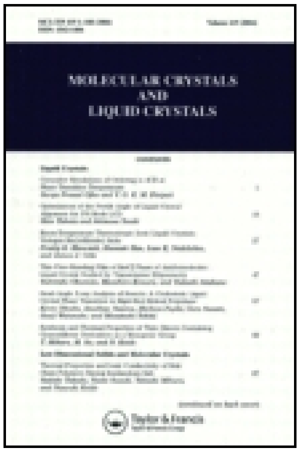

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Statics and Dynamics of Wetting

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STATICS AND DYNAMICS OF WETTING

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Abstract Recent theoretical and experimental studies on the wetting of smooth, isotropic solid surfaces by simple liquids are presented. These simple models should help for a future discussion of more complex situations including anisotropic surfaces and liquid crystals.

INTRODUCTION

Wetting phenomena are presently the subject of many theoretical and experimental studies.[1-3] At the macroscopic scale, contact angles of non wetting liquids,[4,5] or spreading velocities of wetting ones[6-8] are measured. At the microscopic scale, the detailed structure of the liquid edges is investigated by interferometric [9] and ellipsometric methods.[10-13]

The main results of these studies can be summarized as follows :

- The microscopic structure of a liquid edge is not similar to its macroscopic structure. This is due to the presence of interactions whose range does not exceed a few thousand Ångströms. [3]

- In most cases, the macroscopic and the microscopic parts of the liquid edge can be treated separately. [1] Universal laws, which depend only on the bulk liquid properties, hold at the macroscopic scale,[14] whereas the microscopic structure is controlled by thin films properties.[1-3]

- A relevant quantity for discussing the wetting behaviour of a liquid on a (smooth) solid surface is the spreading parameter S :[1]

$$S = \gamma_{SO} - \gamma - \gamma_{SL}$$

where the γ's are the interfacial tensions between solid and vacuum (γ_{SO}), liquid and vacuum (γ), solid and liquid (γ_{SL}). Neither γ_{SO} nor γ are true equilibrium quantities : as a matter of fact, molecular exchanges with the gas phase are assumed to be negligible, at least at short times.

According to the sign of S, the more favourable case is the dry surface ($S < 0$, non wetting liquid), or the surface covered by a thick film of liquid ($S > 0$, wetting liquid). For $S < 0$, a finite equilibrium contact angle θ_e is reached : the liquid does not spread on the solid.
For $S > 0$, the liquid spreads spontaneously and the instantaneous contact angle $\theta(t)$ decreases towards zero with increasing time t.

However, the sign of S gives only a first indication of the liquid behaviour. For a detailed discussion, the properties of thin films must be considered.

THIN FILMS PROPERTIES

Liquid films are thin when their thickness is in the range of molecular interactions.

Interactions in thin Films. Disjoining Pressure

Let us consider a thin liquid film of thickness z on a flat, smooth, solid surface. The excess free energy per unit area of interface can be written as :

$$E(z) = \gamma + \gamma_{SL} + P(z)$$

$$P(z) \to 0 \quad \text{for } z \to \infty$$

P(z) is the interaction energy between gas and solid across the film. This interaction can be characterized as well by the disjoining pressure $\pi(z)$:[3]

$$\pi(z) = -\frac{dP}{dz} \quad \text{or} \quad P(z) = \int_z^\infty \pi(\zeta)\,d\zeta$$

If $\pi(z)$ is positive, it tends to thicken the film. If it is negative, it tends to thin it.

Short Range and Long Range Interactions

Various interactions usually contribute to $\pi(z)$. "Short range" interactions -i.e. for molecular thicknesses- depend on the very details of the liquid and solid microscopic structures. They include physical or chemical bonding and orientational effects at the interfaces. [2-3] "Long range" interactions are mostly controlled by the bulk properties of the phases and obey more general laws.[1-3]

Examples of these long range contributions are dipole induced interactions -van der Waals forces.
In isotropic media, they can be written as

$$\pi(z) = \frac{A}{6\pi z^3} \qquad \text{for } z \lesssim 200\ \text{Å}$$

$$\pi(z) = \frac{B}{z^4} \qquad \text{for } z \gg 200\ \text{Å}$$

A is an effective Hamaker constant for the interaction gas/solid across liquid. [3,15] In anisotropic media, various attempts to calculate van der Waals contributions have been proposed, with[16-18] or without[19] explicit reference to liquid crystals.

Screened coulombic interactions are of importance in electrolyte solutions.[3,15] Water[3] has a peculiar behaviour which is not yet totally understood.

Shorter range interactions (quadrupolar,[20] hydrogen bonding...) belong to the wide class of short range contributions. No systematic theoretical description has been proposed yet. The behaviour of films and thin liquid edges depends on the thinning or thickening effect of the disjoining pressure and on the value of S (which might be considered as the limit of P(z) at close contact).

STATIC SITUATIONS

Static situations correspond to non wetting cases ($S < 0$) or final spreading equilibrium state ($S > 0$).

Non Wetting Case : $S < 0$

Due to the disjoining pressure, the microscopic contact angle differs from the macroscopic one.[1-3] This local distortion of the edge profile extends typically over the range of $\pi(z)$.

In liquid crystals, ordering effects at interfaces are induced by angle-dependent contributions in $\pi(z)$.[16-20] If these contributions are dominant, they impose the local equilibrium contact angle (Figure 1, adapted from reference 1.).

In some cases they can be strong enough to prevent spreading even for (small) positive S values.[1]

Wetting Case : Final Spreading Equilibrium

The wetting case corresponds to a positive (thickening) disjoining pressure. As a result, there is a minimum thickness for a spreading film, which is a balance between the driving force for spreading (S) and the disjoining pressure.

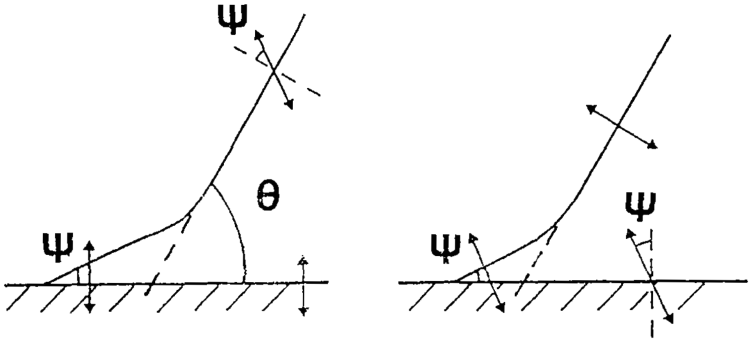

FIGURE 1. The local contact angle Ψ ensures the compatibility between preferred orientations at solid/liquid and liquid/gas interfaces.

The minimum thickness e_c is given by the implicit equation [1]

$$S = P(e_c) + e_c \Pi (e_c)$$

For van der Waals forces and isotropic media

$$e_c = \frac{1}{2}\sqrt{\frac{A}{\pi S}}$$

No calculation is available yet in more complex cases.

THE DYNAMICS OF WETTING $S > 0$

Although no complete description of the spreading dynamics has been given yet, the most important conclusions have been established by de Gennes and Joanny.[1]

For describing the behaviour of an advancing liquid edge, it is usually possible to treat separately the macroscopic part -characterized by the macroscopic velocity U(t) and the macroscopic contact angle θ(t) -and the microscopic structure. This structure is a thin film developing in front of the macroscopic edge, called the precursor film. A schematic picture is given on the Figure 2.

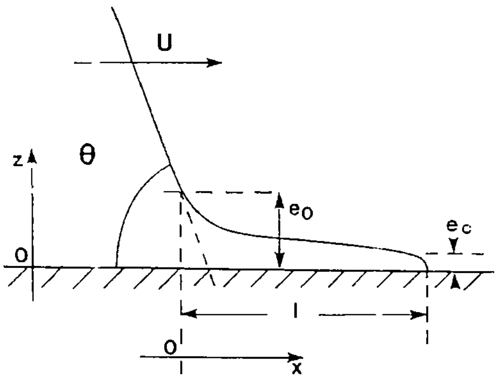

FIGURE 2. The macroscopic edge (left) is characterized by the angle θ (t) and the velocity U(t). The precursor film (right) has a maximum thickness e_0, a minimum thickness e_c and a length l.

Macroscopic Behaviour

Both theory [1,2,6,21] and experiments[6,9,14] have shown that, within a good approximation, [22] a general relation exists between θ and U :

$$\theta = f\left(\frac{\eta U}{\gamma}\right) = f\ (Ca)$$

f is an universal S-shaped function which can be explicitly calculated at low Ca. [1,6]

$$\theta \simeq K\ (Ca)^{1/3} \qquad K \simeq 4$$

$$Ca < 10^{-2}$$

η is the liquid viscosity.

This result can be used for predicting the rate of spreading of macroscopic droplets in the low θ limit [1] and gives good agreement with experiments. [6-9] For droplets, the large θ situation is not expected to obey simple spreading laws and the few theories and experimental results available up to now are still tentative.[23]

The Precursor Film

The universality of the macroscopic laws is due to the presence of the microscopic precursor film. In contrast with the macroscopic edge, which depends only on the bulk liquid properties (η and γ), the precursor film reflects the details of the solid/liquid/gas interactions.

For van der Waals interactions and isotropic media (the only case which is theoretically tractable up to now), the length of the precursor is, for $U \neq 0$:

$$l \approx \frac{1}{3\eta U} \sqrt{\frac{AS}{\pi}}$$

Its maximum thickness at the crossover with the macroscopic edge is[1]

$$e_0 \approx \frac{1}{\theta} \sqrt{\frac{A}{6\pi\gamma}}$$

Its minimum thickness is e_c.

For $U = 0$, the precursor length is given by a diffusion equation[24]

$$l \approx \sqrt{Dt}$$

$$D = \frac{1}{3\eta} \sqrt{\frac{AS}{\pi}}$$

A Tentative Discussion

The main point in the preceding results is the possibility to treat separately the macroscopic and the microscopic parts of the edge. This conclusion is expected to remain valid for the spreading of (possibly) anisotropic liquids on (possibly) anisotropic surfaces, as long as spreading is actually achieved.

For example, if the solid surface is smooth at the macroscopic scale ($\gtrsim$ μm), the usual spreading laws for droplets [1,6-9] might be observed and the wetted spot might remain a circle.[25]

Obviously, the precursor characteristics will be completely different. The corresponding distorded domain at the edge of the drop (see Figure 1) will still have a reduced extension, but the associated interaction energy is not negligible. It can play a role in the selection between competing anchoring directions during spreading process[25] and is certainly a dominant term for the late stages of spreading.

For the moment, spreading processes in molecularly anisotropic systems have not been investigated theoretically.

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