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Reply to “Kinetics of reactive wetting”

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Abstract

This letter provides an extension of an earlier paper [Scripta Mater 36(1997)645] on the rate of diffusion-limited reactive wetting, in which the analysis is extended to include the influence of local reaction kinetics, and underlying assumptions are discussed in response to a recent paper by Yost [Scripta Mater 42(2000)801]. © 2001 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

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Introduction

The subject of interest in this short communication is that of a drop of liquid metal, placed upon a flat solid substrate which it wets poorly, and which spreads gradually on this solid thanks to the formation of a new phase along the liquid/solid interface, this new phase being significantly better wetted by the liquid than the original solid surface. The rate of spreading of the drop is limited by the rate at which this new phase can grow along the liquid/solid/atmosphere triple line, and spreading stops when the drop becomes sufficiently flat that the (low) angle of contact of the liquid on the new solid phase is attained.

Specifically, we are interested in the case where it is a solute element contained within the liquid that reacts with the solid along the triple line to form the new, better wetted, reaction phase upon which the drop spreads. In this case, as we have pointed out earlier [1], two phenomena can limit the rate of formation of the new phase: (i) the intrinsic rate of the reaction itself, and (ii) the rate of supply of solute to the triple line. Although

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several mechanisms for transport of solute from the drop bulk to the triple line can be envisaged (interfacial diffusion, vapor transport, . . .), we focus on the case where the most rapid pathway for solute transport is through the liquid (see Fig. 1 of Ref. [1]).

We provided in Ref. [1] a simplified analysis of this diffusion problem, which is compared with data in Refs. [2,3]. A recent article published in this journal by Yost [4] has raised questions on this analysis and has suggested broadening it to incorporate the influence of local reaction kinetics. The present communication is a follow-up on this contribution.

Lack of validity of the analysis in Ref. [1] for published data showing diffusion control

On the basis of observed spreading kinetics published in Refs. [2,5], it is stated by Yost that the analysis of Ref. [1] can only be valid at spreading rates so low as to be characteristic of chemical reaction (and not diffusion) control of triple line motion. Yost's reasoning is that in practical cases which display features of diffusion control, the rate of spreading dR/dt , where R is the drop radius and t is time (keeping our original notation) does not obey:

$$\frac{dR}{dt} \ll \frac{D}{R} \quad (1)$$

where D is the diffusion constant for the solute in the liquid. Satisfaction of this equation is stated by Yost to be the condition for "quasi-equilibrium or slow flow". This, of course, is equivalent to the requirement that the Peclet number Pe' defined by:

$$Pe' = \frac{R}{D} \left(\frac{dR}{dt} \right) \quad (2)$$

be significantly less than one.

The assumption that the local Peclet number be significantly below one is indeed in general necessary for convective solute transport to be negligible, this allowing in turn the problem to be analyzed by solution of Fick's law only; however, we wish to stress that the selection of Pe' of Eq. (2) is not the appropriate Peclet number, such that obeyance of condition (1) is not required for the analysis of Ref. [1] to be valid. We agree that the local liquid velocity u near the triple line scales (in the absence of other convection sources such as thermosolutal convection) roughly with the drop spreading rate dR/dt . On the other hand, there is no reason to adopt the drop radius as the appropriate length scale L entering the definition of the relevant Peclet number, $Pe = Lu/D$. Rather, as was pointed out in Ref. [1], L should be taken as the width b of the diffusion layer, measured from the triple line, i.e. the width of the region within which significant diffusion takes place. As was shown in Ref. [1], b is close to $10 \mu\text{m}$ under usual experimental conditions, which is $<R$ by two or three orders of magnitude with usual drop sizes. Specifically, for the data in Fig. 2 of Ref. [2], we have $dR/dt \leq 2 \times 10^{-5} \text{ m s}^{-1}$ and $D \approx 4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, such that the relevant Peclet number will be $<5 \times 10^{-2}$, verifying the requirement $Pe \ll 1$.

Thus, although the analysis presented in Ref. [1] is certainly approximate, there is no reason to doubt its basic validity for the values of R , dR/dt and D relevant to experiments reported in Ref. [2]. Rather, as was stated in that reference, the most reasonable explanation is that the analysis does not fully describe the data because of an added phenomenon, which we proposed could be the presence of continued formation of the reaction product behind the triple line. The validity of this proposal is the subject of current investigation.

Similarity of the two approaches

It is stated by Yost that his analysis [4] is similar to that presented in Ref. [1]. We wish to point out that the two are in fact quite different. Both are indeed solved in cylindrical coordinate systems and are based on a solution of Fick's law; however, the reference frame and associated symmetry invoked differ. In Ref. [1], the curvature of the triple line was neglected; hence the problem is defined as one that features cylindrical symmetry about an axis coincident with the triple line, the triple line thus being locally assimilated to a straight line. The analysis of Ref. [4] on the other hand seemingly centers the problem around the axis of symmetry of the drop itself. All diffusion is thus assumed in Yost's treatment to take place horizontally, along planes parallel to the surface of the solid. With this assumed diffusion path geometry, the only flux lines that reach the triple line are located within the liquid/solid plane of contact, and the no-flux condition across the drop free surface is violated. To compensate for this, Yost then multiplied the thus-derived horizontal radial flux by $\cos(\phi)$ (Eq. (3) of Ref. [4]) and integrated the resulting expression in ϕ between 0 and θ . Both the solute flow path and the final equation thus differ significantly between the two analyses.

For values of D and spreading time t near their realistic upper bounds (near 10^{-8} $\text{m}^2 \text{s}^{-1}$ and 10^3 s respectively), the diffusion zone width, which extends from the triple line to distance $b = a \exp[1/2F(T)]$ (variables a and $F(T)$ are defined in Ref. [1], in which this expression unfortunately appears with the factor 2 missing) may become commensurate with the droplet radius. If, also, convection within the bulk drop is negligible it may then become necessary to take into account the triple line curvature in solving the problem. For such circumstances, an approach which incorporates, as does that of Yost, the rotational symmetry about the droplet central axis becomes necessary. We note, however, that the simultaneous occurrence of long time and high diffusivity is not expected in practice since high diffusivity implies rapid triple line motion and, hence, short droplet spreading times (experimentally observed diffusion-limited spreading times are close to 10^2 s with D nearer 10^{-9} $\text{m}^2 \text{s}^{-1}$ [2,3,5]).

Incorporation of reaction kinetics in the analysis of Ref. [1]

The analysis of Ref. [1] can also readily be extended to incorporate the influence of finite reaction kinetics, following the usual series scheme used in the analysis of kinetic

processes. To this end, Eq. (11) of Ref. [1] is rewritten with C_a , the local solute concentration in the liquid along the triple line, instead of the equilibrium concentration C_e :

$$\frac{dR}{dt} = \frac{2DF_{(t)}}{en_v} (C_0 - C_a)\theta \quad (3)$$

(n_v is the number of moles of reactive solute per unit volume of the reaction product, e is the reaction product thickness at the triple line, and C_0 is the bulk drop concentration). Writing a local kinetic equation linking dR/dt and C_a , one obtains two equations for two unknowns (C_a and dR/dt), from which dR/dt is simply deduced. For example, if one opts to describe local reaction kinetics at the triple line using the simple linear law:

$$\frac{dR}{dt} = k(C_a - C_e) \quad (4)$$

where k is a constant, the rate of spreading is predicted to be:

$$\frac{dR}{dt} = \frac{\frac{2DF_{(t)}}{en_v} (C_0 - C_e)\theta}{1 + \left(\frac{2DF_{(t)}}{ken_v} \theta\right)} \quad (5)$$

which indeed tends toward the expected reaction-control and diffusion-control limits as (D/k) tends towards infinity and zero, respectively. We note, however, that local reaction kinetics can be governed by relatively complex phenomena, such that more involved relations than Eq. (4) may obtain; a specific case will be exposed in forthcoming work by one of the present authors (N.E.) and his collaborators.

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