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Growth of a wetting layer in a flowing binary-liquid mixture at bulk coexistence

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Using reflectivity, we observe the effect of steady fluid flow on the growth of gravity-thinned wetting films in a binary-liquid system of nitromethane and carbon disulfide at bulk coexistence. The substrate is a horizontal borosilicate glass surface. The growth process is driven by the substrate-liquid interaction and opposed by a gravity-induced pressure gradient. We find that the steady-state wetting-layer thickness increases with the stirring rate in qualitative agreement with the hydrodynamic theory of Kayser, Moldover, and Schmidt [J. Chem. Soc. Faraday Trans. 2 **82**, 1701 (1986)] for wetting-layer development. We observe diffusion-limited exponential buildup of the wetting layer toward steady state. The steady-stirring experiments presented here are compared with earlier random stirring results. Finally, we find that at high stirring rate the bulk liquid-liquid interface becomes unstable against the formation of liquid droplets. This instability is responsible for a fast growth mode of the wetting layer.

I. INTRODUCTION

Recently growth phenomena and pattern formation at surfaces have attracted attention. While considerable progress has been made towards an understanding of nucleation and spinodal decomposition in bulk systems,[1] we have much to learn about such processes as they occur on surfaces. As will be shown here, a wetting system at bulk coexistence can be exquisitely sensitive to driving forces. It is believed that for a binary-liquid mixture at coexistence, wetting-layer growth can be a very slow process.[2] We discovered,[3] however, that for a binary-liquid mixture of nitromethane and carbon disulfide at coexistence, a thick (≈ 500 nm) steady-state wetting layer composed of the nitromethane-rich (N^*) phase grew on a horizontal borosilicate glass substrate at the bottom of a sample cell in a few hours if the system was randomly stirred at a rate on the order of 1 Hz. The spectator phase [carbon disulfide–rich (C^*)] is denser than the N^* wetting phase. Hence the wetting film was thinned by gravity. Kayser, Moldover, and Schmidt[2] (KMS) suggested that such a thick wetting layer might be understood by taking hydrodynamic flow into consideration. In this article we report new experimental results on how fluid flow can control wetting-layer growth and steady-state behavior. In these experiments stirring is steady (we will refer to this as *regular* stirring) as opposed to random.

In order to control the fluid flow in our sample cells (see Fig. 1), we constructed floating cylindrical stirrers which were driven by a uniformly rotating system of permanent magnets. The rotation rate f could be varied between 0 and 5 Hz continuously. Because of axial symmetry of the sample cell and the small liquid gap between the glass substrate and the bottom of the stirrer, the flow pattern can be well approximated by a planar rotor parallel to a stationary, flat substrate.[4,5] KMS showed that an important feature of this stirring geometry is that a well-defined diffusion boundary layer (thickness $=L_{\mathrm{DBL}}$) is formed near the glass substrate.[2] Outside the diffusion boundary layer the chemical stratification of the C^* phase is eliminated by convection. In this region, the chemical potential is the same everywhere and is equal to the value at bulk coexistence. Inside this boundary layer, the bulk liquid behaves like a quiescent C^* phase, with diffusion driving molecular transport. The chemical potential (field conjugate to chemical concentration, the order parameter) at the substrate therefore differs slightly from that at bulk coexistence by

$$\delta\mu=\Delta\rho\, g L_{\mathrm{DBL}} \ , \tag{1}$$

where $\Delta\rho$ is the mass density difference between the coexisting phases and g is the acceleration of gravity (when there is no stirring, we expect to use the height of the spectator phase in place of L_{DBL}). From KMS we have

$$L_{\mathrm{DBL}}\approx(D/\nu)^{1/3}\delta=(D/\nu)^{1/3}[\nu/(2\pi f)]^{1/2}\sim f^{-1/2} \ . \tag{2}$$

Here D is the mutual diffusion constant, ν is the kinematic viscosity,[6] and δ is the (viscous) boundary layer thickness. We estimate[7] that at the temperature of greatest interest for the observations discussed here ($\approx$ 10 K below the critical mixing point) and the maximum stir rate employed (5 Hz) $L_{\mathrm{DBL}}\approx 13$ μm. Under the same conditions the viscous boundary layer thickness is ≈ 100 μm. Thus, the diffusion boundary layer is not drastically perturbed by fluid motion. KMS refers to this situation as "gentle" stirring.

Inside the diffusion boundary layer, wetting layers form as a result of the combined forces of gravity (through $\delta\mu$) and substrate-liquid interactions. We define the substrate-liquid interaction potential (Refs. 8 and 9) V as the free energy of the wetting system as a function of the thickness of the wetting layer l. For the sake of simplicity, we hypothesize that V is a power-law

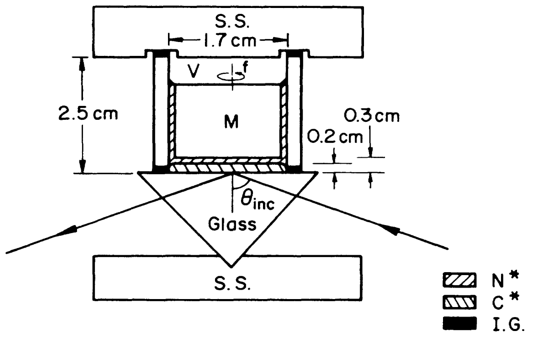

FIG. 1. Sample cell schematic. Side view. V denotes vapor phase, N* the nitromethane-rich phase, C* the carbon-disulfide-rich phase, S.S. the stainless-steel plates, I.G. the indium gaskets (thickness exaggerated), and M the cylindrical mixer. The rotation axis for the mixer is marked by f. The side wall is a Pyrex glass cylinder. The mixer is magnetically driven. The substrate (marked Glass) is a borosilicate glass prism. The cell is held under compression by screws (not shown) connecting the stainless-steel plates. The line indicates incident and reflected light. θ_{inc} denotes the angle of incidence.

function of l (the approach taken in this paper can be generalized if this is not the case)

$$V(l)=A/l^{p} . \tag{3}$$

Since this interaction favors the formation of the wetting layer, A is positive. While experiments that are sensitive to $V(l)$ have been performed, most notably the measurement of the equilibrium thickness of a wetting layer upon approach to bulk coexistence,[3] we feel that the current knowledge of $V(l)$ is not sufficiently precise to quantitatively test the predictions made in this paper.[10]

Combing the substrate-liquid interaction potential with the chemical potential contribution mentioned above gives the free energy per unit area of the system as a function of wetting-layer thickness

$$F(l)=l\,\delta\mu+V(l) . \tag{4}$$

If we minimize F with respect to l, we get the mean-field thickness (as in Ref. 8)

$$l\sim(\delta\mu)^{-1/(p+1)} . \tag{5}$$

We therefore expect that for the present stirring experiment the steady-state thickness of the wetting layer L_{ss} depends on the stir rate according to

$$l_{\text{ss}}\sim f^{1/[2(p+1)]} . \tag{6}$$

II. EXPERIMENTAL DETAILS

In this experiment (for aspects of the experiment not discussed here, see Ref. 3), two different sample cells were employed. They were filled with carbon disulfide and nitromethane of $99^{+}\%$ purity[11] at the critical volume fraction[12] [0.6014±0.006 (our measurement uncertainty) volume fraction of carbon disulfide]. The two cells differed in the material used for the stirrer and the glass-cleaning procedure applied to the glass substrate. Cell 1 used a Macor[13] stirrer and was cleaned with ethylenediamine tetra-acetic acid (EDTA) following a procedure similar to H-3 described in Ref. 9).[14] Cell 2 used a Pyrex stirrer and was cleaned with chromic acid, as in our original random stirring work.[3] For the first two weeks of observation the two cells gave the same results. Over three months of observation, cell 1 showed a remarkable aging effect. Although the critical temperature changed by only ≈ 1 mK per day over the three month period, the measurements of the reflectivity as a function of temperature just above the critical point suggested that the surface had switched its preference in adsorption from nitromethane to carbon disulfide. As explained in Ref. 15 this is indicated by a change in the slope of the reflectivity as a function of temperature from negative to positive, respectively. Cell 1 therefore fortuitously provided an example of a substrate that was not attractive to the material forming the wetting layer of interest. It was used only for this purpose in this report. Cell 2 showed no such aging effect over the same duration of time—wetting by the N^{*} phase persisted. The critical temperature for cell 2 changed by approximately $+3$ mK per day. A third sample cell which had been cleaned with EDTA did not show the aging effect after more than a year of observation. We suspect that the special aging behavior of cell 1 was a result of using Macor glass. All sample cells were loaded under an inert (Ar) atmosphere. For all experiments, the samples were at liquid-vapor coexistence.[16]

III. SAMPLE SHEARING

Over the range of stirring rate ($0<f<5$ Hz) and temperature ($\Delta T\equiv T_c-T>1$ K) employed our liquid system was not drastically sheared. The reasoning is as follows. We define τ_{fluc} to be the relaxation time of concentration fluctuations and S to be the shear rate. Using the velocity field for our system given in Ref. 5 we find that for our system $S\leq 2.4\times10^{3}\ \text{sec}^{-1}$ overall (the greatest value is inside the viscous boundary layer). According to Ref. 17

$$\tau_{\text{fluc}}=\frac{16\eta}{k_B T}\xi^{3} .$$

We find that all our observations were made with $S\tau_{\text{fluc}}\leq 2\times10^{-4}$ ($\ll 1$), i.e., very weak shearing. We also found that the bulk transition was hardly affected by the shearing; bulk T_c was lowered by about 1 mK at the maximum shear rate, consistent with the theory of Onuki and Kawasaki.[18] From experiments on binary-liquid mixtures,[19,20] we find that in the weak shear regime the flow birefringence should be very small. Therefore flow birefringence should be of no consequence in the interpretation of our reflectivity measurements of wetting-layer thickness. This allows us to use data for a quiescent mixture in the analysis of our stirred system.

IV. OPTICAL PROBE

We used *frustrated total internal reflection* to measure the thickness of growing wetting layers as in our earlier random stirring work (see Ref. 3 for details not given here). The wetting layer was modeled as a dielectric slab consisting of N^* phase sitting between two homogeneous dielectrics, the glass substrate and the C^* (spectator) phase.[21] Let θ_c be the critical angle for the following optical system: semi-infinite spaces of glass and N^* in contact. In this experiment we used an angle of incidence (1.271 rad from normal) closer to glancing than θ_c. At this angle, the reflectivity of the system with no wetting layer was low (≈ 0.015). Under these circumstances, when a wetting layer is present, the reflectivity is a monotonically increasing function of the layer thickness l, a great convenience in the analysis. The incident light was s polarized. We used the following values (see discussion in Ref. 3) for the refractive indices for the N^* phase, C^* phase, and the glass substrate (n_{N^*}, n_{C^*}, and n_{glass}, respectively):

$$n_{\text{glass}}^2 = 2.2955 \ ,$$

$$n_{N^*,C^*}^2 = 2.206 \mp 0.62 t^{\beta} \ ,$$

where t (defined in Ref. 7) is the reduced temperature, $\beta = 0.32$,[12] and the $-$ and $+$ signs correspond to the N^* and C^* phases, respectively. The incident laser beam (wavelength is 633 nm, beam diameter is approximately 1 mm) was attenuated to a power level of 300 μW in order to make the local laser heating effect on wetting-layer thickness (discovered in earlier work[3]) negligible.

V. SAMPLE PREPARATION: REMOVAL OF THE WETTING LAYER

In order to observe the development of a wetting layer, specimens were first prepared by burning off the wetting layer (while stirring) in the following manner. The thermostat bath temperature was increased by a fraction of degree Kelvin over a period of ≈ 10 min. This had been found, as reported earlier,[3] to give an abrupt drop in reflectivity. The reflectivity remained at a low value after continued heating. We interpret this to indicate the complete (for the purposes of this work) removal of the wetting layer. The physics of burning can be easily understood as follows. Since the critical point is an upper demixing point, a fast increase in cell temperature results in an undersaturation of nitromethane in the C^* phase. Since the small amount of nitromethane in the wetting layer is adjacent to the bulk C^* phase it disappears quickly after burning. This idea can also be applied to the reverse process, temperature quenching (as was also used in Ref. 3). By quickly lowering the thermostat temperature, we produced a nonequilibrium wetting layer of thickness ≥ 1 μm. Since this results in near total reflection, this signal was used to normalized the reflectivity data.

VI. "BULK" INTERFACIAL INSTABILITY

In visual observations of the sample, it was noticed that at sufficiently high stir rates the *bulk* liquid-liquid interface became unstable. At a fixed temperature, the behavior as a function of stir rate can be divided into four regimes.

(i) For $0 \leq f < f_0$, there was no evidence of breakup of the interface. We found that for ΔT ($\equiv T_c - T$) ≈ 8 K, $0.56 < f_0 \leq 2.2$ Hz.

(ii) For $f_0 \leq f < f_1$ droplets appeared in the bulk fluid, but the bulk liquid-liquid interface was well defined.

(iii) As f approached f_1 from below, the bulk interface developed long-wavelength waves of increasing amplitude.

(iv) At $f = f_1$, the bulk interface completely broke up into jets of droplets.

We suspect that the appearance of droplets for $f_0 \leq f < f_1$ may be associated with departures of the motion of the mixer from steady rotation. Abrupt reorientations of the mixer may have contributed higher shear to the fluid than which would have been present had the mixer been noise-free in this regime of stirring.

The breaking wave phenomenon observed at $f = f_1$ can be understood as a Helmholtz instability due to shear along the bulk interface. It is expected[22] that

$$f_1^4 \sim \sigma g (\rho_{C^*} - \rho_{N^*})(\rho_{C^*} + \rho_{N^*})^2 / \rho_{C^*}^2 \rho_{N^*}^2 \ .$$

Here ρ_x is the mass density of phase x. Near the critical mixing point σ (the surface tension) $\sim t^{\mu}$ and $\rho_{C^*} - \rho_{N^*} \sim t^{\beta}$. Since $\mu \approx 1.26$,[23] we expect $f_1 \sim t^{0.40}$. Figure 2 shows the threshold stir rate for this instability obtained by visual observation at various temperatures. A power-law fit gave $f_1 \sim t^{0.32 \pm 0.04}$ as plotted. This is a smaller exponent than expected. We speculate that the disagreement may be due to the fact that the stirred bulk

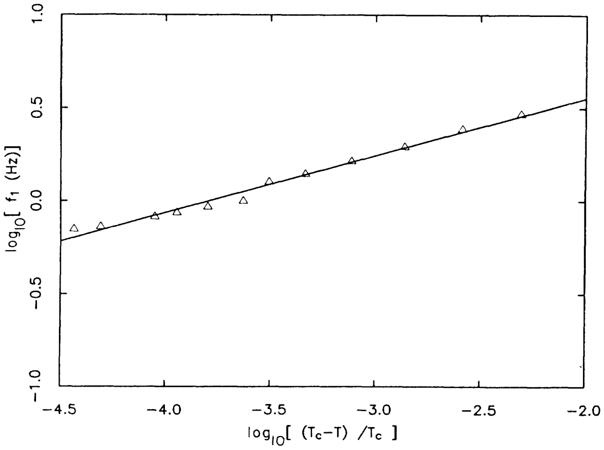

FIG. 2. Stir rate for threshold of bulk liquid-liquid interface breaking (Helmholtz instability) (f_1) vs reduced temperature. Visual observation of the interface at a fixed temperature with increasing stir rate gave the frequency at which the instability appeared. Line is the power-law fit discussed in the text.

liquid-liquid interface was not flat as was assumed in the theory. Nevertheless, the observations are in qualitative agreement with theory.

VII. WETTING-LAYER DEVELOPMENT: LONG-TIME BEHAVIOR

In earlier (Ref. 3 and unpublished) work we had found that random stirring gave wetting layers with a steady-state thickness (statistical variation of $+6\%$ with time) for a single sample at a typical temperature over a wide range of temperature (at least $4 \leq \Delta T \leq 21$ K). For the regular stirring work reported here we performed growth measurements at fixed temperatures and stir rates. We chose to restrict the sample temperature to a narrow band $7.3 \leq \Delta T \leq 9.4$ K within the aforementioned range. For each run, the sample temperature after the complete removal of the wetting layer by a burn was constant to $\pm \leq 0.2$ mK. It took ≈ 4 min to stabilize the sample temperature after the end of each burn. Samples were stirred at all times. Figures 3(a) and 3(b) show growth observations of reflectivity as a function of time for a wide range of stir rates. Time zero is defined as the time at which the temperature stabilized after a burn. The same observations, expressed as wetting-layer thicknesses, are shown in Fig. 4. The nonwetting reference substrate shows the expected low value of reflectivity. For this system, the reflectivity increased by a slight amount, 0.0035, over the course of the observation. This is an insignificant increase compared to that observed with the wetting sample. For the wetting substrate, two different stirring regimes for wetting-layer development with time can be clearly seen.

A. Low flow rate: Steady state

For $f < f_0$ (no breakup of the bulk interface), the wetting-layer thickness leveled off at a constant thickness for sufficiently long times. In this case, the wetting layers were visually observed to be flat and mirrorlike. Examples of this *steady-state* behavior are shown in Figs. 3(a) and 4 for $f \leq 0.56$ Hz. In this regime, the steady-state wetting-layer thickness increased as the stirring rate increased, as shown in Fig. 4. Over the range of stir rate under discussion ($0.05 \leq f \leq 0.56$ Hz) L_{DBL} varied between 132 and 38 μm and δ varied between 1000 and 300 μm (respectively for the minimum and maximum stir rate). Note that at the lowest stir rate the viscous boundary layer thickness δ was comparable to the height of the spectator phase (2000 μm, see Fig. 1). We may well expect the appearance of this new length scale to alter the flow pattern and the consequent wetting behavior.

Figure 5 gives a plot of wetting-layer thickness at long times versus stir rate. We see that the statistical error in wetting-layer thickness is small. The dominant uncertainty in the absolute value of the layer thickness is systematic. It arises in the conversion from reflectivity to wetting-layer thickness. There are five sources of this error.

(a) As discussed in Ref. 3, there is uncertainty in the refractive index of the spectator phase. We find this quantity by extrapolation of high-temperature ($T \gg T_c$) reflectivity where the contribution of wetting layers is slight. We also perform nonequilibrium background measurements which permit the measurement of the reflectivity of the spectator phase without a wetting layer in the temperature range of interest. In these experiments, we continuously heat the sample to eliminate the wetting layer by burning while the bulk liquid was subjected to random stirring. See Fig. 3(a) of Ref. 3 for an

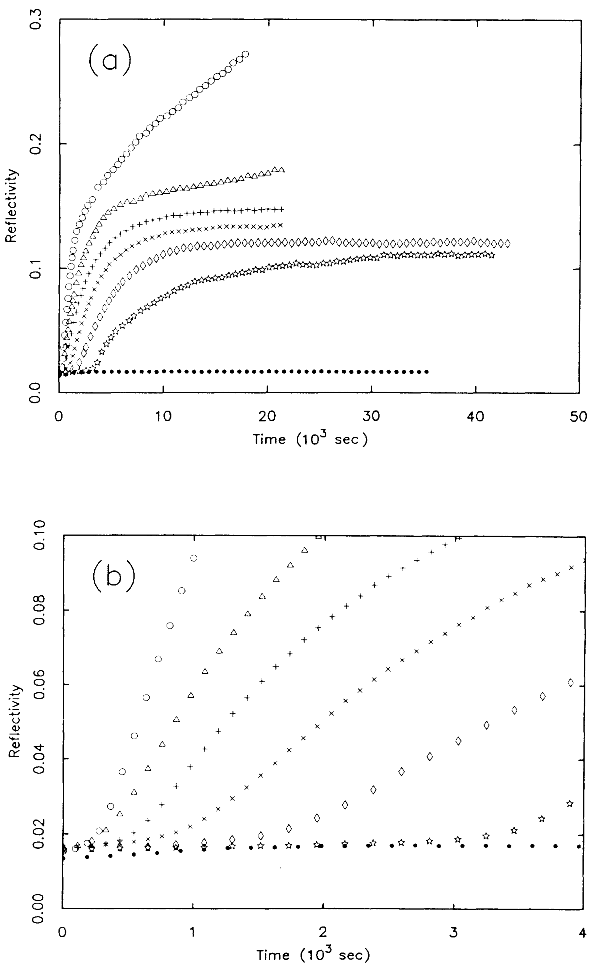

FIG. 3. Reflectivity vs time for wetting-layer formation and growth. The observations are for fixed temperatures [$T_c - T(\equiv \Delta T)$ between 7.3 and 9.4 K] at different fixed stir rates (f). (a) Full time range (abscissa covers 50×10^3 sec); (b) early development. No droplets were visible in the bulk for $f \leq 0.56$ Hz. Droplets were visible for the $f = 2.2$-Hz run (see text for more discussion on the stability of the bulk liquid-liquid interface). Symbols are as follows: solid circles, nonwetting reference (aged cell 1, see text for preparation), $f = 0.18$ Hz, $\Delta T = 8.3$ K; (all other symbols are for cell 2); open stars, $f = 0.05$ Hz, $\Delta T = 9.4$ K; open diamonds, 0.12 Hz, 8.4 K; crosses, 0.28 Hz, 8.2 K; pluses, 0.56 Hz, 7.9 K; open triangles, 1.1 Hz, 7.6 K; and open circles, 2.2 Hz, 7.3 K.

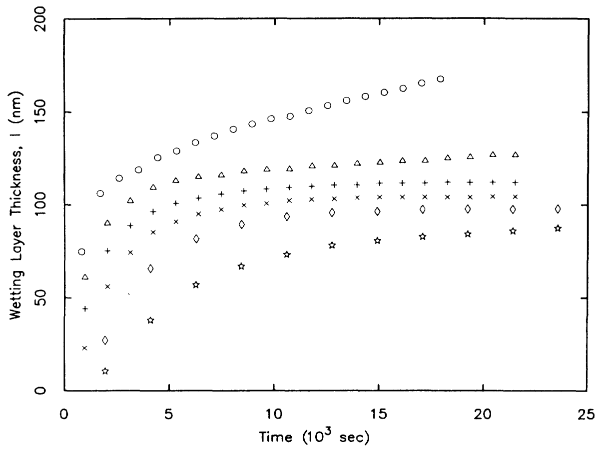

FIG. 4. Wetting-layer thickness as a function of time for different stir rates. Companion to Fig. 3. Symbol designations are the same.

example of such an observation. We conservatively expect from such work that the refractive index of the spectator phase at the critical temperature is between 1.47 and 1.49. The variation of this quantity with temperature is found in the same measurements, as discussed in Ref. 3. The uncertainty in the spectator phase refractive index contributes an uncertainty of ±10% in l.

(b) The second source of uncertainty in the absolute wetting-layer thickness is due to uncertainty in the variation of the order parameter (ϕ is the volume fraction of carbon disulfide) with the refractive index of the liquid. This matter is again discussed in Ref. 3. There we calculated that $dn^2/d\phi \equiv B = 0.77$. From experiments[3] we find that $0.69 < B < 0.87$ by combining the published values for the coexistence curve[12] with the nonequilibrium temperature ramp experiments discussed above. This contributes an uncertainty of ±8% to l.

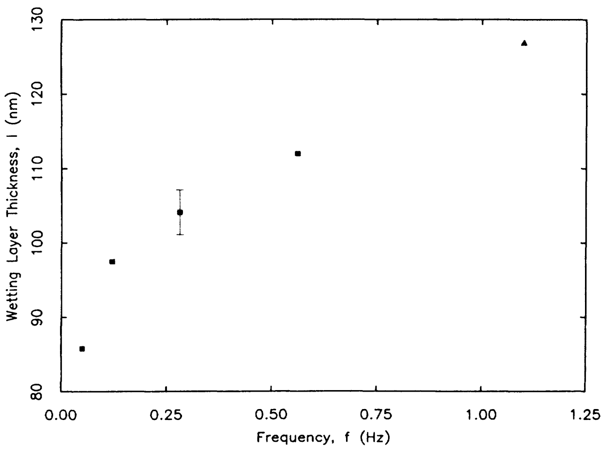

FIG. 5. Wetting layer thickness vs stir rate. Measurements are from Fig. 4 data at time $=2.2\times10^4$ sec. The triangle indicates that the steady state may not have been reached. The error bars are statistical only. The error in converting reflectivity to *absolute* wetting-layer thickness contributes an uncertainty of less than ±36%. The trend of increasing layer thickness with increasing stir rate is independent of both errors.

(c) Strain birefringence in the substrate can change the polarization of the incident light beam, adding a third contribution to the uncertainty in absolute wetting-layer thickness. As a worst case, we consider a shift from s- to p-polarized light. s-polarized light reflected from a 120-nm-thick wetting layer gives a reflectivity identical to that of p-polarized light reflected from a 129-nm-thick wetting layer. We therefore estimate a maximum uncertainty of ±8% in l due to depolarization of the probe beam in the substrate.

(d) Possible variations of the index of refraction near the substrate surface are the fourth source of uncertainty in the absolute wetting-layer thickness. Both polishing and acid leaching of borosilicate glass increase the relative concentration of SiO_2 near the surface, changing the index of refraction relative to its bulk value.[24–27] We choose three possible models for this surface film, in all three cases assuming that the film is a slab of constant refractive index n_f and thickness d_f. Measurements far from coexistence for a noncritical composition (see Ref. 3) gave a reflectivity of $(1.0\pm0.2)\times10^{-3}$ when the bulk substrate and the single-phase liquid had identical indices of refraction. This reflectivity value was used to determine d_f for each model.

Model 1. We assume that the surface film is homogeneous-fused silica with $n_f = 1.457$ (Ref. 28) and $d_f = 13$ nm.

Model 2. Yokota *et al.*[29] found that for polished borosilicate glass, $n_f = n_{\text{glass}} - 0.005$. We fit d_f rather than using Yokota's value and find $d_f = 160$ nm.

Model 3. Zhdanov[27] measured a pore volume fraction of roughly 0.13 in surface films formed by acid leaching. We assume a surface film composed of 87% fused silica and 13% air, and find $n_f = 1.441$, $d_f = 10$ nm using a Bruggeman effective-medium model.[30]

Since we have not extensively characterized our surface, we include a fourth model for comparison.

Model 4. We assume that the glass substrate is homogeneous, with no surface film.

The widest variation in wetting-layer thickness found by comparing all four models is 10% for the range of wetting-layer thicknesses given in Fig. 5. We take this as our uncertainty in l due to substrate surface films.

(e) Finally, calculations of wetting-layer thickness by a slab model neglect the substrate surface roughness. Vedam and Malin[31] found that silica polished with cerium oxide had a surface roughness of 10 nm. We model a rough glass surface by assuming that a 10-nm layer at the glass-liquid interface is 50% glass and 50% N^*. Again we use a Bruggeman effective-medium model to compute the index of refraction. If we interpret wetting-layer thickness as volume of N^* per unit area, the results of this model and for a smooth interface model differ by less than 0.1% for the wetting-layer thicknesses of Fig. 5. Therefore, we can neglect substrate surface roughness.

We find that the small increase in wetting-layer thickness (≈ 25 nm) with increasing stir rate observed for stir rates between 0.05 and 0.56 Hz (see Fig. 5) is not only significant compared to statistical errors but also independent of the systematic conversion errors just discussed (we estimate less than $\pm 36\%$). We interpret this increase as that described by the KMS theory in Eq. (6). Note that the singularity in Eq. (6) expected at $f=0$ is unrealistic. In fact, as mentioned earlier, effects of finite sample size may be expected to appear at the lowest stir rate measured.

B. High flow rate: Sustained growth

For $f>f_0$, we no longer observed a leveling off of the wetting-layer thickness as a function of time in Fig. 4. The wetting layer kept growing over the period of observation. See, as an example, the $f=2.2$ Hz curve in Fig. 3(a). It was noticed visually that such growth was due to continuous deposition of N^* phase droplets onto the glass substrate. This gave an inhomogeneous appearance to the wetting layer. This is in contrast to the growth by the diffusion of nitromethane molecules across the diffusion boundary layer observed at slow stirring rates.

VIII. EVOLUTION AND GROWTH

For sufficiently low stir rates [regime (i), $f<f_0$], we found that wetting-layer development with time towards steady-state behavior showed at least two characteristic periods.

(1) As seen from Fig. 3(b), [for regime (i) and regime (ii) also] we found that rapid wetting-layer growth occurred after an initial startup period of $\approx 3000-250$ sec, a time which decreased with stir rate. Recall that the runs began ≈ 240 sec after the end of each burn. Following KMS, we can estimate the incubation time for wetting-layer development, assuming that the diffusion boundary layer is established

$$\tau_{\rm DBL}=L^2_{\rm DBL}/D \; . \tag{7}$$

Using this expression to find $\tau_{\rm DBL}$ at $T-T_c=9$ K, we get $\tau_{\rm inc}=24$ and 2.2 sec at $f=0.05$ and 0.56 Hz, respectively. This is about a factor of 110 shorter than what we find in Fig. 3(b). We conclude that diffusion in the diffusion boundary layer is not the controlling factor in the early development of the wetting layer. We speculate that incomplete homogenization of the spectator phase above the diffusion boundary layer after the burning has ended may play a role (the critical-point mixing theory of Ref. 32 may be applicable). Whatever the explanation, we can quantify this process by defining a startup time $\tau_{\rm start}$ as the time it takes to increase the reflectivity by $\Delta R=0.005$ after the beginning of each run. We arbitrarily chose ΔR to be comparable to the increase in reflectivity seen for the nonwetting substrate [see Fig. 3(b)]. Using the data from both stirring regimes (i) and (ii) in Fig. 3(a), we find the power-law relation shown in Fig. 6, $\tau_{\rm start}\sim f^{0.72\pm0.1}$. We find that the exponent in this relation depends crucially on the value of ΔR used in the definition of the startup time, e.g., $\Delta R=0.025$ gives an exponent of 0.6. A theory of bulk-mixing and wetting-layer formation that can explain this behavior is needed.

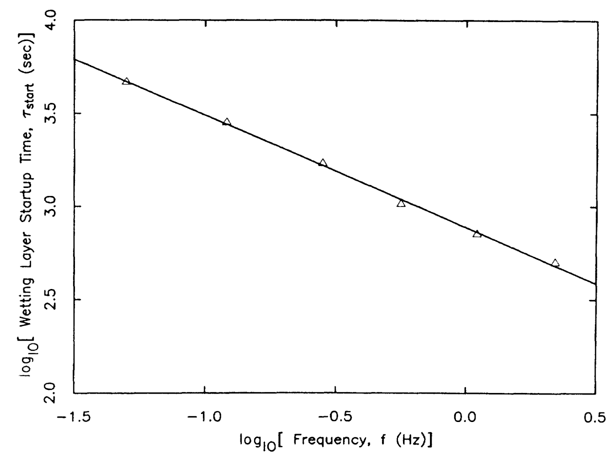

FIG. 6. Time for initial wetting-layer development ($\tau_{\rm start}$) vs stirring rate (f). See text for definition of $\tau_{\rm start}$. Line is a power-law fit.

(2) The approach (for $f<f_0$) to the steady-state wetting-layer thickness was exponential (see for example Fig. 7, for time beyond 2.5×10^3 sec). The relaxation time $\tau_{\rm grow}$ is seen from Fig. 4 to weakly depend on stir rate for $0.05\le f\le 0.56$ Hz.

We can show that the wetting-layer interface is well defined throughout this growth period (KMS calls this quasistatic growth). From KMS, we expect that growth will be quasistatic so long as $l_{\rm qs}\ll l$, where l is the layer thickness at the time of interest, and $l_{\rm qs}$ is defined to be

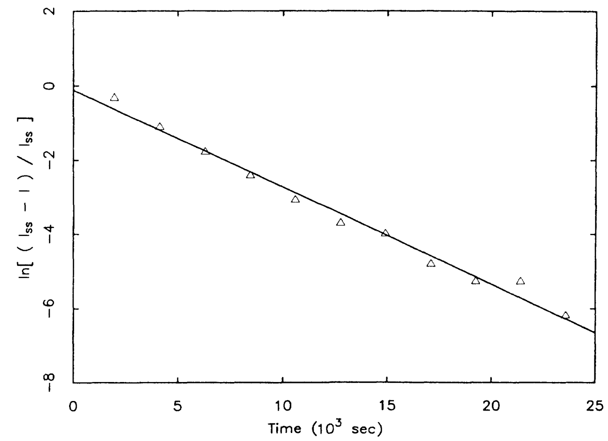

FIG. 7. Fractional deviation of wetting-layer thickness (l) from the steady-state value ($l_{\rm ss}$) vs time: demonstration of the exponential growth of late stage wetting-layer development. For this run, $\Delta T=8.2$ K, $f=0.28$ Hz (the data are the same as the crosses in Fig. 3). The fit shown has $l_{\rm ss}=105$ nm and relaxation time $=\tau_{\rm grow}=3.8\times10^3$ sec.

$\dot{l}\tau_{\text{DBL}}$. In other words, the wetting layer cannot be growing too fast. We can test this condition on the example of Fig. 7, where exponential growth gives $\dot{l}=(l_{\text{ss}}/\tau_{\text{grow}})e^{-t/\tau_{\text{grow}}}$. Here, t is the time from the start of the run. We see that $l_{\text{qs}}<0.1$ nm for t beyond 2.5×10^{3} sec. Comparing this to the layer thickness, we see that the quasistatic condition is well-satisfied throughout this time period.

The driving force behind the growth of the wetting layer toward the steady state is the unfavorably high free energy for small l in Eq. (4) produced by the substrate-liquid interaction [represented by $V(l)$]. The gravity force gives a pressure gradient which opposes growth.[2]

We can understand the role of diffusion in the observed approach to steady state via thickening by considering the depletion layer concept discussed by Lipowsky and Huse.[33,34] They argue that there is a nitromethane-deficient zone just ahead of the growth front of thickness L_{deplete} which grows with time as $L_{\text{deplete}}\approx(Dt)^{1/2}$. From the earlier discussion, we find that L_{deplete} reaches L_{DBL} in a short time ($\tau_{\text{DBL}}<10$ sec) compared to τ_{grow}. Thus we are not able to apply the final results of Lipowsky and Huse since they considered growth processes when the depletion zone was much smaller than the effective sample size (L_{DBL} in our experiment). Rather, we have a wetting layer which is growing in a steady-state manner toward a source of wetting material which is essentially a fixed distance away (since $l<l_{\text{ss}}\ll L_{\text{DBL}}$ always). Because the system is in steady state as it grows, the concentration of nitromethane (x_N^s) in the spectator phase is a linear function of distance from the substrate ($D\nabla^2 x_N^s=\partial x_N^s/\partial t=0$).

As shown in the appendix, the approach to steady state is expected to be exponential, as was first predicted by KMS.[35] As was discussed earlier, this is indeed what we observe. The time constant is expected to be

$$\tau_{\text{grow}}\sim L_{\text{DBL}}(d^2V/dl^2)^{-1}_{l=l_{\text{ss}}} . \tag{8}$$

The first factor is due to the diffusion bottleneck. Since we are treating the stirred wetting system as an equilibrium system with $\delta\mu$ controlled by L_{DBL} in Eq. (1), we expect[8] to approach a *continuous* transition as $f\to\infty$ [and $\delta\mu\to0$ from Eq. (2)]. This is signaled by an infinitesimally curved minimum in $F(l)$ about l_{ss} in Eq. (4). The expected critical slowing down is reflected in the second factor in Eq. (8). We can predict how τ_{grow} scales with stir rate by substituting Eqs. (6) and (2) into (3) and (8)

$$\tau_{\text{grow}}\sim f^{1/[2(p+1)]} .$$

This result for $p=2$ (nonretarded van der Waals force) can also be found in KMS by combining Eq. (6) with KMS Eq. (3.31).

IX. RANDOM STIRRING: COMPARISON

In the random stirring experiments at bulk coexistence we consistently observed very thick (400–600 nm) steady-state wetting layers in the temperature range used here.[3] Despite variations in the shape and performance of the inverted teardrop-shaped mixer used, this result was the same for the three sample cells employed. The motion of the mixer was chaotic, with a fundamental frequency of $\approx1-5$ Hz, comparable to the rotation frequency of the mixer in the regular stirring experiments discussed here. In the temperature range under discussion ($\Delta T\approx10$ K), the liquid-liquid interface was well-defined in the random stirring experiments. In these experiments, a *steady-state* wetting layer was achieved after a complete burnoff of the wetting layer in behavior similar to the steady-state results for regular stirring ($f<f_0$) (90% of the steady-state thickness for random stirring was recovered within $1.4-2.9\times10^{4}$ sec for $\Delta T\approx8-10$ K). These wetting layers are at least a factor of 4 thicker than the thickest layer observed in the steady-state regular stirring ($f<f_0$) experiments discussed here. We conclude that random stirring can be more effective than regular stirring in transporting nitromethane throughout the lower bulk phase.

X. SUMMARY

We find that the steady-state thickness of a regularly stirred, gravity-thinned wetting layer in a binary liquid at coexistence is enhanced by stirring, in qualitative agreement with the hydrodynamic theory for wetting-layer development given by Kayser, Moldover, and Schmidt.[2] We also find a high rate stirring regime in which the bulk liquid-liquid is unstable and the wetting-layer growth is unlimited over the observation interval employed. The initial development period for a wetting layer after it is removed by a rapid increase in thermostat bath temperature is characterized but not understood. We observe exponential decay of the wetting-layer thickness with a well-defined liquid-liquid interface toward the steady-state value in a manner that is diffusion limited. A prediction is made for the competition between diffusion and critical slowing down as the wetting system approaches coexistence by increased stirring. We have found that random stirring, as practiced in earlier experiments, can be considerably more efficient than regular stirring in supporting wetting-layer growth through convection. In summary, controlled stirring of a sample at bulk coexistence gives a new look at wetting-layer dynamics and steady-state behavior. The challenge before us is to interpret these results quantitatively using descriptions for the free energy of the substrate-liquid interaction such as that provided by Kayser[36] or phenomenologically through equilibrium experiments which measure dV/dl through the observation of the wetting-layer thickness as a function of temperature difference from coexistence.[3]

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APPENDIX: EQUATION OF MOTION FOR THE APPROACH TO STEADY STATE

Following[37] the method of Lipowsky and Huse,[33] we can arrive at the growth law for the approach to steady state. By mass conservation

$$\bar{\rho}\,\dot{l} \approx [1/(x_N^s - x_C^w)]D\bar{\rho}(\partial x_N^s/\partial z)_{z=l^+} .$$

Here the subscripts C and N refer to carbon disulfide and nitromethane, respectively. The superscripts w and s refer to the wetting (N^*) and spectator (C^*) phases, respectively. x denotes mole fraction at coexistence. $\bar{\rho}$ is the number density of the spectator phase. z is the distance from the substrate. The second factor on the right-hand side of the equation is the number flux of nitromethane through the spectator phase. We have used the fact that the perturbation in the concentration in the spectator phase due to the diffusion of nitromethane toward the wetting layer is slight compared to the equilibrium concentration difference between the spectator and wetting phases. The position $z = l^+$ is just ahead of the wetting-layer growth front. Because the concentration profile in the spectator phase relaxes quickly compared to the motion of the wetting layer we have

$$(\partial x_N^s/\partial z)_{z=l^+} = \Delta x/L_{\mathrm{DBL}} ,$$

where $\Delta x \equiv x_N^s(z=l^+) - x(z=L_{\mathrm{DBL}}^-)$. We also expect that

$$\Delta x = (\partial x/\partial \mu)_{\mathrm{spectator}}\Delta\mu ,$$

where $\Delta\mu$, the difference in the field conjugate to the order parameter, is defined in a manner similar to Δx. Following Ref. 33, we expect that

$$\bar{\rho}(x_N^w - x_N^s)\Delta\mu = -\partial F/\partial l .$$

Note that we use a different definition for V than that in Ref. 33. We combine these relations to yield (saving only f-dependent terms)

$$\dot{l} \sim (1/L_{\mathrm{DBL}})(\partial F/\partial l) .$$

For $l \approx l_{\mathrm{ss}}$ we have

$$\partial F/\partial l \approx (\partial^2 F/\partial l^2)_{l=l_{\mathrm{ss}}}(l - l_{\mathrm{ss}}) .$$

Therefore, we have exponential relaxation of l toward l_{ss} with a time constant

$$\tau \sim L_{\mathrm{DBL}}(\partial^2 F/\partial l^2)^{-1}_{l=l_{\mathrm{ss}}} .$$

We can express the second factor on the right-hand side of this relation in terms of $V(l)$ by differentiating Eq. (4).

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[1] W. I. Goldburg, in *Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems,* edited by Sow-Hsin Chen, B. Chu, and R. Nossal (Plenum, New York, 1981), p. 383.

[2] R. F. Kayser, M. R. Moldover, and J. W. Schmidt, J. Chem. Soc. Faraday Trans. 2, **82**, 1701 (1986).

[3] X. Wu, M. Schlossman, and C. Franck, Phys. Rev. B **33**, 402 (1986).

[4] R. F. Kayser (private communication).

[5] H. Schlichting, *Boundary Layer Theory* (McGraw-Hill, New York, 1979), p. 229.

[6] $\nu = \eta/\rho$ where η is the dynamic viscosity and ρ is the mass density.

[7] *International Critical Tables of Numerical Data, Physics, Chemistry and Technology,* edited by E. W. Washburn (McGraw-Hill, New York, 1928), Vol. 7, (F. Giordani) p. 213 for viscosities, and Vol. 3, (G. P. Baxter) p. 23 and (R. F. Brunel and K. Van Bibber) 28 for densities. We get $\eta \approx 4\times 10^{-3}$ poise and $\rho \approx 1.1$ g/cm^{-3} for temperature between 63 and 53 °C by averaging the pure liquid values. We find D using the Kawasaki-Stokes-Einstein relation [B. Chu, S. P. Lee, and W. Tscharnuter, Phys. Rev. A 7, 353 (1973)] $D = k_B T/(6\pi\eta\xi)$. Here, k_B is Boltzman's constant, T is the temperature (K), and η is the low-frequency dynamic viscosity (the above reference shows that this is a good approximation). We find ξ, the correlation length [$\approx \xi_0^- t^{-\nu}$, where $t \equiv |T_c - T|/T_c$ is the reduced temperature with respect to the critical temperature in units of degrees Kelvin (we measure $T_c \approx 63.3$ °C)] from our turbidity measurements above the critical point (we get $\xi_0^+ \approx 0.2$ nm assuming $\nu = 0.62$ [see A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 57 (1983)]) and the amplitude ratio $\xi_0^+/\xi_0^- \approx 1.9$ [see D. Beysens, A. Bourgou, and P. Calmettes, Phys. Rev. A **26**, 3589 (1982)].

[8] R. Lipowsky, Phys. Rev. B **32**, 1731 (1985).

[9] K. Abeysuriya, X. Wu, and C. Franck, Phys. Rev. B **35**, 6771 (1987).

[10] Specifically, we are concerned that the results for the exponent p reported in Ref. 3 should be reinterpreted in light of the possibility of a substrate surface layer as described in Sec. VII A (d) of this paper. This was suggested to us by M. R. Moldover and has been confirmed by our subsequent calculations.

[11] Aldrich Chemical Company Stock Nos. 15470-9 and 23073-1, respectively.

[12] E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan, and S. V. Subramanyam, Phys. Rev. Lett. **32**, 284 (1974).

[13] Corning Glass.

[14] The only significant variation in the procedure was that the exposure time was 24 hours for both EDTA and nitric acid.

[15] J. A. Dixon, M. Schlossman, X. Wu, and C. Franck, Phys. Rev. B **31**, 1509 (1985).

[16] In this report "coexistence" will henceforth refer to the coexistence of two liquid mixture phases, unless otherwise noted.

[17] D. Beysens, M. Gbadamassi, and B. Moncef-Bouanz, Phys. Rev. A **28**, 2491 (1983).

[18] A. Onuki and K. Kawasaki, Ann. Phys. (N.Y.) **121**, 456 (1979).

[19] D. Beysens and M. Gbadamassi, Phys. Rev. Lett. **47**, 846

(1981).

[20] Y. C. Chou and W. I. Goldburg, Phys. Rev. Lett. **47**, 1155 (1981).

[21] We used the solution to Maxwell's equations for this problem given by M. V. Klein, *Optics* (Wiley, New York, 1970), pp. 582–585.

[22] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1984), p. 241.

[23] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982), p. 265.

[24] K. Kinosita, in *Progress of Optics,* edited by E. Wolf (North-Holland, Amsterdam, 1965), Vol. 4, p. 85.

[25] D. L. Malm and J. E. Riley, Jr., J. Electrochem. Soc. **129**, 1819 (1982).

[26] A. Iqbal, S. C. Danforth, and J. S. Haggerty, J. Am. Ceram. Soc. **66**, 302 (1983).

[27] S. P. Zhdanov, in *The Structure of Glass* (Consultant's Bureau, New York, 1958), p. 125 [translation of *A Conference on the Structure of Glass* (Academic of Sciences, Moscow, 1953)].

[28] *Handbook of Chemistry and Physics,* edited by R. C. Weast (Chemical Rubber Company, Boca Raton, 1982), p. E-379.

[29] H. Yokota, H. Sakata, M. Nishibori, and K. Kinosita, Surf. Sci. **16**, 265 (1969).

[30] D. E. Aspnes and J. B. Theeten, Phys. Rev. B **20**, 3292 (1979).

[31] K. Vedam, and M. Malin, Mater. Res. Bull. **9**, 1503 (1974).

[32] R. Ruiz and D. R. Nelson, Phys. Rev. A **24**, 2727 (1981).

[33] R. Lipowsky and D. A. Huse, Phys. Rev. Lett. **57**, 353 (1986).

[34] KMS also give a general argument for the approach to steady-state behavior.

[35] Ref. 2, p. 1713.

[36] R. F. Kayser, Phys. Rev. Lett. **56**, 1831 (1986).

[37] Suggested by D. Huse (private communication).