

steady states and their associated stabilities for combinations of constraints reported in ref 1. The model and associated parameter values are given in Table I. The ranges and scan increments in each constraint are listed in Table II as two-dimensional grids of  $k_0$  and reactant concentration. A four-variable empirical rate law model much like that in Table I was first used by Epstein and co-workers<sup>10</sup> to give a near quantitative description of bistability in the iodate-arsenous acid system. One- and two-variable reductions of the four-variable model have provided remarkably accurate descriptions of the system with arsenous acid in stoichiometric excess.<sup>3-6</sup>

Our search for potentially oscillatory behavior yielded only single stable steady states or one unstable steady state lying between two stable steady states. Thus, according to these model calculations the system is either monostable or bistable, but is not oscillatory for the conditions reported in ref 1.

Based on findings in the bromate-cerium(III) system,<sup>11-13</sup> oscillatory behavior might be expected in the iodate-arsenous acid system near the critical point. We carried out an exhaustive search for oscillatory behavior near the critical point for the conditions of Figure 5 in ref 1 and for excess iodate conditions in ref 2 and excess arsenous acid conditions in ref 5.<sup>14</sup> In no case did we find any behavior other than monostability or bistability.

Of course, model calculations can never disprove a claim of oscillatory behavior. Even with the past successes of the model presented here, it may still contain deficiencies. However, we believe that these calculations, along with our observations of the sensitivity of the system to experimental fluctuations, suggest that the nonperiodic oscillations reported in ref 1 are not the result of an oscillatory chemical reaction.

In the absence of deterministic oscillatory behavior, another possible source for nonperiodic oscillations might be thermal fluctuations. Theoretical results of Nicolis and Turner<sup>15</sup> show that near the critical point thermal fluctuations become much larger in magnitude. We have observed an extreme sensitivity to experimental fluctuations near the critical point and hysteresis limits but have yet to find evidence for stochastic behavior arising from thermal fluctuations, presumably because the experimental fluctuations are much larger in magnitude than the thermal fluctuations and both are magnified at these points. We believe that the nonperiodic oscillations reported in ref 1 do not arise from thermal fluctuations, but rather from a sensitivity to experimental fluctuations resulting from the high reactant concentrations utilized in that study. We repeated the experiments reported in Figure 3 of ref 1 with a Pt electrode (Orion Model 96-78) and found *periodic* oscillations that coincided with the pulsations of our peristaltic pump. The maximum amplitude of these oscillations was much smaller than that of the nonperiodic oscillations reported in ref 1. Interestingly, even with arsenous acid in stoichiometric excess, a visually detectable iodine concentration was generated in the reaction mixture. A calculation using the empirical rate law model in Table I showed that at these high reactant concentrations the Roebuck reaction becomes rate determining, thereby resulting in an accumulation of iodine. We believe that the large amplitude nonperiodic oscillations reported in ref 1 resulted from a high sensitivity of the Pt electrode to molecular iodine coupled with a shorter time scale for reaction (due to high reactant concentrations) than the time scale for complete mixing of the reaction mixture.

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Registry No. Iodate, 15454-31-6; arsenous acid, 13464-58-9.

Department of Chemistry  
West Virginia University  
Morgantown, West Virginia  
26506-6045

N. Ganapathisubramanian  
Kenneth Showalter\*

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## Relevance of Prewetting on the Stability of Transient Foams in Partially Miscible Liquids

*Sir:* In a recent letter, Gracia, Varea, and Robledo explained the stability of certain transient foams in binary liquid mixtures by prewetting phenomena. We show that such an explanation which is valid for infinite thickness films (early times) cannot be valid for finite thickness films (later times) at thermodynamic equilibrium. We propose a nonequilibrium mechanism to explain the foam stability.

In a recent letter,<sup>1</sup> Gracia et al. proposed a theoretical explanation for the stability of transient foams in the one-phase region of a binary liquid mixture. Their calculation was based on calculating nonuniform prewetting profiles between vapor and bulk liquid regions. They considered macroscopic films (with an infinite thickness) and showed that, in the prewetting region, liquid films are best maintained due to the increased stiffness of their interfaces toward adsorption. However, even in this prewetting region a liquid film is unstable due to long-range van der Waals forces. During the early stages of their life transient foams are macroscopic and the study of ref 1 is relevant; however, at later times finite thickness films in the prewetting region are subject to an additional force.

(i) At thermodynamic equilibrium this force is always attractive thus the foam instability is enhanced.

(ii) If, due to slow diffusion along the film the composition of the film remains fixed, the force on the film can be *repulsive* and thus can *stabilize* the foam. We study briefly these two situations.

In permanent foams, the stabilizing agent is a surfactant that reduces the interfacial tension and thus favors the appearance of a film structure. However, a transient foaminess was observed<sup>2</sup> in some binary liquid mixtures under agitation, for example, when nitrogen is bubbled through a binary mixture of diisobutylcarbinol and ethylene glycol. Foaminess was more pronounced in the vicinity of the consolute point and was only observed in the one-phase region.<sup>2</sup>

Our model is based on the analogy between the effect of *prewetting* layers on the foam stability and the effect of *adsorbed* polymer layers (in a good solvent) on the interaction between two planar surfaces as studied experimentally by Klein<sup>3</sup> and co-workers and theoretically by de Gennes.<sup>4</sup> At thermodynamic equilibrium the interaction between the plates is always attractive. However, due to the long relaxation times for polymer desorption, the adsorbed polymer concentration remains, in practice, constant. For this nonequilibrium situation, the two polymer layers repel each other.

We consider a film of thickness  $z = d$  which is in contact with a bulk AB mixture where the concentration of the A liquid (the one that prefers to wet the vapor wall) is  $C_b$  and the system is in the prewetting state as can be seen in Figure 1. The free energy functional  $\gamma$  is

$$\gamma[C, C_s] = \int_0^d \left[ \frac{1}{2} a \left( \frac{\partial C}{\partial z} \right)^2 + W(C) \right] dz + 2(\gamma_0 - C_s \gamma_1) \quad (1)$$

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(2) S. Ross and G. Nishioka, *J. Phys. Chem.*, **79**, 1561 (1975).

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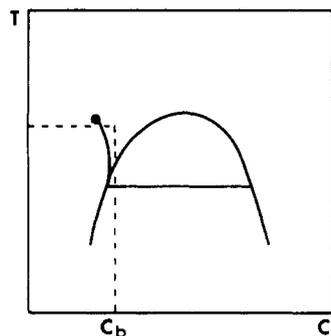


Figure 1. A typical bulk concentration  $C_b$  which lies in the prewetting region.

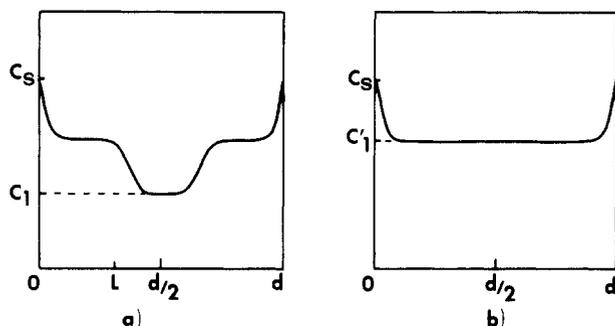


Figure 2. Schematic concentration profiles in the prewetting region. The vapor walls are at  $z = 0$  and  $d$ , and  $C_s$  and  $C_1$  are the concentrations at  $z = 0$  and  $d/2$ , respectively. In (a)  $d > 2L$  whereas in (b)  $d < 2L$ ,  $L$  being the prewetting layer thickness.

The first term is a gradient term which describes the short-range interaction. It is different from the Kac-like nonlocal interaction that was introduced in ref 1 but, since this interaction is also short range, we do not expect the difference to be relevant. The second term is the difference between the bulk free energy density  $F(C)$  and its corresponding tangent at the bulk concentration  $C_b$ .<sup>5</sup> The third term is a surface term which expresses the preferential adsorption at the wall, and  $C_s$  is the surface concentration. Notice that

$$W(C) \equiv F(C) - F(C_b) - \frac{\partial F(C_b)}{\partial C_b}(C - C_b) \quad (2)$$

is equal to  $F(C) - \mu_b C - \pi_b$  where  $\mu_b$  and  $\pi_b$  are the bulk chemical potential and the osmotic pressure, respectively; hence by construction it has a minimum and it vanishes at  $C = C_b$ .

We will now calculate the force on the film due to its finite thickness in two different situations: (i) thermodynamic equilibrium and (ii) irreversible film formation due to a constant surface excess.

(i) At thermodynamic equilibrium, a minimization of the free energy functional (1) with respect to  $C$  and  $C_s$  gives the equilibrium

concentration  $C(z)$ . The force between the two surfaces is simply  $f = -\partial\gamma/\partial d$ , calculated with the equilibrium profile. Doing the variation on (1) we get  $f = -W(C_1)$  where  $C_1 = C(d/2) \geq C_b$  is the concentration at the middle of the film. Since  $W(C_1) > W(C_b) = 0$  as was discussed above, the force on the film is *always* attractive. For thick films, Figure 2a,  $d > 2L$  where  $L$  is the prewetting layer and  $C_1 \approx C_b$  so that the force is almost zero. On the contrary, for thin films, Figure 2b,  $d < 2L$  and  $C_1 > C_b$  (in the prewetting region) thus the force is nonnegligible. From this simple reasoning we conclude that at equilibrium the prewetting phenomena does not enhance foam stability, it rather adds an extra attractive force. An explicit calculation of the force can be done by specifying  $W(C)$  in (2). Close to the consolute point we choose  $W(C)$  to be the Widom free energy.<sup>6</sup> For thin films  $C_s > C_1 > C_b$ , the force scales like  $f \sim -kT/d^3 < 0$ , whereas for thick films it is decaying exponentially with  $d$ . The crossover between the two regimes occurs as the film thickness  $d$  approaches twice the prewetting layer thickness,  $d = 2L$ . A similar result for an attractive force was derived by Nightingale and Indekeu<sup>7</sup> using somewhat different considerations.

(ii) If the formation of the film is fast enough, and if diffusion or convection along the film is slow, the film is not kept at thermodynamical equilibrium but rather at a given surface excess  $\Gamma = \int_0^d C(z) dz$ . In this case, the profile should be calculated by minimizing (1) with the constrain that  $\Gamma$  is fixed. By introducing a Lagrange multiplier  $\mu$ , the problem reduces to minimizing  $\gamma - \mu\Gamma$  which is equivalent to replacing  $W(C)$  by  $\tilde{W}(C) = W(C) - \mu C$ . The force is now given by  $f = -\tilde{W}(C_1) = -W(C_1) + \mu C_1$  and it can be either repulsive or attractive depending on the value of  $\mu$ . Following ref 4, we find that, for large values of  $\Gamma$  and within the Widom approximation,  $f \sim kT/d^3 > 0$ , thus the force is repulsive. This force is in direct competition with the van der Waals force which has the same power law decay ( $\sim 1/d^3$ ) but is attractive. Hence, for thin films, the foam stability depends on the relative strength of these two forces. For thick films, the dominant force is the attractive one and we expect the average film thickness to be of the order of  $2L$ .

In summary, we showed why transient foam stability cannot be explained from simple equilibrium considerations; instead we proposed a nonequilibrium explanation for long times. It still remains to be explained on dynamical grounds by a detailed study of diffusion-convection modes coupled to peristaltic modes why such a nonequilibrium process takes place.

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Laboratoire de Physique de la Matière Condensée  
Collège de France  
C.N.R.S. - UA 792  
F-75231 Paris Cedex 05, France  
David Andelman  
Jean-François Joanny\*

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