

Note

Response to the comment on [J. Colloid Interface Sci. 253 (2002) 196] by J. Eggers and R. Evans

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Abstract

We examine the comment on our paper [J. Colloid Interface Sci. 253 (2002) 196] by Eggers and Evans and show that the assertions made there have no foundation in fact nor in scientific substance.

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The comment by Eggers and Evans on [1] is really a comment on the theory developed in [2] and used to analyze the data in [1]. The theory was published more than a decade ago and has since been applied to different problems by many workers so that it is hardly “recent” as remarked by the authors. Below, we address the points raised in the comment starting with the most important ones.

(1) The key assertion in the comment is that, as the authors “believe,” the surface tension relaxation time for both liquid–vapor and liquid–solid interface can be estimated as $\tau \approx 10^{-18}$ s, and hence no surface tension relaxation ever takes place in hydrodynamic processes, including dynamic wetting, which are characterized by much longer time scales. This assertion is spectacularly wrong as one can show in several different ways. First, the value of 10^{-18} s is obtained by dividing the size of a molecule of a simple fluid by the speed of light. In fact, as is well known, the relaxation of an interface toward its equilibrium state is a *dissipative* process, whereas the propagation of an electromagnetic wave is not. To estimate the rate of a dissipative process by considering a nondissipative process, as the authors do, is a mistake of principle. The formation of an interfacial structure, which is what the surface tension relaxation process is about, is as-

sociated with re-arrangement of molecules in the interfacial layer and mass exchange between the interface and the bulk, in other words with molecular, not photon, motion. In this connection, it is worth mentioning that in the theory developed in [2] the interface formation process is described in the framework of irreversible thermodynamics and shown to be driven by the difference between the chemical potentials in the bulk and the surface phase, i.e., to be a dissipative process of a diffusion type. This theory applied in [1] to 8 experimental curves for liquids with viscosities spanning almost three decades allowed us to describe all of them without any ad hoc adjustments from one curve to another. The estimates for τ (ranging from nano- to microseconds depending on viscosity) were obtained as an outcome of the experimental study with all assumptions clearly stated.

Second, the experimental literature on the issue (e.g., [3]) shows that the surface tension relaxation times of pure liquids, as well as of mixtures, are many orders of magnitude larger than 10^{-18} s.

Third, dynamic wetting experiments also show that the authors’ “belief” that the surface tension is always constant in all fluid flows is in conflict with physical reality. The Young equation

$$\sigma_1 \cos \theta = \sigma_3 - \sigma_2, \quad (1)$$

which defines the macroscopic notion of the “contact angle” θ as it introduces this concept into fluid mechanics, relates

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θ to the surface tensions σ_1 , σ_2 and σ_3 acting on the contact line from the three interfaces. It has been shown by analyzing experiments on dynamic wetting (e.g., [4,5]) that the velocity dependence of the measured dynamic contact angle, as well as its dependence on the flow field, cannot be attributed entirely to free-surface bending near the contact line; the actual (Young's) angle θ does vary when the contact line is moving. Molecular dynamic simulations show this as well [6]. Once the dynamic contact angle θ deviates from the static value, one has to conclude from equation (1) above that at least one of the surface tensions σ_1 , σ_2 or σ_3 acting on the contact line is *not* the same as at equilibrium. Hence, the surface tension relaxation, from a nonequilibrium value at the contact line to the equilibrium one away from it, is bound to take place. Then, physical mechanisms of the interface formation have to come into play. The simplest mathematical model of these mechanisms is what Shikhmurzaev's theory [2] is all about.

(2) The bulk of the comment is devoted to the surface equation of state

$$\sigma = \gamma(\rho_0^s - \rho^s), \quad (2)$$

which the authors singled out from the model [2]. Its meaning is as follows. As is well known from experiments and molecular dynamic simulations, at equilibrium, for any given temperature, the interfacial layers of liquid adjacent to the gas phase and to the solid boundary have, in general, different densities and different surface tensions. The density can be characterized integrally as the mass per unit area of the interfacial layer, i.e., as the surface density ρ^s , just as the surface tension σ is also an integral across the layer of the momentum flux distribution. Thus, the surface density can be used, together with the temperature, as parameters characterizing the state of the interfacial layer; hence in [2] the interface is considered as a *two*-parametric thermodynamic system. For a particular class of processes, namely *isothermal* (or, more generally, *barotropic*) flows, this system becomes one-parametric with $\sigma = \sigma(\rho^s)$. The simplest phenomenological equation of state correlating σ and ρ^s in such a process, as the interface evolves from one equilibrium state to the other, is a linear one, i.e., (2). A more general equation of state is described in [2]. It is worth emphasizing that since the theory in [2] is the first one incorporating the process of interface formation into fluid mechanics, one should use the simplest self-consistent mathematical model of this process until experiments indicate the necessity to generalize it and the direction in which to go.

Eggers and Evans begin by claiming that (2) “makes no sense. Firstly, as explained in [7, p. 31], surface density as introduced by Gibbs cannot be an intrinsic property of the surface of a pure liquid.” Beautifully argued with just one flaw: the surface density in [2] is *not* the one introduced by Gibbs. Gibbs considers the equilibrium thermodynamics of *excess* quantities. In contrast, the theory developed in [2] considers the whole of the interfacial layer as a thermodynamic system

in a nonequilibrium process of interface formation and characterizes it via integral quantities, such as σ and ρ^s . This approach makes it possible to treat both the liquid–gas and liquid–solid interface in a unified way. Hence the authors' arguments related to the interfacial structure, “dividing surface,” etc. are irrelevant and misleading: in [2] the internal structure of the interface is not considered. Here the authors simply misrepresent the issue.

The authors go on: “Secondly, the surface is not an independent thermodynamic system that would allow relations between its extensive and intensive parameters to be defined. . . .” One might notice that the same argument applies to “fluid particles” in classical fluid mechanics and other open systems, where the methods of irreversible thermodynamics have been successfully used for half a century. As is well known, continuum mechanics *defines* a thermodynamic system via its constitutive equations together with transport and dissipation mechanisms. The properties of the resulting model are then tested against independent experiments, which is the ultimate test for every theory, not speculations about different models operating with different concepts. On this count, Shikhmurzaev's theory has, so far, performed exceptionally well, being uniquely able to describe all key experiments in the field of dynamic wetting without any ad hoc adjustments (e.g., [1,2,8,9]). Furthermore, this theory has been successfully applied [10], again without any ad hoc alterations, to removing unphysical singularities (infinite velocities and pressures) from the mathematical description of the capillary breakup of liquid threads. These singularities have been championed by Eggers for many years [11] and are now removed.

(3) To illustrate the above criticisms of (2), the authors talk about the density profiles inside the interfacial layer, the consequences of setting the thickness of this layer equal to zero ($h = 0$) and the temperature variations. This illustration, however, is again misrepresenting the issues. Indeed, a check of the authors' statements against what is actually written in [2], or a glance at Eqs. (1)–(6) of [1], would baffle the reader since in the theory developed in [2] and briefly recapitulated in [1] one would find neither an interfacial thickness h nor profiles of any quantities across the interfacial layer: as already explained above, the interfaces are characterized in terms of their integral properties (σ , ρ^s , etc.). Hence the authors' musings over the interfacial structure and what the surface tension for different h is likely to be are simply not relevant to the theory they are commenting on: the theory has no h in it!

In [1], we *estimate* the values of all macroscopic phenomenological coefficients involved in the theory by using estimates for the interfacial layer thickness (at *equilibrium*) and other microscopic properties, similarly to how one would estimate, say, the viscosity coefficient in the bulk or the bulk density via molecular properties of the medium. To set $h = 0$ in such an estimate (Eq. (13) of [1]), as the authors do, is like setting the intermolecular distance equal to zero in an estimate for the bulk viscosity or density—the resulting ab-

surdity rests with the authors. Ironically, they argue for the interface at equilibrium being a diffuse one and then... set $h = 0$ in our estimate, Eq. (13) of [1], although the subscript $1e$ explicitly states that the estimate is considering the *equilibrium* state of the interface (1 refers to the liquid–gas interface and e stands for “equilibrium,” as explained in the text). Furthermore, the actual values for h used in the estimate are *given*. Here the authors’ misrepresentation of our paper is more than obvious.

As pointed out above, Eq. (2) relates σ and ρ^s at a *given* temperature so that speculations about what would happen to h if the temperature is varied and how the density profiles inside an interfacial layer might then evolve are not related to the issue and can only mislead the reader.

(4) In the last paragraph of the comment, the authors suggest subtracting the effects of interfacial bending for “a correct interpretation of experimental data.” We can report that these effects have been carefully examined in a separate study for our systems, and it was shown that for the spatial resolution of our measurements, which was about $20\ \mu\text{m}$ (not “say, $10^{-4}\ \text{m}$ ”), these effects leave the contact angle within the experimental error and hence make absolutely no impact either on the qualitative conclusions or on the quantitative estimates obtained in our paper. It should also be pointed out here that qualitatively equating, as the authors do, the case of perfect wetting with a precursor film in front of the

main body of fluid and the case of partial wetting, where there is no such film, is simply wrong: these two cases are well known to be qualitatively very different.

Thus, we have to conclude that none of the authors’ assertions can stand close scrutiny and some show a wanton disregard of the facts. Nevertheless, we welcome this opportunity to dispel some of the misconceptions that appear from time to time in connection with ongoing research on dynamic wetting.

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