Steady motion of the three phase contact line in model Langmuir-Blodgett systems

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Summary

The forced steady motion of the three phase contact line in model Langmuir-Blodgett systems is studied. Different "Y"-multilayers served to vary the dynamic behaviour of the contact perimeter at constant viscosity, density and surface tension of the subsolution. The specific velocity dependences of the receding contact angle \( \theta_r \) and dynamic capillary height \( L_c \) stress the significance of the three phase contact line properties in the kinetics of wetting in the whole steady velocity range. The presentation of the experimental results in the Blake and Haynes theoretical scale confirms this conclusion.

The deviation from the theoretical trend observed with arachidic acid system at high velocities is related to the bulk drag force which becomes significant under these conditions. A model considering the drag force location in a receding meniscus at high withdrawal velocities is proposed, in which the Blake/Haynes relation is taken as a boundary condition of the bulk hydrodynamic problem. The latter is assumed to be similar to the problem of film entrainment by a moving solid wall. The experimental data show good agreement with the equation obtained on the basis of the proposed model.

I. Introduction

Wetting of a solid surface is characterized by the angle which the gas/liquid interface makes with it along the three phase contact line. At equilibrium the static value of this contact angle is determined by the solid/gas, solid/liquid and liquid/gas interracial tensions. When the liquid is moving a dynamic contact angle is established, the latter reflecting the balance between driving and drag forces in the system. A single-valued dependence exists between this angle and the contact line velocity. The explicit form of this relationship depends on the location of the drag forces and the adopted model of their calculation.

When low speeds are considered, it is usually assumed that the dynamic meniscus has a quasi-equilibrium shape. In this case the kinetics of wetting is restricted by the dissipation of energy in the three phase contact region (1). At higher speeds the static shape approximation might lead to considerable errors (2). The exact solution of the problem of the dynamic profile meets with substantial difficulties. For this reason various hydrodynamic models are used, merely assuming the bulk nature of the drag forces in the system.
When a solid is withdrawn at a constant speed $U$ from a liquid which does not wet it completely ($0^\circ < \theta_r < 90^\circ$), the receding contact angle $\theta_r$ and the contact line velocity $V$ do not change in time. This steady motion is characterized by the equality $|V| = |U|$. At higher velocities the steady $\theta_r$ become smaller and at a given $U$-value the solid wall entrains a liquid film. This phenomenon is known in the literature as “dynamic wetting” and the velocity at which it occurs is termed “critical velocity of dynamic wetting” (3).

By means of model Langmuir-Blodgett systems it was shown (4) that the value of $U_{cr}$ strongly depends on the specific properties of their three phase contact regions. This means that the dynamic behaviour of the contact line plays an important role in the whole steady range of velocities ($0 < U < U_{cr}$).

In the present paper the steady motion of the contact perimeter is analyzed in more detail. As in (4), different model Langmuir-Blodgett systems having identical bulk properties are investigated.

II. Experimental

Langmuir-Blodgett multilayers of the “Y”-type built up by monolayer transfer of insoluble surfactants bearing various hydrophilic groups served to model different behaviour of the three phase contact line. Thus one could vary the interactions occurring there between the functional groups of the last transferred monolayer (a) and that being transferred (b) - figure 1. In all cases bulk viscosity, density and liquid/gas interfacial tension were held constant. (The monolayer transfer was carried out under barostatic conditions $\Delta a = \text{const.}$.) The insolubility of the monolayers on the liquid surface as well as the automatic maintainance of constant $\sigma$ exclude any influence of grad $\sigma$ on the hydrodynamics of the process.

II.1 Experimental technique, materials and substances

Multilayers were built up at constant surface pressure of 30 dynes/cm by the standard Langmuir-Blodgett technique (5). An automatic feed-back Langmuir-Adam balance (6) was used. A lifting device ensured a strictly vertical motion of the solid substrate at a speed ranging from 0.05 cm/s to 2.5 cm/s. A glass cylinder with sufficiently large diameter was used as a solid support, so that its external meniscus did not differ from that near a flat wall.

Fig. 1. Schematic presentation of the process of Langmuir-Blodgett multilayer creation. TPCL – three phase contact line

Photographs of the meniscus profile were taken at suitable magnification under static as well as dynamic conditions and the values of the corresponding contact angles were measured therefrom. Due to the saddle-like shape of the meniscus a local value of the contact angle at a given point of the wetting perimeter was thus obtained. For this reason the $\theta_r$-values were rather scattered.

Simultaneously with the photographic determination of $\theta_r$ the height $L_c$ of the three phase contact line above the liquid level was measured using a cathetometer. The horizontal line of the wire cross was adjusted to intercept the irregularities of the contact line, i.e. $L_c$ was averaged along its whole observable part. This $L_c$-value reflects the dynamic behaviour of the three phase contact perimeter in the whole steady range of velocities. As shown below, the dynamic contact angles photographically obtained at high velocities are not directly related to the interactions in the region of the contact perimeter.

Arachidic acid C19H39COOH and its methyl ester C19H39COOCH3 (Merck - additionally recrystallized) were used to prepare the model multilayers. In both cases pH = 2 was maintained in the aqueous subsolution (1·10^{-2} M HCl). Under these conditions the arachidic acid dissociation is completely suppressed (7). Thus an interaction between non-ionic functional groups takes place in the region of the three phase contact line.

All water was doubly distilled. The hydrochloric acid used for pH adjustment was of A. R. grade. The glass cylinders were cleaned using a mixture of conc. HNO3 and conc. H2SO4 and treated with dichlorodimethylsilane. Systems of more than 5 transferred monolayers were used for the $\theta_r/U$ and $L_c/U$ measurements in order to avoid the influence of the glass substrate (8).

II.2 Results

Figures 2 and 3 represent the dependence of $\theta_r$ and $L_c$ on $U$ for both investigated model systems. The static capillary height $L_{st}$ was deter-