibrium, K^{net} is zero and $K^+ =$

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[1] Yin, T. P. *J. Phys. Chem.* **1969**, *73*, 2413.

[2] Strella, S. *J. Appl. Phys.* **1970**, *41*, 4242.

[3] Ogarev, V. A.; Timonina, T. N.; Arslanov, V. V.; Trapeznikov, A. A. *J. Adhes.* **1974**, *6*, 337.

[4] Karnik, A. R. *J. Photogr. Sci.* **1977**, *25*, 197.

[5] Tanner, L. H. *J. Phys. D: Appl. Phys.* **1979**, *12*, 1473.

[6] Starov, V. M. *Kolloidn. Zh.* **1983**, *45* (6), 1154.

[7] Chen, J. D. *J. Colloid Interface Sci.* **1988**, *122* (1), 60.

[8] Diez, J. A.; Gratton, R.; Thomas, L. P.; Marino, B. *J. Colloid Interface Sci.* **1994**, *168*, 15.

[9] de Gennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827.

[10] de Gennes, P. G.; Cazabat, A. M. *C. R. Acad. Sci.* **1990**, *310*, 1601.

[11] Dodge, F. T. *J. Colloid Interface Sci.* **1987**, *121* (1), 154.

[12] Cherry, B. W.; Holmes, C. M. *J. Colloid Interface Sci.* **1969**, *29*, 174.

[13] Blake, T. D.; Haynes, J. M. *J. Colloid Interface Sci.* **1969**, *30*, 421.

[14] Hayes, R. A.; Ralston, J. *Langmuir* **1994**, *10*, 340.

[15] De Coninck, J.; D'Ortona, U.; Koplik, J.; Banavar, J. R. *Phys. Rev. Lett.* **1995**, *74* (6), 928.

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$K^- = K^0$. Blake and Haynes assumed the driving force for the wetting line to be the out-of-balance surface tension force $\gamma_{LV}(\cos(\theta^0) - \cos(\theta))$, where γ_{LV} is the surface tension of the liquid. Using Eyring's activated-rate theory for transport in liquids gave the final relationship between θ and v as

$$v = 2K^0\lambda \sinh\left[\frac{\gamma_{LV}(\cos(\theta^0) - \cos(\theta))}{2nk_BT}\right] \tag{1}$$

where n is the number of adsorption sites per unit area, k_B is Boltzmann's constant, and T is the temperature. This molecular theory is independent of geometry. It has been routinely applied in the case of capillary displacement and for plunging tapes but may also be applied to spreading drops.

For small drops, gravity can be neglected and the shape of the spreading drop will approximate a spherical cap.[1] The geometry of a spherical cap is characterized by the following relationship:

$$r = \left[\frac{3V}{\pi}\frac{\sin^3(\theta)}{2 - 3\cos(\theta) + \cos^3(\theta)}\right]^{1/3} \tag{2}$$

where V is the drop volume, r is the base radius, and θ is the instantaneous contact angle. If we assume no evaporation, the volume is constant; hence,

$$\frac{\partial r}{\partial t} = -\frac{\partial \theta}{\partial t}\frac{(1 - \cos(\theta))^2}{(2 - 3\cos(\theta) + \cos^3(\theta))^{4/3}} \tag{3}$$

Equations 1 and 3 are a linked set of partial differential equations with two adjustable parameters: $a = 2K^0\lambda$ and $b = \gamma_{LV}/2nk_BT$. These equations can be solved numerically to give θ. We developed a program to find the values of a and b for the best fit to a given set of experimental data. The differential equations are solved with a fourth-order Runge–Kutta algorithm. The difference between the numerical data and the theoretical curve is then minimized with a downhill simplex method. The equilibrium contact angle is determined independently, by letting the drop spread until there are no further changes with time.

Let us now present our microscopic simulations based on molecular dynamics. The model is defined in terms of the interactions between the atoms. Two types of atoms have to be considered: fluid and solid. To characterize the interactions, we use Lennard-Jones potentials of the form $U_{ij} = C_{ij}d^{-12} - D_{ij}d^{-6}$ where ij stands for fluid or solid and d denotes the distance between the two atoms. For computational convenience, the tails of the potentials are cut off at the distance 2.5 in units of fluid core size. This means that we take into account only short range interactions. The coefficients C and D are related to the standard Lennard-Jones parameters ϵ and σ in the following way: $C = 4\epsilon\sigma^6$ and $D = 4\epsilon\sigma^{12}$. Most of the simulations were developed with $C_{ff} = D_{ff} = 1.0$, $C_{ss} = 35.0$, $D_{ss} = 5.0$, and $C_{sf} = D_{sf} = 0.3$, 0.4, or 0.5. In order to solve Newton's equations, we need to ascribe masses to the fluid and solid atoms. To give comparable time scales for the solid and liquid, we choose $m_{solid} = 50m_{fluid}$. To model the molecular structure of the liquid, we also add an extra interaction between adjoining atoms of the form $U_{conf} = D_{conf}d^6$ with $D_{conf} = 1.0$. Although this interaction is rather simple, it forces the atoms within one molecule to stay together and reduces evaporation considerably. The solid atoms are strongly pinned by an harmonic potential to sites on a one-layer fcc lattice; typically, we use 40 000 atoms to represent the wall. This provides an atomic representation of the substrate surface.

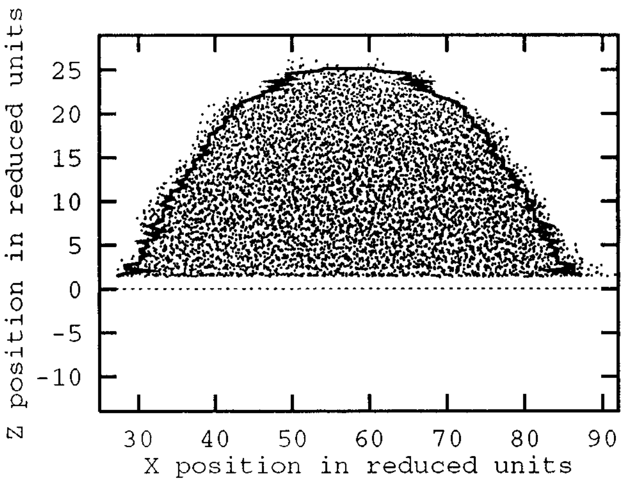

Figure 1. Computed profile of the drop based on the layer density analysis (solid line). The solid top layer is located at the height 1.7 (not shown).

Another set of 1600 16-atom chains is used to model the liquid droplet, which will be spherical far away from the solid surface. Once the two systems are equilibrated, we let the drop approach the substrate very slowly and observe the positions of the atoms as a function of time. Initially, we maintain the temperature of the complete system constant, but once the drop begins to spread, we keep the temperature of only the solid constant, so as to mimic the dissipation of energy between the solid and the liquid. The time is measured in standard units $(m\sigma^2/\epsilon)^{1/2}$. Although the model described above is very simplistic, it nevertheless contains the basic ingredients to reproduce the experimental results within realistic computation times.

To compute the associated contact angle, we proceed as follows. First, we subdivide the liquid droplet into several horizontal layers of arbitrary thickness. The constraint on the number of layers is provided by the need to maximize the number of layers whilst ensuring that each layer contains enough molecules to give a uniform density. For each layer, we locate its center by symmetry and compute the density of particles as a function of the distance to the center. We then locate the extremity of the layer as the distance where the density falls below some cutoff value, usually 0.5, as shown in Figure 1. To check the consistency of the method, different layer thicknesses and cutoff values were considered; these gave almost identical results.

These methods enable us to construct the complete profile of the drop and to determine how it evolves with time. The best circular fits through the profiles were always situated within the region where the density dropped from 0.75 to 0.25, except in the first few layers above the substrate. This indicates that the simulated drops always retain their spherical form during spreading, except very close to the solid surface. Indeed, we expect the profile to be perturbed in the vicinity of the solid for energetic and entropic reasons.[16] To avoid this problem, we investigated the profile as a function of the number of layers used, from top to bottom. Evidently, to reproduce the macroscopic thermodynamics of the drop, we need to consider enough layers and to stay sufficiently far from the substrate. The circular fit using all the experimental points except the last ten above the substrate leads to stable results for drops with more than 20 000 atoms. Thus, we are able to measure the contact angle θ as a

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(16) De Coninck, J.; Dunlop, F.; Menu, F. *Phys. Rev. E* **1993**, *47* (3), 1820.

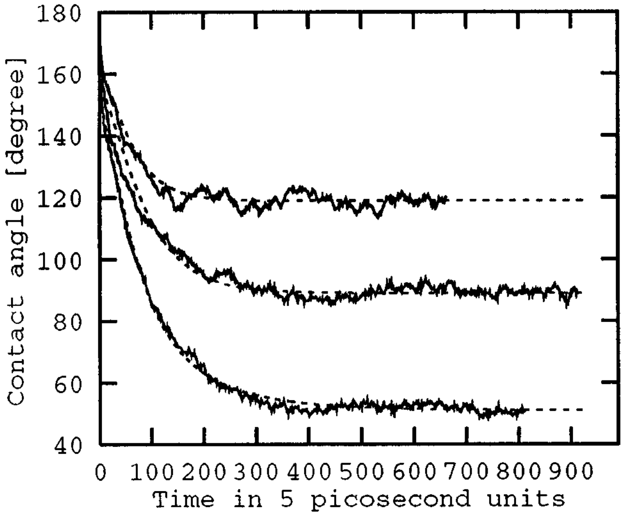

Figure 2. Dynamics of contact angle for three different liquid/solid interactions, from top to bottom C_{sf} = 0.3, 0.4 and 0.5.

function of the number of time steps during our simulations. Typical results are presented in Figure 2 for the three different interactions, where for the sake of clarity we have translated the curves to the same starting time, 0, at which the drop is just touching the wall in each of the three simulations. We have also plotted the best fit given by the molecular kinetic theory (dotted lines). If we arbitrarily choose the unit distance to be 5 Å, the unit mass to be 10 times the mass of hydrogen, and the temperature of the solid to be 300 K, then the time unit in the figure is 5 ps. The values chosen for these parameters do not affect the spreading behavior, but they are necessary to compare the values of a, b, and K^0 with true experimental results. Clearly, the equilibrium contact angle depends strongly on the solid−liquid interactions and decreases with increasing interaction, as expected.

The three computer experiments were fitted simultaneously, to find the best value of b for the three curves. The parameter b should be the same for all the experiments, since it depends only on the liquid and solid lattice characteristics and is independent of the interactions between solid and liquid. The resulting b is 0.21 ± 0.06. Because this value is relatively small, eq 1 will always be operating in its linear limit where v is proportional to $\gamma_{LV}(\cos(\theta^0) - \cos(\theta))$. We hope to extend the test to higher values of b in later simulations. The a values are shown in the Table 1. Also shown are the values for K^0, calculated from a, assuming that λ is equal to the lattice spacing. To estimate the probable errors, we looked at the variation of the parameters caused by perturbing the experimental data with random noise. The noise on the contact angle was uniformly distributed about the measured value with a range of ±5°. The results are qualitatively comparable with those of experiments using real liquids.[17]

Table 1. Relationships between the Parameters Obtained from Molecular Dynamics and Molecular−Kinetic Theory

$C_{sf} = D_{sf}$	θ^0 (deg)	a (m/s)	K^0 (10^{10} s^{-1})	K^0_{count} (10^{10} s^{-1})
0.3	119 ± 3	170 ± 36	14 ± 3	9.8 ± 1.2
0.4	89 ± 2	108 ± 18	8.6 ± 1.5	8.1 ± 1.8
0.5	51 ± 2	74 ± 6	5.9 ± 0.6	5.7 ± 1.8

With molecular modeling, we are also able to measure the jump frequency, K^0, directly. At equilibrium, we counted the number of molecular displacements per unit time, vertically into or out of the layer of liquid molecules adjacent to the solid surface. These vertical displacements effectively determine the velocity of wetting. A net flux into the layer causes the wetting line to advance whilst a net flux out of the layer causes the wetting line to recede. At equilibrium the net flux must be zero. Only displacements of length greater than 0.8λ were considered in order to avoid counting unsuccessful displacements where the atom simply made harmonic oscillations about its initial site. Varying the threshold for the displacements within reasonable limits does not significantly change the result. The number of jumps was divided by the local density to find the jump frequency per molecule. As expected, at equilibrium, $K^+ = K^- = K^0$, and the frequency is higher in the vicinity of the contact line. As shown in Table 1, the values for the counted K^0, denoted K^0_{count}, compare well with the frequencies obtained from the fitted curves. The jump frequency decreases with increasing solid−liquid interaction. This is expected because the liquid molecules are bound more strongly to the solid sites with higher solid−liquid interaction, resulting in less frequent displacements. The errors on the counted frequencies were estimated from the variation of K^0_{count}, over long periods at equilibrium.

In this article we have shown that a well-designed molecular dynamics simulation containing a sufficiently large number of atoms can be used to model the spreading of a liquid drop on a solid surface. We have also shown that the evolution of the drop may be modeled using the molecular−kinetic theory of wetting, or more precisely that the driving force behaves as $(\cos(\theta^0) - \cos(\theta))$. Furthermore, we have demonstrated that the effective molecular parameters in the theory are consistent with those arising directly from the simulation. These results provide strong support for the underlying validity of the molecular−kinetic theory of wetting. They also amply demonstrate the power of molecular dynamics simulations in relating the macroscopic dynamics to the microscopic properties of the system.

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(17) Blake, T. D. In *Wettability*; Berg, J. C., Ed.; Marcel Dekker: New York, 1993; p 251.