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A two-step Monte Carlo method for wetting on heterogeneous surfaces

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Abstract. A new Monte Carlo method is described for studying the equilibrium shapes of fluids on solid surfaces when the contact angles on the surface are smaller or equal to $\pi/2$. The method minimizes the energy of the system by consecutively applying two distinct annealing mechanisms. The method is tested for some simple analytically solvable cases and, as an example, applied to a more complex geometry.

1. Introduction

Wetting of a solid by a liquid in equilibrium with vapour phase is a commonly observed and used phenomenon in the natural and technological world. Since the pioneering work of Laplace [1] and Young [2] the problem has been extensively studied both from theoretical [3–5] and experimental [4–6] aspects. Although it has a long history, the spreading of a liquid over the surface of a solid remains a complex problem. The final shape of the liquid depends not only on the surface energies of the interfaces but also upon the roughness of the surface [7, 8] and the manner in which the liquid is placed on the solid [10–13]. Even if we consider smooth surfaces and neglect hysteresis effects the possible heterogeneity [14] in the contact angles on the surface could cause serious technical problems and in general the problem is unsolvable by analytical approaches only. In this sense, numerical methods or computer simulations are very useful. The problem is twofold: (i) what are the states of minimal energy of the system and (ii) what is the kinetic to reach them? In this paper we will address only the first aspect.

Fixing the boundaries of the fluid surface, and thus the contact interface between the fluid and the solid surface, the problem is numerically solvable in a very elegant manner by using the '*Surface Evolver*' elaborated by Braake [15, 16]. The '*Surface Evolver*', is free software accessible on the Internet (http://www.geom.umn.edu/software/evolver/html/) and is available for all main operating systems and machines. The *Evolver* evolves the surface toward minimal energy by a gradient descent method. The energy considered in the problem can be a combination of surface tension, gravitational energy, squared mean curvature, user-defined surface integrals or knot energies. The *Evolver* can handle arbitrary topology, volume constraints, boundary contact angles, prescribed mean curvature, crystalline integrands, gravity and constraints expressed as surface integrals. Besides

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its large applicability to other physical and engineering problems it is very useful for determining the equilibrium shapes of fluid surfaces whenever the surface boundaries are fixed. However in case we are interested in minimizing the energy of the system by not *a priori* fixing the contact surface between the fluid and the solid (which is the problem considered in the present paper) other methods should be elaborated. In the problem proposed by us we are looking for a local energy minimum both as a function of the form of the triple line and the shape of the fluid surface.

Regarding computer simulations, the two main techniques, the molecular dynamics (MD) and Monte Carlo (MC) methods have already been applied. Theoretical aspects of the drying and wetting transitions have been investigated on microscopic scales by MD [17, 18]. The dynamics of a liquid-droplet spreading on a solid surface was considered by MC simulations using solid-on-solid (SOS) models or non-volatile Ising-lattice-gas (ILG) models with particle number conservation in [19–21] and [22, 23], respectively. Although these two models (SOS, ILG) describe qualitatively well many wetting phenomena, recently a more complex model was also considered [24]. In their paper, [24], Andersen and Brechet proposed a new macroscopic Hamiltonian for the wetting of a solid by a liquid in the immersion geometry, which has been applied to heterogeneous surfaces with spatial variations in the local contact angle. This method allowed one to compute the triple line shape and position in the chosen geometry where the liquid 'climbs along a vertical wall', namely the Wilhelmy plate [25]. Due to the specific role of gravity, the situation corresponding to this immersion geometry is quite different from the most common experimental cases where a droplet of liquid spreads along the horizontal surface of a solid. While the proposed macroscopic Hamiltonian can also be easily generalized for this latter problem, the MC method used in [24] will not work. The qualitative reason for this is that during the proposed MC simulation the fluid surface will not be smooth enough, and thus the dynamics will not be able to drive the system in the minimal energy configuration. Indeed, the thermal energy needed to re-arrange the surface shape is comparable to the energy change associated to spreading in the 'horizontal geometry', and so to suppress the roughness of the liquid–vapour surface leads to anomalous fluctuations of the triple line position. The situation is quite different for the 'Wilhelmy plate' geometry where the energy cost due to gravity stabilizes the triple line. As a result of this difference, the simple MC method used in [24] has to be modified using more refined algorithms to deal with geometries where gravity is not relevant. The present paper intends to contribute in this sense.

In the following we will present a 'two-step' MC method which works well also for the spreading phenomenon. The method will be tested on some simple, analytically solvable cases and than used for a more complex situation.

2. The method

The relevant physical quantities of the problem are the surface tensions γ_{LG}, γ_{LS} and γ_{SG} for the liquid/gas, liquid/solid and solid/gas interfaces, respectively. These three quantities are related to the local equilibrium contact angle θ, through Young's relation:

$$\gamma_{LG}\cos(\theta) = \gamma_{SG} - \gamma_{LS}. \tag{1}$$

In the case $\theta < \pi/2$, following [24], we can construct a macroscopic Hamiltonian for the wetting problem. Discretizing the surface of the solid on a square lattice with the lattice

constant 'a', and considering the height of the liquid on a site with coordinates (i, j) as h_{ij}, the Hamiltonian of the system can be written as

$$H = \sum_{i,j}(\gamma_{SG} - \gamma_{LS})\delta(h_{ij})a^2 + \gamma_{LG}\frac{a^2}{4}\sum_{i,j}[F_{ij}(i+1, j; i, j+1) + F_{ij}(i-1, j; i, j-1) + F_{ij}(i+1, j; i, j-1) + F_{ij}(i-1, j; i, j+1)] + \frac{a^2}{2}\rho g\sum_{i,j}h_{ij}^2 \tag{2}$$

where:

$$F_{xy}(b, c; d, e) = \bar{\delta}\left(\frac{h_{xy} + h_{bc} + h_{de}}{a}\right)\left(1 + \left(\frac{h_{xy} - h_{bc}}{a}\right)^2 + \left(\frac{h_{xy} - h_{de}}{a}\right)^2\right)^{1/2} \tag{3}$$

$$\delta(x) = \{1 \text{ for } x = 0, 0 \text{ for } x \neq 0\} \tag{4}$$

$$\bar{\delta}(x) = \{0 \text{ for } x = 0, 1 \text{ for } x \neq 0\}. \tag{5}$$

We denoted by g the gravitational constant and by ρ the density of the liquid. The first two terms in (2) describe the surface energies of the interfaces and the last the gravitational potential energy contribution. It is important to note that in the case of heterogeneous surfaces γ_{SG} and γ_{LS} are position dependent, and so thus also is the θ local equilibrium contact angle. Using Young's relation the normalized Hamiltonian can be written as

$$\frac{H}{\gamma_{LG}a^2} = \sum_{i,j}\delta\left(\frac{h_{ij}}{a}\right)\cos(\theta_{ij}) + \frac{1}{4}\sum_{i,j}[F_{ij}(i+1, j; i, j+1) + F_{ij}(i-1, j; i, j-1) + F_{ij}(i+1, j; i, j-1) + F_{ij}(i-1, j; i, j+1)] + \frac{\rho g a^2}{2\gamma_{LG}}\sum_{i,j}\left(\frac{h_{ij}}{a}\right)^2 \tag{6}$$

which obviously reduces to the continuum description when $a \to 0$.

To find the configuration of the h_{ij} values which minimizes the Hamiltonian (6) we used a 'two-step' MC method. The outline of the method is as follows.

(I) Fixing a given configuration of lattice sites $\{A_0\}$ on which there is liquid ($h_{ij} \neq 0$), by MC simulated annealing we drive the liquid on these sites to its minimal energy ($E_{min}\{A_0\}$) shape.

(II) Mapping all the probable site configurations for the liquid spread-out ($\{A_i\}$) we look for their energy minimum ($\min[E_{min}\{A_i\}]$), and for the corresponding liquid surface shape.

Separation of the MC algorithm in these two steps is necessary in order to prevent anomalous fluctuations of the triple line or unphysical roughness of the liquid surface. Both steps will now be discussed in some detail.

(I) When a site configuration on which liquid exists is chosen ($\{A_0\}$), finding the minimal possible value of (6) and the corresponding liquid surface shape is realized by the following MC method.

(1) The amount of liquid is divided into N boxes with base a^2. Their heights will be considered as units.

(2) These N units are randomly distributed on the chosen sites, giving initial h_{ij} heights.

(3) By using (6) we calculate the energy (E_i) of this configuration.

(4) Driven by the local curvature of the liquids surface (and thus by the local Laplacian pressure) we change the heights of the liquid on the sites of a randomly chosen P_{ij} sublattice

(P_{ij} contains the sites $[i, j]$, $[i+1, j]$, $[i, j-1]$ and $[i+1, j-1]$). On the site where the local curvature determining quantity $\kappa_{l,m} = h_{l+1,m} + h_{l,m+1} + h_{l-1,m} + h_{l,m-1} - 4h_{l,m}$ is minimum (and thus the local Laplacian pressure is maximum) we lower the height by unity, and on the site where $\kappa_{l,m}$ is maximum we increase the height by unity. In the case when we have several sites with maximum or minimum values of κ we choose randomly among them. We forbid the liquid to be on sites not belonging to the chosen configuration and we also forbid the liquid to leave a chosen site.

(5) We calculate the new energy (E_f) of the system. We accept the change with the classical Metropolis probabilities (1 if $\Delta E = E_f - E_i < 0$, and $\exp(-\Delta E/kT)$ if $\Delta E > 0$). The temperature used here has no physical meaning since, on the scale of capillary length, thermal fluctuations have no influence. The use of the Boltzmanian factor must be understood only as a numerical trick which drives the system in the neighbourhood of minimal energy configurations.

(6) We repeat (4)–(6) until equilibrium fluctuations are obtained. This is usually achieved after 1000 trials/site.

(7) The temperature is consecutively lowered until the system is trapped in the minimal energy configuration.

This curvature driven evolution (which mimics surface diffusion) allows a more rapid convergence due to the fact that the liquid surface will be much more smooth during the simulation, and thus the minimum energy state much more rapidly achieved. Although this will raise some complications in writing the code, the gain in computing time is considerable. There are also many minor tricks used to make the algorithm competitive. We mention in this sense the use of a fast and tested random number generator with repetition period of order 2^{59}, the calculation of ΔE only from the local changes in h_{ij} and the use of dynamic memory allocations.

(II) If we would like to map all possible site configurations on a lattice of size L^2, we would need to repeat the MC annealing 2^M ($M = (L/a)^2$) times. Due to the fact that for each configuration we would need to calculate the energy by the procedure described in (I), this would become technically impossible when the lattice sizes are reasonably large. In order to get the configuration of sites occupied by the liquid for the global minimum energy we need to build efficient searching rules. Unfortunately, we do not have general recipes in this sense. The idea would be to make use at the maximum of the symmetries of the problem (if there are some!), to keep the compactness of the liquid layer, to form a first qualitative picture about what the final equilibrium shape would look like (if possible!) or what we are looking for, and to drive the liquid in the neighbourhoods of this. A more general, although computationally much more expensive, MC algorithm can also be considered. This implies changing site by site the form of the triple line, conserving the compactness of the liquid layer. For each new configuration the energy would be computed by the method described in (I), and the changes would be accepted with the already discussed Metropolis probabilities. The temperature in the Boltzmanian factor would have again no physical meaning and it should be lowered consecutively throughout the simulation. This would be the second step in our two-step MC method.

The method consisting of these two steps, (I) and (II), works well if the searching algorithm is properly chosen. Although computationally the method is very time consuming, it gives new perspectives to solve interesting wetting problems. (Generally for obtaining the minimum surface energy of only one configuration with 30×30 sites, on an IBM RISC 6000 39H computer 2–3 min of CPU times were necessary.) In the following we will illustrate its applicability for some simple geometries. It has to be stressed that this method is concerned with finding the equilibrium shapes and disregards kinetic barriers.

3. Test of the method in the case of a translational symmetry

As a test of the method, first we consider an analytically solvable case. On a smooth and uniform surface we consider an infinite long strip of liquid in the manner presented on figure 1.

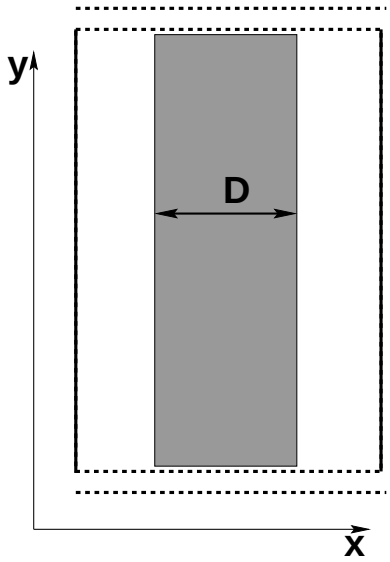

Figure 1. The geometry for testing the method. Liquid strip (dark region) on a surface.

Obviously there is a translational symmetry in the y-axis direction and so, in principle, the problem is one-dimensional. We are looking to answer the following questions:

• Neglecting gravity and fixing the contact angle $\theta = \pi/2$, how does the width in the x spatial direction of the strip (D) vary as a function of the liquids volume per unit length (v)?

• Neglecting gravity and fixing v, how does the width vary as a function of the contact angle?

• Including gravity effects, what will be the thickness of the fluid layer (h) in the limit $v \to \infty$ and $\theta = \pi/2$?

The answers to all these questions are known analytically. These problems are therefore a set of case studies in which we can check the reliability of our numerical method. When gravity is neglected, using elementary variation calculus, it can be proved that the shape of the liquids surface must have a cross section which is an arc of circle, and thus one will easily obtain for $\theta = \pi/2$,

$$D = \sqrt{\frac{8v}{\pi}}. \tag{7}$$

Similarly for fixed v

$$D = \sqrt{\frac{4v \sin^2(\theta)}{\theta - \cos(\theta)\sin(\theta)}}. \tag{8}$$

When gravity is considered and $\theta = \pi/2$, in the limit $v \to \infty$ the liquid layers height on the surface can be approximated as

$$h = \sqrt{\frac{2\gamma_{LG}}{\rho g}}. \tag{9}$$

Considering a lattice of sizes 100×50 with periodic boundary conditions in the y spatial direction, by means of the presented MC method we numerically solved these problems. The parameter determining the strip is D, and so the mapped configurations were strips with different D values. For annealing one configuration with fixed D we considered typically 14 temperatures consecutively lowered by a factor of 2. For each temperature we performed 500 MC steps per lattice sites. The results obtained by computer simulations are compared with the analytical predictions (7), (8) and (9) in figures 2–4. As shown on these figures the method gave fair agreements with the exact results. For the liquid layer height when gravity is considered (figure 4) the discrepancies between analytical and simulation data for small values of v is due to the fact that the liquid strip is not wide enough and thus the real boundary geometry is important. The theoretical approach (9) becomes exact only in the limit $v \to \infty$, when the semicylinder shape of the liquid surface near the triple line can be approximated with a vertical plane surface, without making a considerable error in evaluating the surface energy.

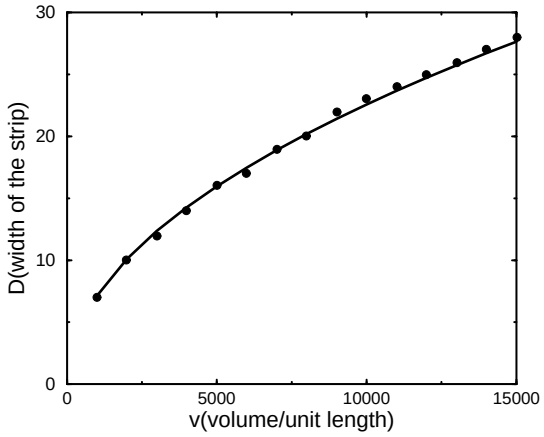

Figure 2. Variation of the liquid strip width (D) as a function of the volume of liquid per unit length (v). The contact angle on the surface is considered $\theta = \pi/2$. The continuous curve is analytical (equation (7)), and the points are simulation results.

4. Application for a more complex geometry

In order to illustrate the applicability of the method for analytically non-solvable cases we considered also a more complex geometry. The solid surface was composed of three regions with sizes L_1, L_2 and $L_3 = l$ in the manner illustrated in figure 5, having contact angles $\theta_1 = \pi/2$, $\theta_2 = \theta$ and $\theta_3 = \theta_1 = \pi/2$. Considering that the liquid is spread out symmetrically around the x and y axis and neglecting gravity, we looked for the aspect

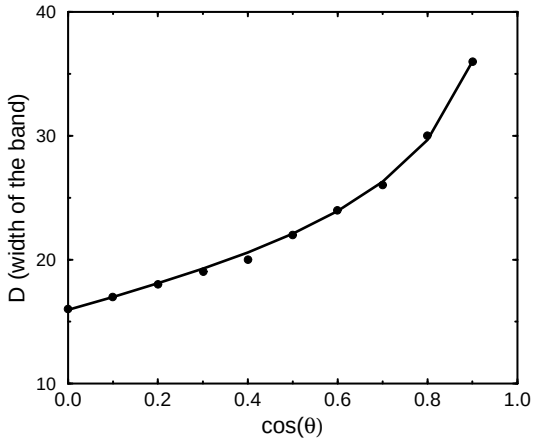

Figure 3. Variation of the liquid strip width (D) as a function of the cosine ($\cos(\theta)$) of the contact angle, when the liquids volume per unit length is kept constant ($v = 100$). MC simulation results (dots) are compared with analytical (continuous curve) predictions (8).

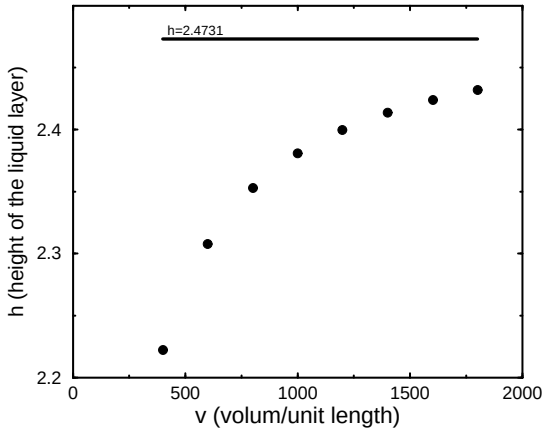

Figure 4. Average height of the liquid layer (h) when gravity is included, as a function of the liquids volume per unit length (v). The continuous horizontal line is the analytical prediction (9) for $v \to \infty$, and the points are simulation results ($\theta = \pi/2$, $g = 9.81$ m s^{-2}, $\gamma_{LG} = 0.03$ N m^{-1}, $a = 0.001$ m and $\rho = 1000$ kg m^{-3}).

ratio $r = R_x/R_y$ of the droplet in the minimal energy configuration as a function of the contact angle θ. It is obvious that in the limit of $\theta = \pi/2$ we must have $r = 1$ and for $\theta = 0$: $r = \infty$, but for $\theta \in (0, \pi/2)$ the problem is difficult to handle analytically.

We considered a lattice of sizes 50×30, $L_1 = L_2 = 10$ and periodic boundary conditions in both spatial directions. The MC simulations were started from the strip considered in the earlier case, considering the total volume for the liquid spread out on the surface $V_0 = 1200$ units. Due to the symmetry with respect to the x and y axis it is enough to determine

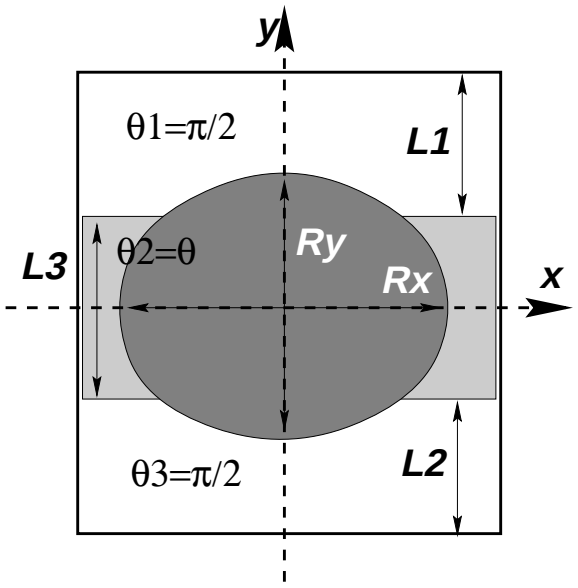

Figure 5. Geometry of the considered contact angle configuration and qualitative shape (darkest region) of the droplet.

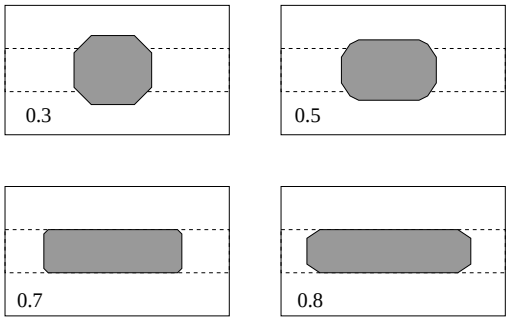

Figure 6. Schematics of the minimal energy configuration of the liquid droplets on the considered surface for four different values of $\cos(\theta)$. The sharp edges are 'lattice effects' ($V_0 = 1200$, $L_1 = L_3 = L_2 = 10$, $\theta_3 = \theta_1 = \pi/2$, $\cos(\theta) = 0.3$, 0.5, 0.7 and 0.8).

the triple lines shape ($y(x)$) only in the first quarter of the plane ($x \geqslant 0$ and $y \geqslant 0$), where this must be a monotonously decreasing function. This curve, constructed on the underlying lattice structure was step by step locally deformed, always satisfying $\mathrm{d}y/\mathrm{d}x \leqslant 0$ and keeping the shape which would yield a 'local' energy minimum for the corresponding liquid configuration.

We drove the system through the configurations with local energy minimums to the global minimum energy configuration.

Six possible values of $\cos(\theta)$ were considered: 0, 0.3, 0.5, 0.6, 0.7 and 0.8. As expected for $\cos(\theta) = 0$ we recover the obvious $r = 1$ value. On figure 6 we plotted some equilibrium configurations of the droplets on the considered surface. The aspect ratios (r) of the droplets in their minimal energy configuration as a function of $\cos(\theta)$ are plotted with dots on figure 7.

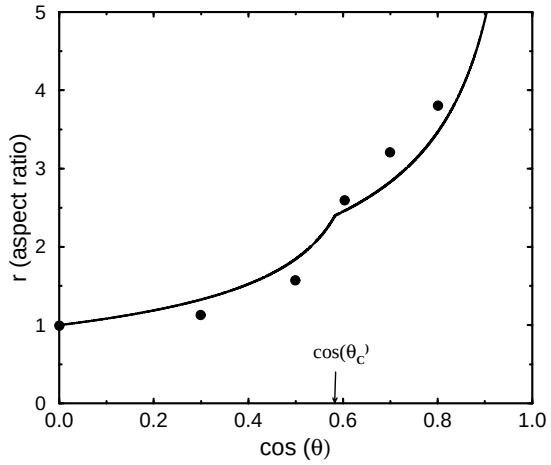

Figure 7. The aspect ratio of the droplet (r) as a function of the cosine of the $\theta_2 = \theta$ contact angle. Dots are simulation results and the full curve is the analytical approach by using the presented rectangular geometry ($V_0 = 1200$, $L_1 = L_3 = L_2 = 10$, $\theta_3 = \theta_1 = \pi/2$).

A qualitative prediction for the r aspect ratio as a function of the contact angle θ can also be obtained by approximating the form of the liquid droplet with a rectangle of size $L_x \times L_y$ and a constant height h. If $L_y > l$ and neglecting gravity the total energy of the system can be written as

$$W = \gamma_{\mathrm{LG}} \left(L_x L_y + \frac{2V}{L_y} + \frac{2V}{L_x} \right) - \gamma_{\mathrm{LG}} L_x l \cos(\theta) \tag{10}$$

where $V = L_x L_y h$ is the volume of the droplet. Minimizing W with respect to L_x and L_y we find a system of equations with the unknowns L_x and L_y:

$$L_x = \frac{2V}{L_y^2} \tag{11}$$

$$\frac{1}{2Vl\cos(\theta)} L_y^4 + \frac{1}{l\cos(\theta)} L_y + 1 = 0. \tag{12}$$

Solving the fourth-order equation with *Mathematica* (see the Appendix) one can determine the value of L_y,

$$L_y = y_2 = \frac{\sqrt{A}}{2} + \frac{\sqrt{-2b/a\sqrt{A}}}{2} \tag{13}$$

which is acceptable only when $y_2 > l$. L_x is immediately calculable now using equation (11).

For values of the wetting angles giving $y_2 < l$ it is easy to realize that the fluid will be trapped in the central region and we will have $L_y = l$ independently of θ. There will thus be a critical value θ_c under which this is realized. In this region the equilibrium value of L_x is obtained by minimizing the expression (10) for W as a function of L_x considering

$L_y = l$ constant. As result for $\theta < \theta_c$ one would obtain

$$L_x = \sqrt{\frac{2V}{l(1-\cos(\theta))}}. \tag{14}$$

Knowing the values of L_x and L_y for each possible value of θ, the $r = L_x/L_y$ aspect ratio is analytically calculable.

In figure 7, in comparison with the simulation data, the aspect ratio $r = L_x/L_y$ obtained by the above analytical approach as a function of $\cos(\theta)$ is plotted with a continuous line. Although the geometry of the droplet considered in our theoretical approach is very approximate, we can observe that our simulation data are in good agreement with the expected behaviour.

5. Conclusions

As a conclusion, in the present paper we have proposed a 'two-step' MC method for finding the minimal energy configuration of liquids wetting solid surfaces. The method was tested and applied for some simple geometries. Comparison with exact or approximate analytical solutions shows good agreement with the obtained simulation data. In principle, the method could be applied for all complex geometries, being technically limited only by the necessary computer time. For a fixed configuration of fluid occupied lattice sites our method is slower and thus computationally more expensive than the already discussed Surface Evolver. The main advantage and difference to this is in the fact that we are looking for a local energy minimum without an *a priori* imposed triple line. Not only is the shape of the fluid surface unknown but also the form of the triple line. Smart searching algorithms applicable for each problem separately are important, in order to improve the efficiency of the method.

Acknowledgment

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Appendix

By using *Mathematica* one can find the solutions of the fourth-order equation (12) as

$$y_{1,2} = \frac{\sqrt{A}}{2} \pm \frac{\sqrt{-2b/a\sqrt{A}}}{2} \tag{15}$$

$$y_{3,4} = -\frac{\sqrt{A}}{2} \pm \frac{\sqrt{2b/a\sqrt{A}}}{2} \tag{16}$$

where a, b and A stand for

$$a = \frac{1}{2Vl\cos(\theta)} \tag{17}$$

$$b = -\frac{1}{l\cos(\theta)} \tag{18}$$

$$A = \frac{2^{\frac{1}{3}}4}{(27ab^2 + \sqrt{-6912a^3 + 729a^2b^4})^{\frac{1}{3}}} + \frac{(27ab^2 + \sqrt{-6912a^3 + 729a^2b^4})^{\frac{1}{3}}}{2^{\frac{1}{3}}3a}. \tag{19}$$

The acceptable (real and $L_y > l$) solution for L_y is

$$L_y = y_2 = \frac{\sqrt{A}}{2} + \frac{\sqrt{-2b/a\sqrt{A}}}{2} \tag{20}$$

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