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Dissolving interfaces in the presence of gravity

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Dynamic surface light scattering from dissolving interfaces in binary mixtures of tunable density contrast shows that the surface tension of the interface between the upper and lower phases of the mixture dissolves more slowly for a mixture of higher density contrast. Even for a lower density contrast mixture, the dissolution is still slower than would be expected from naive application of equilibrium diffusion arguments. The factor most likely to be responsible for this anomalous dissolution is gravity, through a mechanism based on the competition between diffusion and sedimentation across the interface. [S1063-651X(99)02801-9]

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The process of dissolution of a liquid interface between two miscible liquids should be a highly nonequilibrium and nonlinear process and therefore is not well understood. However, if gravity does not retard the dissolution, the slowest process we might think of is diffusion. Anything other than diffusion, and especially convective effects, should naturally speed the mixing process, so diffusion should set a lower limit for the speed of dissolution. Analytic techniques based on the mean field dynamics of soft Ising spins, as well as molecular dynamics simulations [1], agree with a diffusion-like law for the decrease of the interfacial surface tension.

Surprisingly, a few years ago it was reported [2] that the effective interfacial tension of the interface between the phases of an isobutyric acid and water binary mixture (made miscible by rapidly raising the temperature into the one-phase region) disappears even slower than predicted by a naive use of diffusion. It was pointed out that the anomalously slow dissolution might be caused by the stabilizing effect of gravity. Simulations of the interfacial dissolution were carried out [3] in the presence of a gravitylike pinning field, without including an order parameter dependent mobility [4], and at short times after it started, the dissolution was not significantly different from the dissolution in the absence of the field, unless the field was made so strong as to freeze the interface entirely.

In this paper we report the results of an experiment designed to investigate the possible role of gravity in producing the anomalously slow interfacial dissolution reported in Ref. [2]. In this experiment we tune the density contrast across the dissolving interface and observe its effect on the rate of interfacial dissolution.

For our test system we have chosen a near-critical cyclohexane and methanol (CM) mixture [5]. The two components are naturally well density matched; the density difference between the phases at a temperature 225 mK below T_c is 2×10^{-3} g/cm^3. The density contrast can be tuned by mixing in deuterated forms of the components. We have performed dynamic surface light scattering (SLS) experiments to study interfacial dissolution in a CM mixture and in a cyclohexane and deuterated methanol d_4 (CDM) mixture, which provided a density contrast about 8 times larger than the nondeuterated sample. We also prepared a cyclohexane+deuterated cyclohexane+methanol mixture [6] (CDCM) of deuterated fraction 1.65%. Its density contrast, obtained from the measurement of the capillary length as in Ref. [7], is about 5 times smaller than the density contrast for CM. However, due to this very small density difference between the upper and lower phases, the mixture started flowing along the walls of the cell when the temperature was raised. The integrity of the CDCM's interface was destroyed by the convection and we could not continue our dynamic surface light scattering experiments with this mixture.

The cells filled with CM and CDM mixtures were vertical glass cylinders about 12 cm in height and 5 cm in diameter. For the entrance and exit of our laser signals, two small regions of the cylinder's lateral surface were replaced by two facing optically flat glass windows. The cells were immersed in a thermally stabilized water bath whose temperature was controlled to ±0.1 mK over time intervals less than 1 h and to ±1 mK over intervals of a few days. The critical temperature T_c, above which the system can attain one-phase equilibrium, was determined at first by measuring the relative volumes of the two equilibrium phases at several temperatures within 500 mK of T_c and then monitored by turbidity measurements. In this method, T_c is determined to ±2 mK.

To prepare an initial state with an equilibrium interface, we let each mixture reach thermal and composition equilibrium at a temperature 225 mK below the critical temperature. Then to initiate interface dissolution, we abruptly raised the temperature to a final state above T_c. Before and after changing the temperature we recorded the autocorrelation function of the light scattered by the capillary waves on the interface between the phases of the mixture. For a binary mixture near its critical temperature, due to the smallness of the interfacial tension, the capillary waves are overdamped and the autocorrelation function is well represented by a decaying exponential with the relaxation time $\tau=2(\eta_1+\eta_2)/\sigma q$ [8], where η_1 and η_2 are the viscosities of the two liquids, σ is the interfacial tension, and q is the wave number of the scattered light. Thus the autocorrelation function measurements provide the surface tension in a rather direct fashion.

Immediately after raising the temperature the interface typically lost its flatness due to collective motions of the bulk liquid caused by temperature gradients. When the heating time was of the order of a few minutes the gradients were sufficiently small that the interface maintained its integrity. The interface of CDM was typically less affected by the

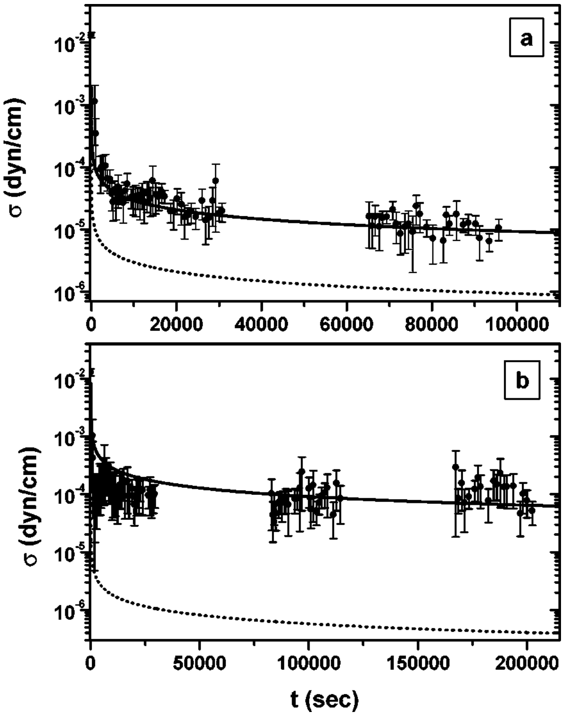

FIG. 1. Effective interfacial tension of the dissolving interface for binary mixtures of (a) cyclohexane and methanol and (b) cyclohexane and deuterated methanol. The dotted lines show the interfacial tension in a naive diffusion model, expected to provide an upper limit for the interfacial tension in the absence of gravity, corresponding to the equilibrium diffusion constant D. The continuous lines show the best fit of the data with the naive diffusion model, corresponding to an effective diffusion constant D_{eff}. In (a) the initial temperature is 225 mK below T_c and the final temperature is 35 mK above T_c; $D=4.7\times10^{-9}$ cm^2/sec and $D_{eff}=(4.8\pm2.2)\times10^{-11}$ cm^2/sec. In (b) $T_c-T_i=225$ mK, $T_f-T_c=172$ mK, $D=1.4\times10^{-8}$ cm^2/sec, and $D_{eff}=(5.1\pm3)\times10^{-13}$ cm^2/sec.

temperature gradients, presumably due to a larger interfacial restoring force caused by a higher density difference that cuts the long-wavelength deformations of the interface. In about 30 min the mixture typically reached thermal equilibrium and it became possible to resume measuring autocorrelation functions.

The relaxation times of the autocorrelation functions for CM and CDM at two-phase equilibrium had the same magnitude and were in agreement with the known values of the surface tension [7] and viscosity [9] of CM. After the temperature was raised, the relaxation times increased by two to three orders of magnitude in approximately 20 min. The viscosity is known not to differ significantly in the range of temperatures covered by the experiment [9], so for simplicity we assumed it to be constant. Thus the increase in relaxation time was taken to indicate an expected sharp decrease in interfacial tension. After the dramatic initial increase in relaxation time, the two systems differed markedly in their rate of further changes of relaxation time, with the CDM system exhibiting extremely slow dissolution.

TABLE I. Comparison between the equilibrium diffusion constant D and the effective diffusion constant D_{eff}, obtained by naively fitting the experimental data with the diffusion model. In all experiments the initial temperature is T_c-225 mK.

Mixture	$T_{final}-T_c$ (mK)	D_{eff} (cm^2/sec)	D (cm^2/sec)
CM	35	$(4.8\pm2.2)\times10^{-11}$	4.7×10^{-9}
CM	52	$(3.7\pm1.7)\times10^{-11}$	6.0×10^{-9}
CM	95	$(1.4\pm0.7)\times10^{-10}$	9.1×10^{-9}
CM	173	$(1.8\pm1.3)\times10^{-10}$	1.4×10^{-8}
CDM	35	$(1.8\pm1.2)\times10^{-12}$	4.7×10^{-9}
CDM	61	$(3.9\pm3.0)\times10^{-13}$	6.7×10^{-9}
CDM	172	$(5.1\pm3.0)\times10^{-13}$	1.4×10^{-8}

Figure 1 shows the measured interfacial tension for CM [Fig. 1(a)] and CDM [Fig. 1(b)] obtained from the SLS experiments, over a time of 2 days for CM and 3 days for CDM. Some features of the data can be discussed in comparison with the expectations of a naive diffusion model whose one adjustable parameter, the diffusion constant D, can be expected to capture a measure of the speed of interfacial dissolution. In Fig. 1 the dotted lines result from calculations in such a model using the known equilibrium diffusion constant of the system. In this naive diffusion model of the interface [2], the density gradient inside the interface of thickness $L=\sqrt{Dt}$ can be considered to be constant. An effective interfacial tension, which controls the excess free energy for distorting the flat interface, can be defined even for a nonequilibrium dissolving interface [10,3]

$$\sigma\propto\int\left(\frac{dc}{dz}\right)^2 dz, \tag{1}$$

where c is the local composition and z is the direction normal to the interface. Thus the interfacial tension can be taken to be proportional to L^{-1}. We can calculate the interfacial tension in this model by using the fact that the initial equilibrium interface thickness is of the order of the correlation length (which is 1.6×10^{-6} cm for the initial temperature in our experiments $T_i=T_c-225$ mK).

The interfacial tension clearly disappears even more slowly than predicted by this diffusion model. If we now extend the model, using the diffusion constant as an adjustable parameter to quantify the data, we obtain the solid curves shown in Fig. 1. The best fit for CM yields an effective diffusion constant two orders of magnitude smaller than the equilibrium diffusion constant. For CDM the difference is even larger, roughly four orders of magnitude. In addition, the fit is bad: The continuous line goes down like $t^{-1/2}$ while the data do not. A comparison between D_{eff} and D for both mixtures is shown in Table I. In all cases D_{eff} is significantly smaller than the equilibrium constant with a much more pronounced effect for the deuterated mixture.

Since the only major difference in the properties of CM and CDM is a different density contrast between the upper and lower phases, we assume that the drastic difference in the rate of dissolution of the interface is caused by gravity. It is known that gravity can induce equilibrium concentration gradients in binary mixtures near the critical temperature [11]. Even though in some cases these concentration gradients may not be neglected, the magnitude of these effects is much too small to explain our experiments.

TABLE II. L, the interface thickness extracted from the results obtained in the surface light scattering experiments, vs R^*, the thickness selected by the competition between diffusion and sedimentation across the interface.

Mixture	$T_{final}-T_c$ (mK)	L (10^{-4} cm)	R^* (10^{-4} cm)
CM	35	9.0±5.0	4.9
CM	52	9.9±5.6	5.3
CM	95	11.6±5.8	6.0
CM	173	8.3±6.5	6.8
CDM	35	4.0±1.6	2.5
CDM	61	1.5±0.7	2.8
CDM	172	1.7±0.7	3.5

Gravity could slow down the interface dissolution through a mechanism based on the competition between diffusion and sedimentation over the width of the interface. This competition can be explored with dimensional arguments: Let us consider a domain of radius R, of the order of the interface thickness. We can define a sedimentation time τ_s as the time in which the domain travels a distance equal to its radius under the influence of the gravitational field. Neglecting a multiplying numerical geometrical factor that depends on the shape of the domain,

$$\tau_s=\frac{\eta}{R\Delta\rho g}, \tag{2}$$

where g is the gravitational acceleration and $\Delta\rho$ is the density difference between the liquids. A diffusion time can also be defined; it is the time in which the domain disappears by diffusion

$$\tau_d=\frac{R^2}{D}. \tag{3}$$

At the beginning of the dissolution process the interface thickness is small and the diffusion time is much shorter than the sedimentation time. As a result, any fluctuation will be dissolved rapidly and gravity will not have time to sediment the fluctuation. The process will be dominated by diffusion. However, as the interface thickness increases, the sedimentation time decreases and the diffusion time increases. When the two characteristic times become of the same order of magnitude, gravity might begin affecting the dissolution. Setting the two times equal, we obtain a length scale for the interface thickness R^* at which gravity could slow down the dissolution,

$$R^{*3}=\frac{\eta D}{\Delta\rho g}. \tag{4}$$

For our experiments, this initial diffusion dominated stage should last 1–2 min for CM and about 15–30 sec for CDM. This is a huge time compared to the time scales involved in the simulation [1,3] of the process.

In this picture we have just suggested, fluctuations much smaller than R^* are dissolved in a very short time while those much larger are sedimented before being dissolved; fluctuations of the order of R^* will hang on at the interface and will create a high-density-gradient, inhomogeneous layer of thickness of the order of R^*. An experiment by Vailati and Giglio [12] showed that ''giant fluctuations'' at the interface in binary mixtures exist under conditions that might plausibly be related to those of our system.

Our diffusion/sedimentation competition argument is quite compatible with the results from our surface light scattering experiments. Table II shows that R^* and the average thickness of the interface obtained from the experimental data (L) have the same order of magnitude. The magnitude of the thickness of the inhomogeneous region was extracted from the surface tension data by using Eq. (1) and the simplifying assumption that the concentration difference between the upper and lower planes of the inhomogeneous region does not change in time. To eliminate the influence of thermal conduction effects, which might affect the results at the beginning of the experiments before the sample reaches thermal equilibrium, the results obtained in the first two hours were not considered in the calculation of L.

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