Dynamics of Wetting with a Disordered Substrate: the Contact Angle Hysteresis.

P. Collet(*), J. De Coninck(**) and F. Dunlop(*)

(*) Centre de Physique Théorique, Ecole Polytechnique
91128 Palaiseau, France
(**) Université de Mons-Hainaut - 20 place du Parc, B-7000 Mons, Belgium

(received 22 October 1992; accepted in final form 15 April 1993)

PACS. 05.40 - Fluctuation phenomena, random processes, and Brownian motion.
PACS. 64.60C - Order-disorder and statistical mechanics of model systems.
PACS. 68.10G - Interface activity, spreading.

Abstract. - The edge of an advancing or receding two-dimensional sessile drop is studied using Monte Carlo dynamics and analytical arguments. It is found that for disordered substrates an advancing angle \( \theta_a \) or a receding angle \( \theta_r \), both different from the equilibrium angle, appear and remain stable during a lifetime much larger than the time needed to reach equilibrium with a pure substrate. Much larger means a ratio tending to infinity in the thermodynamic limit.

It is a well-known observation in wetting that a contact angle hysteresis may appear for disordered substrates [1-5], and this phenomenon has been studied theoretically, starting from capillarity theory [6-9]. However, the relationship between this property and the molecular characteristics of the substrate has not yet been clearly elucidated. In the present paper, we use statistical-mechanical ideas and methods to show that, indeed, the disorder of the substrate at the molecular level may induce a contact angle hysteresis in a partial-wetting regime. Hysteresis appears to be an important aspect of the role of disorder in wetting phenomena, and the present study complements the equilibrium statistical-mechanics studies of the problem [10-13].

The disorder that we consider is associated to local variations of the spreading parameter \( S \), and we choose it to be completely uncorrelated from site to site. This corresponds practically to chemical heterogeneities at a low-density limit. What we obtain from our analysis is that there should exist, with probability one in the thermodynamic limit, clusters of impurities which are large enough to trap the interface in a metastable state for a very long time. Very long time means that the scaling of the life time with the size of the system should have an exponent bigger than the exponent for relaxation of a corresponding pure system. At the limit of low density, our results indicate that the difference between advancing and
receding contact angles scales linearly in the density of impurities and quadratically with their magnitude, in agreement with [7, 9].

Our analysis is based on Monte Carlo dynamics of the foot of a two-dimensional drop, in a partial-wetting regime. We have studied a solid-on-solid model, along the lines initiated in [14] for pure substrates, and also a simplified model where the only microscopic random variable is the contact point between the interface and the substrate. In this letter we present results for the second model, which are clearer and more precise. The results for the SOS model will be published elsewhere [15]. Let us also point out that we have studied both strong- and weak-disorder regimes, but always far from the wetting transition. This allows us to neglect thermal fluctuations on the wall ahead of the drop.

We describe the spreading edge of the drop as a triangular wedge of height \( h \) and of length \( l_t \) along the substrate. The bulk of the drop is considered effectively fixed on the time scale relevant for the study of the spreading edge, so that the height \( h \) is fixed while the spreading length \( l_t \) evolves with time \( t \). The contact angle is thus also a function of time, satisfying \( \tan \theta = h/l_t \). The energy function, which will be the basis of Monte Carlo dynamics, is taken as

\[
E_t(l_t) = \sigma \sqrt{h^2 + l_t^2} - \mu l_t + \sum_{i=0}^{l_t-1} \xi_i ,
\]

where \( \sigma \) is the interfacial tension coming from the integration over the internal degrees of freedom, and \( \mu \) is the difference between wall free energies in the absence of impurities. We assume for simplicity that \( \sigma \) does not depend upon the orientation of the interface. The random variables \( \xi_i \) take only two values, 0 with probability \( 1 - d \) (this corresponds to the substrate being pure at site \( i \)) and \( b \) with probability \( d \) (this corresponds to the presence of an impurity at site \( i \)).

The corresponding Monte Carlo dynamics corresponds to an inhomogeneous Markov chain. At zero disorder, starting from an initial length \( l_0 \), it relaxes over time scales of order \( l_{eq} - l_0 \) to an equilibrium state with Boltzmann factors proportional to \( \exp[-\beta E_t(l)] \). In the following, we set \( \beta = 1 \), which means that temperature is absorbed in the definition of \( \sigma, \mu \) and \( b \). We have considered initial conditions corresponding to small and large contact angles. The first striking result is that the spreading length \( l_t \) as a function of \( t \) begins by starting to relax normally towards equilibrium, but then shows a series of plateaux, i.e. values of \( l_t \) around which \( l_t \) remains trapped for a time much larger than \( l_{eq} - l_0 \) before relaxing to the next

**Fig. 1.** - Speed vs. disorder amplitude \( b \), for an initial length \( l_0 = 0.8 l_{eq} \), estimated over a time \( 10 l_{eq} \), with \( \sigma = 4.63, \mu = 4.13 \) and \( d = 0.05 \). The curves correspond to numerical results with \( h = 4 \cdot 10^5, 10^5, 2 \cdot 10^5, 10^6, 4 \cdot 10^6, 16 \cdot 10^6 \), from top to bottom. The error bars are taken from the variance around an average over 100 substrates.
plateau, and so on. The angle corresponding to the first plateau will now be called the
advancing angle, or the receding angle, depending on the initial condition, because this angle
will be the only one observed in the limit of large drops.

It turns out to be quite difficult to determine whether there is a critical value of \( b \) below
which the advancing and receding angles would be equal to the equilibrium angle. We have
used the following strategy: We first fix an angle larger than the equilibrium angle. We start
with this angle and we measure the displacement of the contact point after a time equal to 10
times the distance to equilibrium \( l_{eq} - l_0 \). Dividing the measured displacement by the elapsed
time \( 10(l_{eq} - l_0) \), we obtain an estimate of the speed. We repeat this simulation for various
values of \( b \). The results are given in fig. 1 for different values of \( h \).

We observe that the curves corresponding to increasing values of \( h \) converge to a limiting
curve as \( h \to \infty \). Moreover, the variance associated to the average over the randomly chosen
substrates goes to zero as \( h \to \infty \), which means that the measured quantities are
self-averaging. Two regimes are manifestly distinguishable: one in which the speed is
non-zero, and another one with zero speed, which corresponds to values of the advancing
angle larger than the initial angle. This means that for large enough disorder the advancing
profile remains locked in the initial angle, different from the equilibrium angle, for at least
ten times the characteristic time of return to equilibrium. The conjecture of course is that
this ratio of ten could in fact be taken to infinity in the thermodynamic limit. Although
individual impurities are of bounded size measured at the molecular scale, the size of clusters
of impurities is not bounded. The large clusters, which are almost surely of size of order
\( \log(l_{eq} - l_0) \) times the size of an individual impurity, are responsible for the trapping of
the interface. Almost surely means that in the thermodynamic limit such large clusters exist with
probability one.

In order to characterize this hysteresis phenomenon, we introduce the order parameter
\( \cos \theta_e - \cos \theta_a \), where \( \theta_e \) is the equilibrium contact angle and must obey Young's equation:

\[
\sigma \cos \theta = \mu - db,
\]

and \( \theta_a \) is the advancing angle, i.e. the largest angle at which the interface remains trapped for
long times. Its behaviour obtained from the simulations as a function of the density of impurities \( d \) is given in fig. 2.

At very large disorder, the interface is always locked at its initial angle for any angle

![Fig. 2. Semi-log plot of \( \cos \theta_e - \cos \theta_a \) vs. \( d \), for \( \sigma = 4.63, \mu = 4.13 \) and \( b = 2 \). Solid lines correspond to numerical results with \( h = 4 \cdot 10^4, 10^5, 2 \cdot 10^5, 10^6, 4 \cdot 10^6, 16 \cdot 10^6 \) from bottom right to top left. The initial length was \( l_0 = 5000 \). The advancing angle is measured at time \( 10l_{eq} \), and averaged over 100 substrates. Broken lines correspond to eqs. (9) and (10).](image-url)
between 0 and $\pi$, so that the advancing contact angle is equal to $\pi$ and the receding angle equal to zero.

Let us now give an analytic argument for this hysteresis. Consider a pure flat substrate of length $l$ and molecular length $a_0$. We put at random on top of this substrate impurities of size $a_1$ with density $d$. The average coverage of the substrate by impurities is therefore equal to $a_1 d$. For small density $d$, the probability that there exists somewhere a cluster of impurities of length $\lambda$ can be estimated as

$$P(\lambda) = \min \left( 1, \frac{l}{a_0} (a_0 d)^{\lambda/a_1} \right).$$

(2)

This implies that, with probability going to one as $l$ goes to infinity, the largest cluster has a size

$$\lambda(l) = a_1 \frac{\log (l/a_0)}{\log (1/a_0 d)}.\tag{3}$$

The Monte Carlo dynamics of the foot of the interface may be described by a random walk in a random environment. We now give the transition probabilities. When the moving point is at site $l$, the next position is $l-1$, $l$ or $l+1$. The corresponding transition probabilities are given by the standard arguments. Let $\Delta E_+ = E(l+1) - E(l)$ and $\Delta E_- = E(l) - E(l-1)$. An easy computation using formula (1) gives

$$\Delta E_+ = \sigma \cos \theta - \mu + \xi_l + O(1/h),$$

$$\Delta E_- = \sigma \cos \theta - \mu + \xi_{l-1} + O(1/h),$$

(4)

where $\tan \theta = h/l$. The probability $P_+$ to move from $l$ to $l+1$ is given by

$$P_+ = \begin{cases} 1/2, & \text{if } \Delta E_+ < 0, \\ \exp[-\Delta E_+]/2, & \text{if } \Delta E_+ > 0, \end{cases},$$

(5)

while the probability $P_-$ to move from $l$ to $l-1$ is given by

$$P_- = \begin{cases} 1/2, & \text{if } \Delta E_- > 0, \\ \exp[\Delta E_-]/2, & \text{if } \Delta E_- < 0. \end{cases}$$

(6)

Finally, the probability to stay at site $l$ is $1 - P_+ - P_-$. We consider a situation where the current contact angle is larger than the equilibrium contact angle, so that in the absence of impurity there is a positive drift in $l$. We also assume that the contact angle is less than the equilibrium angle corresponding to a different pure substrate with wall free energy difference $\mu - b$ instead of $\mu$. When we are on a cluster of impurities, there is a negative drift in $l$.

In order to estimate the time needed to cross a cluster of impurities of length $\lambda$ starting at $l_0$, we consider a simpler random walk on the half-line $(l_0, \infty)$ with reflection at $l_0$ and transition probabilities given by eqs. (4), (5) and (6), with $\xi_l = b$ for all $l \geq l_0$ and $\theta$ constant. It is easy to verify that this chain is ergodic and has a unique invariant probability measure given by

$$P(l) = \frac{P_- - P_+}{P_-} \left( \frac{P_+}{P_-} \right)^{-(l-l_0)}.$$
The average $T(\lambda)$ of the time needed to move from $l_0$ to $l_0 + \lambda$ approaches, as $\lambda$ goes to infinity, the inverse of the total weight of the sites beyond $l_0 + \lambda$ in the invariant measure, namely [16]

$$T(\lambda) \left( \frac{P_p}{P_-} \right)^\lambda \to 1, \quad \text{as } \lambda \to \infty.$$

For a cluster of length $\lambda(l)$ given by (3) the corresponding time is equal to

$$T(\lambda(l)) = \exp[\lambda(l)(\sigma \cos \theta - \mu + b)] = \left( \frac{l}{a_0} \right)^{\gamma(\theta)},$$

where

$$\gamma(\theta) = \frac{a_1(\sigma \cos \theta - \mu + b)}{\log (1/a_0 d)}.$$

The previous hypothesis on $\theta$ implies that $\sigma \cos \theta - \mu < 0$, but $\sigma \cos \theta - \mu + b > 0$. When $\gamma(\theta) < 1$, the time required to cross the cluster is much smaller than the typical relaxation time for the pure substrate. When $\gamma(\theta) > 1$, the foot of the interface remains trapped for a time much larger than the typical relaxation time. For an experiment on the time scale of the typical relaxation time, angles $\theta$ such that $\gamma(\theta) > 1$ will not be observed. The advancing contact angle will therefore be the angle-$\theta$ solution of $\gamma(\theta) = 1$, from which we obtain

$$\sigma(\cos \theta_e - \cos \theta_a) = \frac{1}{b a_1} \log (a_0 d \exp[b a_1]).$$

A sufficient condition for $\theta_a > \theta_e$ is therefore, again at leading order in $d$,

$$b a_1 > \log (1/a_0 d).$$

In fact the interface will be stopped by an accumulation of clusters of various scales (smaller than $\lambda(l)$). The highest resulting barrier can be estimated, by a large-deviation calculation where we now take $a_0 = a_1 = 1$ for simplicity, as

$$\Delta E = \frac{(b - \mu + \sigma \cos \theta) \log l}{\log (\alpha/d)},$$

where $\alpha$ is the solution of

$$(\mu - \sigma \cos \theta) \log \frac{\alpha}{d} = (b - \mu + \sigma \cos \theta) \log \frac{1-d}{1-\alpha},$$

satisfying $\alpha > d$. An argument similar to the one given above for the case of a homogeneous cluster of length $\lambda$ then shows that the trapping time near the angle $\theta$ behaves as

$$T(\theta) = \exp[\Delta E] = l^{\gamma(\theta)}.$$

The exponent $\gamma(\theta)$ is less than one for $\theta > \theta_a$ and bigger than one for $\theta < \theta_a$, and $\theta_a$ thus defined is found to obey

$$\sigma(\cos \theta_a - \cos \theta_a) = -db + \log (1 + d(\exp[b] - 1)),$$

which is strictly positive for all $d$ and $b$, and is of order $db^2$ for $d$ and $b$ small. The computation leading to these equations does not involve any approximation but is too long to be given here.
and will be given in a forthcoming paper [15]. Equation (10) gives hysteresis at arbitrarily small disorder, whereas the bound (9) allowed absence of hysteresis at small disorder. The numerical results shown in fig. 2 together with plots of (9) and (10) support eq. (10). The behaviour of $\gamma(\theta)$ as $\theta \to \theta_{eq}$, related to the late stages of relaxation and probably not measurable, can also be computed exactly:

$$\gamma(\theta) = \frac{d(1 - d) b^2}{2\pi (\cos \theta_{eq} - \cos \theta)} \text{ as } \theta \to \theta_{eq}.$$  \hspace{1cm} (11)

One may think that the trapping of the interface at arbitrarily small disorder is special with respect to one-dimensional interfaces, but the analogy with localization cannot be made precise enough to come to a conclusion. A limit law for a random walk in a homogeneous random environment has been obtained [17], but does not apply to our case because the deterministic background is inhomogeneous and the step probabilities are not independent.

***

The authors acknowledge support from the CNRS, the FNRS and the CGRI which made this collaboration possible. This text also presents research results of the Belgian programme on Interuniversity Poles of attraction initiated by the Belgian State, Prime Minister's Office, Science Policy Programming. The scientific responsibility is assumed by its authors.

REFERENCES