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1998 J. Phys.: Condens. Matter 10 L445

(http://iopscience.iop.org/0953-8984/10/27/001)

J. Phys.: Condens. Matter **10** (1998) L445–L451. Printed in the UK PII: S0953-8984(98)94662-8

LETTER TO THE EDITOR

Wetting of rough surfaces

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Received 1 June 1998

Abstract. A theory is presented to describe the wetting phenomena and the contact line depinning as a function of the microstructure of rough surfaces. The noise and fluctuations of the quenched disorder on self-affine rough surfaces play a important role in the analysis of the spreading of liquids on non-planar substrates. By using the long-range noise correlation function, functional relationships that show the influence of surface roughness on the contact angle, the critical surface tension and the depinning of the contact line are derived. Roughness enhances wetting and broadens the three-phase contact line.

Wetting plays a prominent role in many high technology applications from microelectronics, thin film coating, to image formation that involve the spreading of liquids on solid surfaces. From the scientific point of view, the wetting phenomena have been widely studied both theoretically [1] and experimentally [2] in connection with the physics of surfaces and interfaces. The behaviour of liquid partially wetting a smooth solid surface is well understood. However, the case of rough solid surfaces is much less clear, even though roughness is a real-world problem and its value in practical applications is very high. Studies of disordered and inhomogeneous surfaces [3–8] should have significant impact on the problem of wetting of rough substrates. Recent theoretical studies [9, 10] suggest that the surface roughness of a non-planar substrate may enhance wetting, but a quantitative description is still lacking. Therefore, we shall focus our attention on the understanding of the effect of the microstructure of rough surfaces on the partial wetting phenomena.

In this letter, we shall analyse the change in contact angle and determine how it is coupled to the wandering of the three-phase contact line due to the microstructure disorder of a rough surface. The noise caused by the irregular fluctuations on a rough surface is treated as the source of the disorder. The quenched noise, which does not change with time, is usually more important than temporal noise [3, 4] and will be considered in this work. We shall also assume that the wetting fluid spreads slowly on a non-planar substrate. On the basis of statistical physics, the macroscopic wetting phenomena will be linked to the noise correlation function beyond the white-noise limit.

To begin with an ideal situation of flat and smooth solid surfaces, the equilibrium angle of contact θ_0 is determined by the Young–Dupre equation [1]: $\gamma_s - \gamma_{sl} = \gamma \cos\theta_0$. Here γ_s, γ_{sl} and γ are the interfacial free energy per unit area for the solid–vapour, solid–liquid and liquid–vapour interfaces. The contact line of a liquid partially wetting the smooth solid is a straight line chosen to be in the y-direction: $x = 0$. In the real situation of rough substrates, the Young–Dupre equation has to be generalized to include the spatial (x, y) dependent interfacial energy densities and contact angle in the description of the local wetting phenomena:

$$\gamma_s(x, y) - \gamma_{sl}(x, y) = \gamma \cos[\theta(x, y)] \equiv \gamma \cos\big[\theta_0 - \phi(x, y)\big] \tag{1}$$

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where ϕ is due to roughness. The contact line is expected to have the form $x = \lambda(y)$. The contact free energy of the system is the sum of interaction energies with the substrate. It is covered by vapour in the domain of $-\infty < x < \lambda(y)$ and by liquid in the domain of $\lambda(y) < x < \infty$ shown in figure 1. The contact free energy is written as

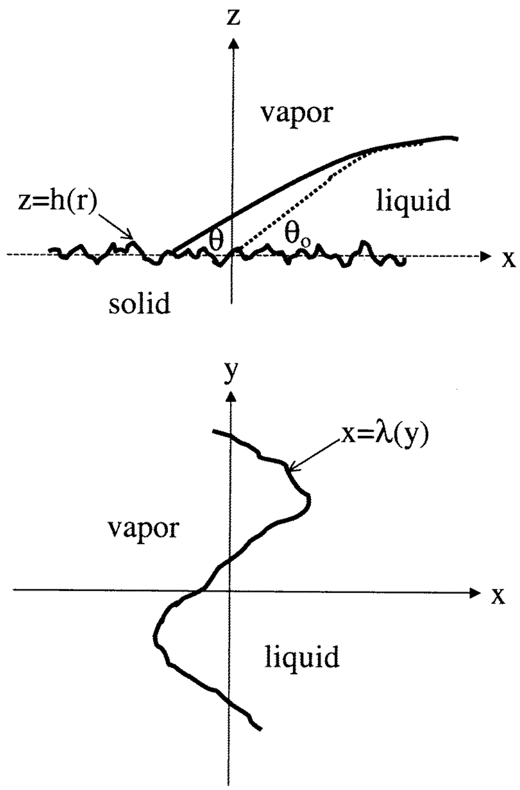

Figure 1. Definitions of the contact angle and the contact line.

$$U_{con} = \int \mathrm{d}y \int_{-\infty}^{\lambda(y)} \gamma_s(x,\ y)\,\mathrm{d}x + \int \mathrm{d}y \int_{\lambda(y)}^{\infty} \gamma_{sl}(x,\ y)\,\mathrm{d}x$$
$$= \int \mathrm{d}y \int_{-\infty}^{\lambda(y)} \left[\gamma_s(x,\ y) - \gamma_{sl}(x,\ y)\right] \mathrm{d}x. \tag{2}$$

The integrals over y are taken over the entire system. The difference in energy between the rough and smooth surfaces is

$$\Delta U_{con} = U_{con} - \langle U_{con}\rangle = \int \mathrm{d}y \int_{-\infty}^{\lambda(y)} \Delta w(x,\ y)\,\mathrm{d}x \tag{3}$$

where

$$\Delta w(x,\ y) = \left[\gamma_s(x,\ y) - \gamma_{sl}(x,\ y)\right] - \langle \gamma_s - \gamma_{sl}\rangle \tag{4}$$

is the local energy density. From equations (1) and (4), a spatial dependent Wenzel roughness [11] can be written as

$$\varepsilon(x,\ y) = \frac{\Delta w(x,\ y)}{\langle \gamma_s - \gamma_{sl}\rangle} + 1 = \frac{\cos[\theta_0 - \phi(x,\ y)]}{\cos\theta_0} \cong 1 + \theta_0\phi(x,\ y) + \dots \text{ for } \theta_0 \ll 1. \tag{5}$$

This equation shows that $\Delta w(x, y)$ is proportional to the local slope $\phi(x, y)$ [1] due to surface roughness. As we shall see later that the Wenzel roughness and energy density are essential to the study of the critical surface tension and contact line depinning, respectively.

Roughness results in local changes in the contact angle and hence the shape of contact lines. Instead of being a straight line in the case of planar substrates, the three-phase contact line tends to wander on the x–y plane due to the roughness shown in figure 1. The spatial dependent angle of contact and locus of wedge intersection fluctuate on an irregular surface in order to find their optimal angle and position via the minimization of the total free energy of surface. Joanny and de Gennes [6] have studied the deformation of a contact line with a small angle of contact. Let us introduce the Fourier transform in space,

$$[\Lambda(q),\ W(q)] = \int_{-\infty}^{\infty} [\lambda(y),\ w(y)]\ \exp(-\mathrm{i}qy)\,\mathrm{d}y. \tag{6}$$

The capillary energy associated with the contact line is given by [6]

$$\Delta U_{cap} = \frac{\gamma\theta_0^2}{2}\int_{-\infty}^{\infty} |q||\Lambda(q)|^2 \frac{\mathrm{d}q}{2\pi}. \tag{7}$$

This energy arises from the increase in the surface area of the liquid–vapour interface. The unusual $|q|$ dependence of the energy function comes from the integration of a q^2 energy over a distance $|q|^{-1}$ as a result of the contact line distortion. The total change in the free energy from equations (3) and (7) is

$$\Delta U = \Delta U_{cap} + \Delta U_{con} = \frac{\gamma\theta_0^2}{2}\int_{-\infty}^{\infty} |q||\Lambda(q)|^2 \frac{\mathrm{d}q}{2\pi} + \int_{-\infty}^{\infty} \Delta W(q)\Lambda(q)\frac{\mathrm{d}q}{2\pi}. \tag{8}$$

Minimizing ΔU with respect to Λ, i.e. $\mathrm{d}(\Delta U)/\mathrm{d}\Lambda = 0$, we obtain

$$\Delta W(q) = \gamma\theta_0^2 |q|\Lambda(q). \tag{9}$$

We shall return to equation (9) when the energy density is determined.

The term rough surface used in this letter refers to an irregular rough surface on which there is no overhanging region, and follows a self-affine description [12, 13]. The height of a continuous rough surface from its smooth reference being represented by the function $h(\boldsymbol{r})$ where $\boldsymbol{r}$ is the position vector on the reference surface $z = 0$ and its magnitude $r = |\boldsymbol{r}| = \sqrt{x^2 + y^2}$. The distribution of surface heights is described by the statistical height distribution $\rho(h)$. It is usually to ensure that h satisfies $\langle h\rangle = \int_{-\infty}^{\infty} h\rho(h)\,\mathrm{d}h = 0$. The root-mean-square height of the surface is equal to $\sigma = [\int h^2\rho(h)\,\mathrm{d}h]^{1/2}$. The standard deviation σ is related to the fluctuation normal to the surface and the correlation length ξ parallel to the surface. Much of the literature assumes that ρ is Gaussian and the surface is defined by σ and ξ. However, we shall go beyond the Gaussian surface in this letter by considering the random rough surfaces that have long-range correlation. Three independent parameters are needed to describe their microstructure [3, 12, 13]. In addition to σ and ξ, the third independent parameter is the roughness exponent α that defines the scaling and fractal properties of the surface: $\langle\Delta h^2(r)\rangle \sim r^{2\alpha}$ for $r \ll \xi$ [3, 4].

In the discussion of surfaces without long-range slope correlation, let us introduce $\Delta h(r) = h(r) - h(0)$ and consider the change of the local slope on a rough surface, which is governed by the stochastic differential equation [5]

$$\frac{\mathrm{d}(\Delta h)}{\mathrm{d}r} = -\frac{\Delta h}{2\xi} + \eta(r) \tag{10}$$

where η is the noise term that is the source of fluctuations of the local slope. Let us first look at the simplest case used in most applications: the noise correlation function is assumed to be uncorrelated white noise [14] with $\langle\eta\rangle = 0$ and

$$\big\langle \eta\big(r_1\big)\eta\big(r_2\big)\big\rangle = A\delta\big(r_1 = r_2\big). \tag{11}$$

The constant A is determined by the requirement of $\langle\Delta h^2\rangle = \sigma^2$. This gives the strength of noise $A = \sigma^2/\xi^2$. In terms of ϕ, its autocorrelation function is related to the noise correlation function by $2\langle\phi(0)\phi(r)\rangle = \langle\eta(0)\eta(r)\rangle$. Taking the spatial average over the range of the correlation length ξ, the noise-induced wetting is determined by

$$\overline{\phi} = \left[\frac{1}{2\xi}\int_0^{\xi}\langle\eta(0)\eta(r)\rangle\,\mathrm{d}r\right]^{1/2}. \tag{12}$$

This equation clearly follows the same concept as that for the root-mean-square height mentioned earlier. Substituting equation (11) into (12) gives $\overline{\phi} = \sigma/2\xi$ that provides a consistent check between equations (10)–(12).

We have just calculated the effect of surface roughness on the change in the contact angle by assuming the noise in the Langevin-like equation, (10), is uncorrelated. The next step is to investigate the influence of correlated noise on the wetting of the self-affine ($\alpha < 1$) surface [3, 12]. The self-affine fractal is statistically invariant under an anisotropic dilatation and is more suitable in the description of surfaces. This is in contrast to the self-similar fractal that is invariant under isotropic dilatation. In the case of noise that has long-range correlation, distant events may have influenced each other. The long-range correlated noise is due to the interactive fluctuations of an irregular surface that carries a memory effect. It serves as the source of disorder in the determination of the noise-induced wetting. Equation (12) is again going to be used in the determination of the change in the contact angle. Introducing the Laplace transform

$$G(p) \equiv L(\langle\eta(0)\eta(r)\rangle) = \int_0^{\infty}\langle\eta(0)\eta(u)\rangle\,\exp(-pu)\,\mathrm{d}u \qquad \text{with } u = r/\xi \tag{13}$$

we obtain the long-range noise correlation function that is the Laplace inversion of $G(p)$ [5]:

$$\langle\eta(0)\eta(r)\rangle = -AL^{-1}\left(\frac{p\sum_{n=1}^{\infty}(-1)^n\frac{\Gamma(2\alpha n+1)}{n!\,p^{2\alpha n}}}{1+\sum_{n=1}^{\infty}(-1)^n\frac{\Gamma(2\alpha n+1)}{n!\,p^{2\alpha n}}}\right) \qquad \text{for } |p| > 1 \text{ and } 0 \leqslant r < \xi \tag{14}$$

where Γ is the gamma function. When $\alpha = 1/2$, the right hand side of the above equation reduces to the delta function mentioned in equation (11). The leading term in equation (14) gives

$$\langle\eta(0)\eta(r)\rangle = \frac{\sigma^2}{\xi^2}\frac{\Gamma(2\alpha+1)}{\Gamma(2\alpha-1)}\left(\frac{r}{\xi}\right)^{2\alpha-2} \qquad \text{for } 1/2 < \alpha < 1 \tag{15}$$

in the limit of $r/\xi \ll 1$. Taking the spatial averages, we obtain the effective Wenzel roughness from equations (4), (5), (12) and (15):

$$\overline{\varepsilon} = 1 + C_\alpha\theta_0\sigma/\xi + \ldots. \tag{16}$$

According to Wenzel [11], $\overline{\varepsilon}$ is the ratio of non-planar-to-planar surface area and it goes to one for the planar system. Equation (16) shows that roughening the surface reduces the contact angle and promotes wetting. The effective energy density is

$$\overline{\Delta w} = \gamma\theta_0\overline{\phi} = C_\alpha\gamma\theta_0\sigma/\xi + \ldots. \tag{17}$$

By definition, the spatially independent $\overline{\Delta w}$ is actually equal to the difference in the work of adhesions between the liquid on a rough surface and that on a smooth surface. The non-dimensional C_α is

$$C_\alpha = \left[\frac{1}{2(2\alpha-1)}\frac{\Gamma(2\alpha+1)}{\Gamma(2\alpha-1)}\right]^{1/2} \qquad \text{for } 1/2 < \alpha < 1. \tag{18}$$

Clearly equations (15)–(18) reveal that the effect of the long-range noise correlation on $\overline{\varepsilon}$ and $\overline{\Delta w}$ is described in terms of α having a value differing from 1/2. C_α is a monotonic increasing function of the roughness exponent and is proportional to $\sqrt{\alpha}$. Of course, the general expression, (14), is needed for higher approximations. For the uncorrelated noise, we get $\alpha = 1/2$, $C_\alpha = 1/2$ and equation (11). In addition to the fluctuations (σ, ξ) of fractal surfaces and the equilibrium properties (γ, θ_0) of smooth substrates, our analysis clearly reveals that the roughness-induced wetting increases not only with the roughness exponent but also with the long-range noise correlation. The fractal structure beyond the white-noise assumption plays an important role.

We are now in a position to return to equation (9). Taking the spatial average of the Fourier inversion of equation (9) and using equation (17) gives

$$\overline{\left|\frac{\mathrm{d}\lambda(y)}{\mathrm{d}y}\right|} = \frac{1}{\theta_0}\overline{\phi} = \frac{C_\alpha\sigma}{\theta_0\xi} + \dots \tag{19}$$

where the average is taken over the range of the correlation length ξ. This equation shows that the slope of the contact line increases with roughness as a function of its strength and long-range noise correlation. By definition, the spatial independent slope is $\overline{\phi} = \overline{|\mathrm{d}h(r)/\mathrm{d}r|}$. Therefore, equation (19) suggests that the slope $\overline{\lambda'(y)}$ amplifies that of the smooth surface by a factor of $1/\theta_0$. As a result, the three-phase contact line is broadened by the roughness of the surface.

The analysis of the Wenzel roughness is useful in addressing another frequently encountered issue in chemical physics with technological significance. The surface energy (or tension) of solid may not be measured directly because of the viscoelastic constraint of the bulk phase, which necessitates the use of indirect methods. Zisman use extrapolated contact angle measurements to define the critical surface tension (γ_{c0}) for planar substrates as [2]

$$\cos\theta_0 = 1 + b\big(\gamma_{c0} - \gamma\big) \tag{20}$$

where $b = -\mathrm{d}(\cos\theta_0)/\mathrm{d}\gamma > 0$ is Zisman's slope of a smooth substrate. γ_{c0} is characterized as an important property of solid surface. In the case of rough surfaces, we can write the effective critical surface tension ($\overline{\gamma}_c$) in the same form:

$$\cos\big(\theta_0 - \overline{\phi}\big) = 1 + B\big(\overline{\gamma}_c - \gamma\big) \tag{21}$$

where $B = -\mathrm{d}(\cos\theta_0 - \overline{\phi})/\mathrm{d}\gamma > 0$ is the yet to be determined Zisman's slope of a rough substrate. Equations (20) and (21) are related to the effective Wenzel roughness by:

$$\cos\big(\theta_0 - \overline{\phi}\big) = \overline{\varepsilon}\cos\theta_0. \tag{22}$$

Combining equations (20)–(22) and using the condition $\overline{\gamma}_c = \gamma_{c0}$ at $\overline{\phi} = 0$, we get

$$\overline{\gamma}_c = \gamma_{c0} + \frac{\overline{\varepsilon} - 1}{b\overline{\varepsilon}} \tag{23}$$

and

$$B = \overline{\varepsilon}b = -\overline{\varepsilon}\frac{\mathrm{d}(\cos\theta_0)}{\mathrm{d}\gamma} > 0. \tag{24}$$

Consider $\gamma_{c0} = 20$ dyne cm^{-1} and $b = 0.025$ for a polymeric surface [2]. In figure 2, the influence of surface roughness on the Zisman plot is calculated from equations (21)–(24). Higher critical surface tension and steeper slope are seen for rougher surfaces. Figure 2 also shows that $\overline{\phi} > 0$ for $\theta_0 < 90°$. Substituting equation (16) into (23) yields

$$\overline{\gamma}_c = \gamma_{c0} + \frac{\theta_0 C_\alpha \sigma}{b\xi} + \ldots . \tag{25}$$

As the roughness increases, the critical surface tension of the solid is raised from γ_{c0} to a value that depends on the strength and range of the correlated noise. For practical applications, it becomes evident from equation (25) that the physical and chemical treatment of low-energy surfaces to improve the adhesion may change $\overline{\gamma}_c$ due to a change in surface chemistry or simply increase $\overline{\gamma}_c$ due to surface roughness.

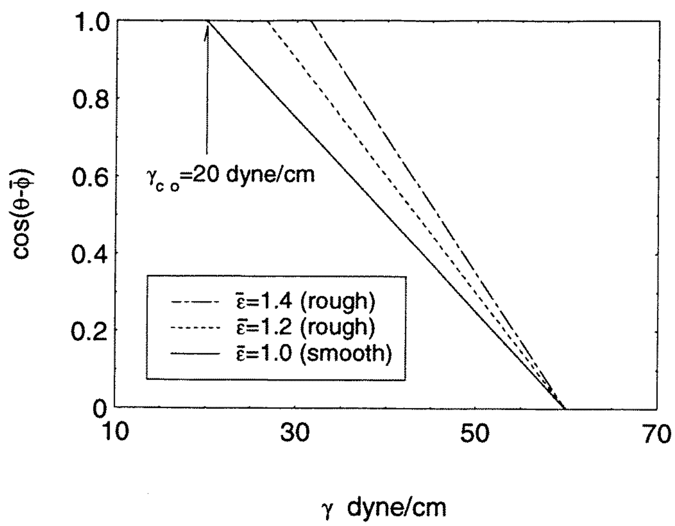

Figure 2. Effect of surface roughness on the Zisman plot.

In summary, a new concept has been developed that enables us to determine the effect of surface roughness on the wetting properties of surfaces from the noise correlation function. The long-range correlated noise is due to the interactive fluctuations of an irregular surface and is treated as the source of disorder in the determination of the noise-induced wetting. Our analysis goes beyond the familiar white noise assumption. Analytical expressions and functional relationships of the contact angle, the critical surface tension and the contact line depinning have been derived as a function of the microstructure of a rough surface. In addition to the fluctuations (σ, ξ) of fractal surfaces and the equilibrium properties (γ, θ_0) of smooth substrates, the noise-induced wetting depends not only on the roughness exponent (α) but also on the strength and range of the correlated noise. Roughening the surface reduces the contact angle, increases the critical surface tension and broadens the three-phase contact line.

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