Contact Angle Hysteresis on Random Surfaces

EUROPHYSICS LETTERS 15 March 1987

Europhys. Lett., 3 (6), pp. 729-735 (1987)

Contact Angle Hysteresis on Random Surfaces.

M. O. ROBBINS (*) and J. F. JOANNY (**)

(*) *Department of Physics and Astronomy, Johns Hopkins University Baltimore,* MD 21218

(**) *Département de Physique des Materiaux, Université Claude Bernard,* 34 *Bd. du* 11 *Novembre* 1918, 69622 *Villeurbanne, France*

(received 12 November 1986; accepted 24 November 1986)

PACS. 68.10. – Fluid surfaces and interfaces with fluids.
PACS. 68.45. – Solid-fluid interface processes.
PACS. 05.40. – Fluctuation phenomena, random processes, and Brownian motion.

Abstract. – Contact angle hysteresis on weakly heterogeneous surfaces is studied using an extension of Imry and Ma's analysis of the random field problem. Deformations of the liquid-vapor interface in response to the heterogeneity are characterized by a length L_d which increases as the magnitude of the heterogeneity decreases. The characteristic energy associated with these deformations is used to find the scale of contact angle hysteresis. In the absence of gravity, contact angle hysteresis occurs for arbitrarily weak heterogeneity. Hysteresis disappears when L_d exceeds the gravitational capillary length, while systems with characteristic size less than L_d show increased hysteresis.

Wetting of solid surfaces has been studied for at least two centuries and is currently a topic of renewed interest [1]. An important parameter which characterizes wetting [2] is the contact angle θ—the angle at which the liquid-vapor interface intersects the solid substrate (fig. 1). This angle is determined by the competition between interfacial energies for liquid-vapor (γ_{LV}), liquid-solid (γ_{LS}) and solid-vapor (γ_{SV}) interfaces. If the spreading power

$$S \equiv \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \tag{1}$$

is positive, the fluid totally wets the solid and $\theta = 0$. For $S < 0$ the solid is partially wet and the contact angle satisfies the Young-Dupré equation

$$\cos\theta = 1 + \frac{S}{\gamma_{LV}} . \tag{2}$$

Experimental measurements of θ reveal substantial hysteresis. Different values are obtained for the advancing contact angle θ_a (obtained after increasing the solid-liquid interface) and receding contact angle θ_r (obtained after decreasing the solid-liquid interface). The origin of this hysteresis has been the focus of much experimental [3] and theoretical [4-8] research. Two major sources have been addressed: hysteresis in surface character and

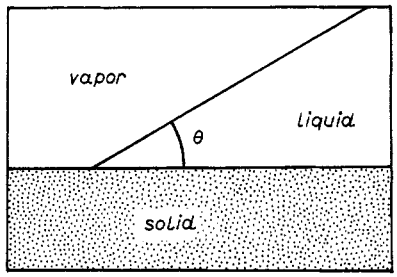

Fig. 1. – The contact angle θ between the liquid-vapor interface and the solid substrate.

heterogeneity of the surface. Hysteresis in surface character may result from deposition of a film of solute on the solid as the liquid recedes. The contact angle hysteresis then results from the difference in S for clean and solute-covered surfaces.

In this paper we consider the second case where hysteresis is caused by surface heterogeneity. The heterogeneity may result from chemical contamination or surface roughness. Chemical contamination causes spatial variations in the interfacial energies determining S. Surface roughness may also be expressed in terms of fluctuations in S. Fluctuations in surface orientation are equivalent to fluctuations in contact angle relative to a fixed orientation [5] and in turn to fluctuations in S (eq. (2)).

Early theoretical treatments [4-6] of contact angle hysteresis considered simple periodic modulations of S such as parallel grooves. The degree of contact angle hysteresis could be calculated from the strength and period of the modulation. However, these results are only valid when the grooves are parallel to the three-phase line—the line where the liquid-vapor interface intersects the solid. More recently, several authors [7, 8] have considered the less artificial case of surfaces with random impurities (localized variations in S). JOANNY and DE GENNES [7] considered hysteresis due to pinning of the three-phase line by *individual* impurities. Their major conclusions were: 1) smooth defects only produce hysteresis if they are sufficiently strong and concentrated, 2) mesa-type defects with sharp discontinuous changes in S always produce hysteresis which scales *linearly* with impurity strength and concentration. POMEAU and VANNIMENUS [8] considered hysteresis on weakly heterogeneous surfaces. They first constructed a nonlinear self-consistent equation for locally stable configurations of the liquid-vapor interface given the spatial variation of S. From this they argued that in the limit of weak heterogeneity contact angle hysteresis is present but small, scaling as the *square* of the magnitude of heterogeneity. However, their argument was based on a discontinuous «checkerboard» model for the variation of S. The work of JOANNY and DE GENNES shows that results for such discontinuous models may be qualitatively different from results for a continuously varying S.

In the following, we re-examine the case of weak heterogeneity using an extension of IMRY and MA'S approach for the random field problem [9]. We find a characteristic length scale, L_d, for deformations of the three-phase line in response to the heterogeneity. For weak heterogeneity, L_d is much larger than the scale of variations in S, and L_d increases as the magnitude of heterogeneity decreases. As in other examples of interfaces pinned by random fields, the three-phase line has many metastable equilibrium positions. It is the energy barrier between these metastable states which is the source of contact angle hysteresis. There is no threshold for contact angle hysteresis in the case of smooth defects (continuous variations in S). Even when individual impurities are too weak to pin the interface, contact angle hysteresis results from pinning by many impurities over L_d. The magnitude of the hysteresis scales as the square of the heterogeneity as found by POMEAU and VANNIMENUS. Modifications in the results occur when other macroscopic lengths such as system size and gravitational capillary length become comparable to L_d.

There are several important assumptions and limitations to our results that should be noted at the outset. As in previous work, we assume that the characteristic length scale for variations in S is macroscopic. At length scales less than $(100 \div 1000)$ Å, van der Waals forces, deformability of the solid surface and other factors modify the form of the interface [1]. The Young-Dupré equation (2) no longer applies. We also assume that thermal fluctuations are negligible because of the large length scales involved. Finally, the Imry-Ma argument is essentially qualitative, giving the approximate scale of important quantities rather than precise numerical values. Indeed, there are many metastable configurations of the three-phase line and there may be substantial variations in the energy and other quantities from one configuration to the next. If thermal fluctuations are small, only one configuration will be accessed on experimental time scales. The particular configuration will depend on the previous history of the line. Our emphasis is on the overall functional dependence of typical results on experimentally controllable parameters recognizing that there may be substantial fluctuations in individual cases.

We consider a horizontal solid surface in the xy-plane with the unperturbed three-phase line at $y = 0$ for a uniform surface, $S(x, y) = \overline{S}$ (fig. 2). Surface heterogeneity produces random fluctuation in S about its mean value $\overline{S}$

$$S(x, y) = \overline{S} + h(x, y) \ . \tag{3}$$

The random component, h, has r.m.s. magnitude $\overline{h}$ and is correlated over a length d (*i.e.* no mesa-type defects)

$$\langle h(r)\, h(r') \rangle \sim \overline{h}^2 \exp\left[- |r - r'|^2 / d^2 \right] \ . \tag{4}$$

The three-phase line will tend to distort to a new position, defined by $y = \eta(x)$, to conform to h. The energy change due to h is

$$U_h = \int \mathrm{d}x \int_0^{\eta(x)} \mathrm{d}y\, h(x, y) \ . \tag{5}$$

However, the deformation also increases the liquid-vapor interface costing surface energy. JOANNY and DE GENNES [7] have considered this energy cost for small θ and small displacements, $q\tilde{\eta}(q) \ll 1$, where $\tilde{\eta}(q)$ is the Fourier transform of $\eta(x)$. Generalizing their

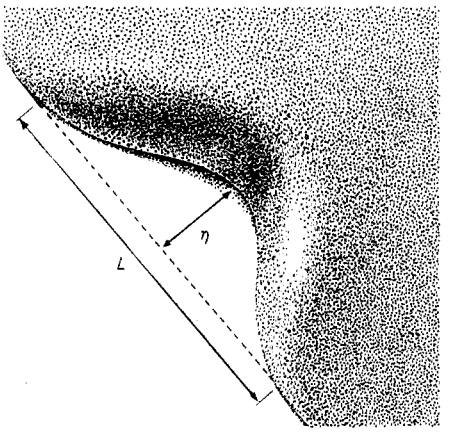

Fig. 2. – Deformation of the liquid-vapor interface to conform to $h(x)$ with characteristic magnitude η over length L. The deformation heals away from the substrate over a length proportional to L.

result to arbitrary θ, we find

$$U_{\text{cap}} \simeq \frac{1}{4}\gamma_{\text{LV}} \sin^2\theta \int \frac{\mathrm{d}q}{2\pi} |q||\tilde{\eta}(q)|^2 . \tag{6}$$

The unusual q-dependence arises because the elastic energy comes from the entire liquid-vapor interface, while η describes the distortion at the three phase line. Deformations of the interface decay exponentially away from the three-phase line with decay length $|q|^{-1}$. Thus the usual quadratic q-dependence of the elastic energy only applies to a region of size q^{-1} giving eq. (6).

Following IMRY and MA [9] and GRINSTEIN and MA [10], we consider the competition between U_{h} and U_{cap} for trial distortions of the three-phase line to determine which are most stable. For a distortion $\eta(x)$ of typical magnitude η over length L (fig. 2), $U_{\text{cap}} \simeq \frac{1}{4}\gamma_{\text{LV}}\eta^2 \sin^2\theta$. The average value of U_{h} is zero because $\langle h \rangle = 0$. However, for any particular distortion the fluctuations in h do not average to zero. The typical magnitude of U_{h} is proportional to the square root of the number of independent regions of size d that the interface crosses as it deforms to $\eta(x)$ and to the typical contribution to U_{h} of the integral (eq. (5)) over each region. The functional form [11] of both factors depends on the relative magnitudes of L, η and d.

Equation (6) is only valid of $L \gg \eta$. As shown below this condition is automatically satisfied for weak impurities. Joanny and de Gennes's calculation [7] of hysteresis due to individual impurities applies when L is of the order of the spacing x between impurities. This corresponds to the case of strong pinning in random field theory [9, 10]. We are interested in the case of weak pinning where the interface is distorted by many impurities acting collectively *i.e.* $L > x > d$. There still remain two distinct cases: $\eta > d$ and $\eta < d$.

For $\eta \gg d$ the area crossed as the three-phase line distorts is many correlation lengths d in each direction. The total number of independent regions is $\sim L\eta/d^2$ and the magnitude of the typical contribution of each region is of order $\bar{h}d^2$. Assuming the random field favours the distortion, the total energy is (1)

$$U(\eta, L) \simeq \eta^2 \gamma_{\text{LV}} \sin^2\theta - \bar{h}d\sqrt{\eta L} . \tag{7}$$

The optimal amplitude η_0 for a given L is found (2) by minimizing eq. (7)

$$\eta_0(L) \simeq (Ld^2\bar{h}^2/\gamma_{\text{LV}}^2 \sin^4\theta)^{1/3}. \tag{8}$$

The corresponding total energy is

$$U_0(L) \simeq -(L^2 d^4 \bar{h}^4/\gamma_{\text{LV}} \sin^2\theta)^{1/3}. \tag{9}$$

The value of U_0 decreases monotonically, suggesting that the longest length scale deformations are most stable. However, shorter deformations can be fit into the same region of the three-phase line. The correct quantity to consider is the energy per unit length, $(1/L)\,U_0(L)$, which becomes *less* negative as L increases. Thus the most stable deformations are those at the shortest length scale. This corresponds to $L_{\text{d}} \sim d(\gamma_{\text{LV}}/\bar{h})^2 \sin^4\theta$, since for $L < L_{\text{d}}$, $\eta < d$ and the assumption used in deriving eq. (9) breaks down. Note that the

(1) In all of the following we will only be interested in scaling laws. We thus systematically drop numerical factors.

(2) This result has already been proposed by D. HUSE (unpublished), see ref. [1], p. 836.

assumption that L is larger than the mean impurity spacing x requires $x < L_d$ or $(\bar{h}/\gamma_{LV} \sin^2\theta) < d/x$. For larger values of $(\bar{h}/\gamma_{LV} \sin^2\theta)$ or x/d the strong pinning analysis of JOANNY and DE GENNES [7] should be used.

For $\eta < d$, the three-phase line does not move across independent regions in the y-direction. The number of independent regions crossed is just L/d and the typical contribution of each region is of order $h\bar{d}\eta$. Following the above analysis we find

$$U(\eta, L) \simeq \eta^2 \gamma_{LV} \sin^2\theta - \bar{h}\eta\sqrt{Ld}\,, \tag{10}$$

$$\eta_0(L) \simeq \sqrt{Ld}\,(\bar{h}/\gamma_{LV} \sin^2\theta)\,, \tag{11}$$

$$U_0(L) \simeq -(Ld\bar{h}^2/\gamma_{LV} \sin^2\theta)\,. \tag{12}$$

The assumption $\eta < d$ breaks down as L increases to the characteristic length L_d calculated above. The energy gained per unit length, E_0, is independent of L, $E_0 \equiv (1/L)\, U_0(L) = -(d\bar{h}^2/\gamma_{LV} \sin^2\theta)$ and scales with the result obtained for $\eta > d$ in the limit $L \to L_d$.

Since all deformations with $d < L < L_d$ produce the same energy gain per unit length, all will be found on the three-phase line. The direction of successive deformations will not be correlated since the surface is random. From eq. (11), $\eta(L) \propto d\sqrt{L/L_d}$. Thus any sequence of deformations with $L < L_d$ will produce a net displacement of the interface by d when the total length of the sequence is of order L_d. The interface will have the form of a random walk in the y direction with steps at regular intervals along the x-direction. The length L_d, is a coherence length or jog length. It measures the length of the three-phase line needed for the interface to distort by d and sample new values of h.

The statistics of the three-phase line at length scales greater than L_d depend on the history of the three-phase line. Since the heterogeneity is random, there are many metastable configurations of the three-phase line, each of which has an energy of order E_0 per unit length and coherence length L_d. Transitions between metastable configurations involve motion of the three-phase line through unfavorable regions of h. As in other treatments of pinning by random fields [9-11] we assume that these barriers scale with $U_0(L)$ for each L: that is that the interface must cross regions which raise the surface energy by about the same amount that it is lowered in the metastable configurations. To find a new metastable configuration, the three-phase line must move far enough to sample a new distribution of h. This distance is of the order of the larger of η_0 and d.

An external force per unit line length, F, acts to displace the three-phase line from its local equilibrium. The interface will move until the derivative of the energy with respect to the displacement of the line, ε, cancels the force $F = -L^{-1}(\partial U/\partial\varepsilon)$. If the force is larger than the maximum value of $|L^{-1}(\partial U/\partial\varepsilon)|$, the contact line will be depinned, moving from one local minimum to the next. Since we know the typical scale of energy variations and the typical length scale for these variations, we can estimate the force per unit length required to depin a distortion of a given size L:

$$F(L) \simeq L^{-1} U_0(L)/\eta_0(L) \approx (\bar{h}^2 \gamma_{LV} \sin^2\theta d^2/L^2)^{1/3}, \qquad L \geqslant L_d\,, \tag{13}$$

$$F(L) \simeq E_0/d \approx (\bar{h}^2/\gamma_{LV} \sin^2\theta)\,, \qquad L \leqslant L_d\,. \tag{14}$$

The maximum of F gives the threshold force for depinning the entire three-phase line, $F_T \approx (\bar{h}^2/\gamma_{LV} \sin^2\theta) \approx (d/L_d)\,\gamma_{LV} \sin^2\theta$. The precise value of F_T will vary from this estimate, but should scale in the same way with experimental parameters. Analogy to the case of charge-density wave pinning suggests that there may be a well-defined depinning force for

the entire line even though each segment interacts with a different distribution of impurities [12].

Experiments measure a macroscopic contact angle θ_M averaged over some length of the three-phase line. For example, in capillary rise experiments the mean height of the three-phase line is measured [5]. According to Young's arguments, there is a macroscopic force associated with the deviation of θ_M from the bare contact angle θ_0 for the uniform surface:

$$F_M = \gamma_{LV}(\cos\theta_M - \cos\theta_0) . \tag{15}$$

In a receding experiment, the macroscopic contact angle starts at a value less than θ_0 and increases in response to F_M. Our analysis shows that when $F_M \sim F_T$ the three-phase line will be pinned by heterogeneity of the solid surface. The value of θ will saturate at $\theta_r < \theta_0$, where

$$\cos\theta_r - \cos\theta_0 \sim (\bar{h}^2/\gamma_{LV}^2 \sin^2\theta_0) \sim (d/L_d) \sin^2\theta . \tag{16}$$

Similarly in an advancing experiment θ will saturate at the value $\theta_a > \theta_0$ given by

$$\cos\theta_0 - \cos\theta_a \sim (d/L_d) \sin^2\theta_0 . \tag{17}$$

Note that contact angle hysteresis is present for arbitrarily weak heterogeneity $\bar{h}$.

So far our analysis has neglected gravity and finite-size effects. Both produce interesting modifications of our results when L_d becomes larger than the relevant macroscopic length scale.

Gravitational energies dominate surface tension on length scales larger than the capillary length $L_c \equiv \sqrt{\gamma_{LV}/\rho g}$, where ρ is the density difference between fluid and vapor and g is the acceleration due to gravity. For $L > L_c$ the energy cost of a distortion of the interface becomes $U = \gamma_{LV}\eta^2 L/L_c$. This increases faster than U_h with increasing L and leads to a decreasing value of $\eta_0(L)$. When the heterogeneity is so weak that $L_d > L_c$, the deformation η_0 never exceeds d. The interface is still rough, but there are no metastable states and thus no contact angle hysteresis.

For systems where the length of the contact line, D, is smaller than L_d, some similar results apply. The three-phase line is rough, but $|\eta| < d$. Only one metastable configuration exists for a given mean position of the contact line. However, there is still contact angle hysteresis, because the energy of the contact line varies strongly with mean position. The contact line samples comparatively few uncorrelated values of h and the magnitude of fluctuations in the energy per unit length is thus large

$$|U|/D \sim \bar{h}d\sqrt{d/D} . \tag{18}$$

Since moving the mean contact line position by d changes the distribution of h, the force per unit length needed to depin the contact line is

$$F_T \approx |U|/dD \sim \bar{h}\sqrt{d/D} \sim \gamma_{LV} \sin^2\theta (d/L_d)\sqrt{L_d/D} . \tag{19}$$

Note that this diverges as D goes to zero. This strong dependence of F_T on D should be observable in experiments on small drops.

In conclusion we summarize the main results obtained. For weak random heterogeneity, distortions of the contact line exist at all length scales. At length scales less than L_d the interface has the form of a random walk. Many metastable configurations of the contact line exist at longer length scales. The ratio L_d/d may be a more easily measured quantity than $\bar{h}^2$. As the strength of the heterogeneity decreases, L_d increases, and the interface becomes smoother.

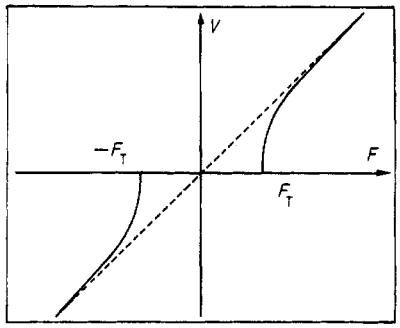

Fig. 3. – Schematic dependence of interface velocity, v, on applied force, F, for uniform (dashed line) and dirty (solid line) substrates.

A force greater than $F_T \sim (\bar{h}^2/\gamma_{LV} \sin^2\theta) \sim \gamma_{LV} \sin^2\theta(d/L_d)$ is needed to depin the distorted interface in the absence of gravity. This leads to contact angle hysteresis: $\cos\theta_r - \cos\theta_a \sim (d/L_d) \sin^2\theta$. In the presence of gravity, the depinning force and hysteresis go to zero when L_d is longer than the capillary length L_c. In contrast the pinning force is larger for drops whose size D is less than L_d: $F_T \simeq \gamma_{LV} \sin^2\theta(d/L_d)\sqrt{L_d/D}$. Experimental tests of the divergence of F_T as D goes to 0 would provide a strong test of our model.

Pinning of the three-phase line has important consequences for the dynamic response of the interface. The velocity must be zero for $|F| < F_T$ and should be depressed for $|F|$ slightly larger than F_T, since the interface will move slowly enough to distort in response to the heterogeneity. A rough sketch of the response is given in fig. 3. The physics should be similar to the motion of charge density waves in a random impurity potential [11, 12]. We plan to study this motion in a future work.

* * *

We have greatly benefited from conversations with D. ANDELMAN, S. GAROFF, P. G. DE GENNES, D. HUSE, L. SCHWARTZ and J. P. STOKES. Support from Exxon Research and Engineering Co. and the National Science Foundation through grant No. DMR-8553271 is gratefully acknowledged.

REFERENCES

[1] DE GENNES P. G., *Rev. Mod. Phys.*, **57** (1985) 827.
[2] For a general description see, ROWLINSON J. S. and WIDOM B., *Molecular Theory of Capillarity* (Oxford University Press, Oxford) 1982.
[3] JOHNSON R. and DETTRE R., *Adv. Chem.*, **43** (1964) 112-136.
[4] MASON S., in *Wetting, Spreading and Adhesion*, edited by J. F. PADDAY (Academic Press, New York, N. Y.) 1978, p. 421; OLIVER J., HUH C. and MASON S., *J. Adhesion*, 8 (1977) 223.
[5] COX R. E., *J. Fluid Mech.*, **131** (1983) 1.
[6] SCHWARTZ L. W. and GAROFF S., *Langmuir*, **1** (1985) 219; *J. Colloid Interface Sci.*, **106** (1985) 422.
[7] JOANNY J. F. and DE GENNES P. G., *J. Chem. Phys.*, 81 (1984) 552.
[8] POMEAU Y. and VANNIMENUS J., *J. Colloid Interface Sci.*, **104** (1985) 477.
[9] IMRY Y. and MA S., *Phys. Rev. Lett.*, **35** (1975) 1399.
[10] GRINSTEIN G. and MA S., *Phys. Rev. B*, **28** (1983) 2588.
[11] For a review of pinning in charge density wave systems see GRÜNER G., *Comments Solid State Phys.*, **10** (1983) 183.
[12] FISHER D. S., *Phys. Rev. Lett.*, **50** (1983) 1486; *Phys. Rev. B*, **31** (1985) 1396.