Note

Comment on "Dynamic wetting by liquids of different viscosity," by T.D. Blake and Y.D. Shikhmurzaev

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Abstract

We comment on a recent theory of dynamic wetting that is based directly upon a model for interface formation, introduced by Shikhmurzaev. We argue that the treatment of surface tension and its relaxation, inherent in the original model, is physically flawed.
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In a recent paper [1], Blake and Shikhmurzaev utilize a model for interface formation, proposed initially by Shikhmurzaev [2,3], to interpret their measurements of the velocity dependence of the dynamic contact angle at a moving contact line. They determine some of the parameters contained in the model, in particular, their viscosity dependence. In this comment, we point out that the key quantities upon which this model is based have no well-defined physical meaning. More specifically, the treatment of surface tension which underlies the theory does not correspond to any known physical mechanism. As a result, the model leads to consequences which are physically unrealistic.

The model in Ref. [1] is based on the fundamental assumption that the surface tension of a *pure liquid* is determined by a 'surface equation of state,' which fixes its value as function of surface parameters (see also [2, Section 2.1]). As an approximation, the surface tension σ is assumed to depend on the 'surface density' ρ^s alone, cf. Eqs. (1) and (4) of [1]:

$$\sigma = \gamma\left(\rho_0^s - \rho^s\right), \tag{1}$$

where γ and ρ_0^s are phenomenological constants. In [1], Shikhmurzaev's model is applied to both the free liquid–gas

and the liquid–solid interface, but we will focus on the former, so there is no need for an index on σ. Equation (1) makes no physical sense *for a pure liquid*. Firstly, as explained in [4, p. 31 ff], surface density as introduced by Gibbs cannot be an intrinsic property of the surface of a pure liquid. It depends solely on the definition of what Gibbs calls the *dividing surface* between the two phases. Conventionally, for a pure liquid, one defines the dividing surface in such a way that the surface density *vanishes* [4, p. 31], a choice which is called the *equimolar surface*. Secondly, the surface is not an independent thermodynamic system that would allow relations between its extensive and intensive parameters to be defined, as is done in [1–3], and as is implied by (1). As pointed out in [4, p. 33], the surface exists only by virtue of the bulk phases that surround it; it does not form an autonomous phase. Hence an expression such as $\sigma = \sigma(\rho^s)$, as given in [1], is meaningless as regards surface thermodynamics, no matter how ρ^s is defined.

We illustrate our criticism further by pointing out two of the consequences of the ansatz (1), which we believe contradict basic principles of surface physics. Equation (13) of [1] states that the surface tension is proportional to the surface thickness h. This is well known not to be the case, see [4]. Of course, h is not really an independent quantity, rather, it is determined by the conditions of thermodynamic equilibrium at the surface. However, by considering, for example, different temperatures, different interface density pro-

files can effectively be realized. Given the interface profile, the surface tension can be calculated essentially by mechanical arguments [4]. (For a slowly varying profile, treated in the square-gradient approximation of Rayleigh and van der Waals, the result is Eq. (1.43) or (3.11) of [4].) If anything, the surface tension will be *larger* for a sharp interface ($h = 0$) than for the real smooth one. The reason is that the real interface shape is one that *minimizes* the total free energy (grand potential) of the inhomogeneous fluid (see [4, p. 54 ff]). Indeed, at high temperatures, when the interface becomes more diffuse, surface tension *decreases* (cf. Figs. 1.5, 1.6, and 6.5 of [4]).

Next, we consider Eq. (14) of [1] for the typical time scale τ, 'required for the interfacial structure formation' [2]. This is supposed to be the timescale over which the surface tension changes from its liquid–vapor value to its solid–liquid value, as fluid elements are swept from the liquid–vapor interface onto the solid. In Eq. (14) of [1] the time τ is claimed to be proportional to the viscosity μ of the fluid, and a specific estimate is given for $\mu = 672$ mPa s, for which the value is supposed to lie between $\tau = 2.5 \times 10^{-6}$ and 8.3×10^{-6} s. We in fact believe that the timescale needed to establish the surface tension of a liquid–vapor or solid–liquid interface is extremely small: force is transmitted with the speed of light, giving $\tau \approx 10^{-18}$ s for molecular sizes. Such a timescale does not depend upon a diffusive or any other transport process. In fact, in [1] we do not find evidence for a convincing 'microscopic mechanism of the interface formation,' nor for a link to time-dependent surface tension.

One might argue that as the authors' estimates are based on their own measurements of a moving contact line, they should provide independent evidence for the consistency of the assumptions of the model. Unfortunately, we do not believe this to be the case. The reason is that the authors' theory refers to what they term the dynamic contact angle θ_d, determined solely by a balance of surface tensions, cf. Eq. (7) of [1]. Viscous forces and, therefore, interface bending does not enter their description. The *measurement* of the interface angle was, however, performed on a macroscopic scale (say, 10^{-4} m). It is well known that the interface near a moving contact line is highly curved [5], which is the result of viscous forces which therefore cannot be ignored. This effect is best appreciated in the case of a perfectly wetting fluid, where the contact line is preceded by a precursor film [5]. Hence no interface formation is taking place, yet on macroscopic scales measured contact angles have a speed dependence consistent with Tanner's law [5]. Thus we suggest that in the partially wetting case, considered here, any effects of interface bending should be carefully subtracted for a correct interpretation of experimental data.

References

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