Simple hydrodynamic model of fast-mode kinetics in surface-mediated fluid phase separation

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We propose here a simple physical model of the fast surface domain growth with the $t^{3/2}$ algebraic law observed for surface-mediated phase separation of symmetric fluid mixtures. This unusually fast coarsening is likely caused by the hydrodynamic spreading of a more wettable fluid phase on a two-dimensional solid surface via bicontinuous fluid tubes. The gradual change in the growth exponent from 1 to 3/2 with an increase in the quench depth can likely be explained by the shape transition of wetting droplets from hemisphere to disk, which is induced by the increase in the wetting power with the quench depth. We also discuss the slowing down of the fast growth mode in the late stage. This slowing down is likely caused by the constraint that domain growth velocity cannot exceed the viscous-dissipation-limit velocity. [S1063-651X(96)12308-4]

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I. INTRODUCTION

Pattern evolution in phase-separating mixtures has been extensively studied from both the experimental and the theoretical viewpoints [1]. Coarsening dynamics has largely been clarified for phase separation in bulk. Since the finding of critical wetting phenomena [2], wetting phenomena have also attracted much attention [3]. Phase separation under an influence of wetting to a solid surface has recently been intensively studied by many researchers both experimentally and theoretically [4]. This problem is important because any experiment on phase separation can never be free from surface effects since we need a container to support a sample. It is also interesting from the fundamental viewpoint to reveal the effects of geometrical confinement and symmetry-breaking surface field on phase-separation behavior. Because of the complex nature of dynamic interplay between wetting and phase separation, however, coarsening dynamics under an influence of wetting has not been fully clarified yet.

Here we focus our attention on one of the unsolved problems: Recently Wiltzius and Cumming *et al.* [5,6] have found the existence of the fast and slow modes for phase separation under an influence of wetting in a quasi-two-dimensional configuration. The most striking feature of their findings is the fast mode of domain growth with the time exponent of 3/2. Shi *et al.* [7] and Harrison *et al.* [8] demonstrated the universality of the fast mode in fluid mixtures and further confirmed that the exponent increases from 1 to 3/2 with an increase in the quench depth. This surprisingly fast coarsening has attracted much attention since it is the fastest coarsening ever known for phase separation [1].

Since then, there have been a few theoretical efforts [9–11] to explain the fast-mode kinetics. Troian proposed a model which couples anisotropic diffusional growth to the process of domain coalescence [9]. She explained the phenomenon on the assumption that there are two length scales, R_B and R_S (B and S stand for bulk and surface, respectively). She derived the growth laws $R_B \sim t^{1/3}$ and $R_S \sim t^{1/2}$. Further, the geometrical constraint of three-dimensional (3D) growth near a two-dimensional (2D) surface increases the effective exponent due to coalescence by a factor of 3 as in the case of the coarsening of breath figures [12]. Thus, she obtained the exponent of 3/2. Marko, on the other hand, considered the hydrodynamic effect and showed that even the fast mode should be slower than the hydrodynamic coarsening [10]. Keblinski *et al.* also pointed out the importance of the hydrodynamic effect based on their simulation [11].

Among these models, only Troian's model has a possibility of explaining the exponent of 3/2. Although her model is an interesting physical model, there have still remained counterarguments [11,9]. Further, her model is based on the assumption that small domains with the slow growth law of $t^{1/3}$ observed by Wiltzius and Cumming *et al.* [5,6] reflect the bulk phase separation. We have recently demonstrated, however, that the small droplet structure is not due to the primary bulk phase separation, but is due to the secondary phase separation likely caused by the interface quench effect unique to hydrodynamic coarsening of symmetric fluid mixtures [13]. Thus, we think that the precondition of Troian's model that phase separation proceeds with droplet morphology is probably not appropriate. More importantly, we think that the diffusional growth can hardly explain such quick growth of domains. We believe that the hydrodynamic coarsening should be responsible for the phenomenon.

In this paper, we propose a simple physical model that the more wettable phase quickly spreads over the surface by a hydrodynamic mode via bicontinuous tubes. In Sec. II, we describe the specific feature of hydrodynamic coarsening of bicontinuous pattern. In Sec. III, we propose a simple model of fast domain growth which can explain the time exponent of 3/2. The predictions based on the model are compared with the experimental results. In Sec. IV, we discuss the spatial correlation between surface domains and the resulting scattering pattern, based on the elementary fast coarsening mechanism of individual wetting droplets derived in the preceding section. In Sec. V, we discuss the remaining problems of our model. Finally we summarize our study in Sec. VI.

II. HYDRODYNAMIC COARSENING OF BICONTINUOUS PATTERN

It is well known that a symmetric fluid mixture phase separates while keeping a bicontinuous pattern and the coarsening proceeds by hydrodynamic tube instability (Siggia's

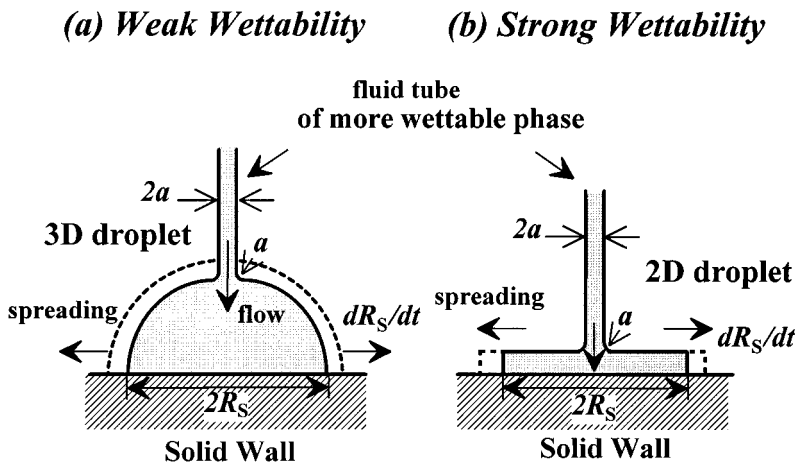

FIG. 1. Schematic figures explaining the wetting dynamics of bicontinuous tubes to the wall which is dominated by the hydrodynamic tube instability: (a) weak wettability case and (b) strong wettability case.

mechanism) [1,14]. The phase-separation process under a geometrical constraint also exhibits this growth behavior for symmetric fluid mixtures [10,15–20]. All the fluid mixtures showing the fast-mode kinetics have nearly critical compositions. Thus, the relevant late-stage coarsening mechanism should be hydrodynamic coarsening caused by tube hydrodynamic instability [1,14].

Our observation of phase-separation behavior in a one-dimensional (1D) capillary strongly supports this fact [15,16]: (i) For nonviscous fluid mixtures, the formation of the wetting layer finishes within a few seconds. Such fast transport of material is possible only by a hydrodynamic process. Further, we have directly observed the pumping process that fluid is supplied via wetting tubes into the wetting layer in the 1D capillary experiment (see Refs. [15,16]). (ii) Linear growth of the wetting layer thickness h ($h \sim t$) has successfully been explained by hydrodynamic transport of fluid from bulk to surfaces [16]. *We believe that this elementary process of the hydrodynamic wetting mode observed in a 1D capillary should be common for a 2D capillary since the thickness of the 1D capillary is much larger than that of a bicontinuous tube.*

III. A SIMPLE MODEL OF FAST SURFACE DOMAIN GROWTH

A. Simple theory

Based on this hydrodynamic coarsening mechanism, we here propose a simple model of the fast surface domain growth [16]. The pressure stemming from the interface tension σ is lowest for a wetting layer because of the smallest curvature of its interface. Thus, there is a pressure gradient between a bicontinuous tube and its wetting part, reflecting the difference in the transverse curvature of the tube between them. This causes a hydrodynamic flow from a tube to a wetting droplet on the wall. Since the pressure gradient between the tube with a radius of a and the wetting layer is $\sim \sigma/a$ over the distance a, the flux of this flow is estimated as $Q \sim (\sigma/\eta)a^2$ [15,16], where η is the viscosity. Thus, the more wettable fluid is continuously supplied to a wetting droplet via a bicontinuous tube [21]. There can be two kinds of wetting droplets depending upon wettability, (a) hemispherical droplets and (b) disklike droplets, as schematically shown in Fig. 1. The shape of wetting droplets is probably closely related to the competition between the driving force for spreading coming from the wetting energy $\Delta\gamma$ ($=\gamma_\alpha - \gamma_\beta$, γ_i: the surface interaction energy for i-phase) and the opposing force due to the liquid-liquid interface energy σ: The former favors a 2D droplet with the large contact area with a solid surface, while the latter favors a 3D droplet with a minimum liquid-liquid interface area. The competition between these two factors can be characterized by the so-called wetting power S, which is defined as $S = \Delta\gamma - \sigma$. Since $\Delta\gamma = \Delta\gamma_0 \epsilon^\beta$ ($\epsilon = \Delta T/T_c$, the reduced temperature; β, the exponent of phase diagram) and $\sigma = \sigma_0 \epsilon^\mu$ ($\mu = 2\nu$) [3], the wetting power S increases with an increase in the quench depth ΔT ($\Delta T = T_c - T$, T_c a critical temperature) in the vicinity of T_c. Thus, 2D droplets are more favored for a deeper quench. Energetically 2D droplets are always favored in the complete wetting region, while kinetically 3D droplets are favored because of less viscous dissipation. This point will be discussed later.

Under strong wettability, the growth of wetting droplets (spreading process) is likely two-dimensional and the thickness of a disklike droplet h is roughly constant with time. This 2D nature of the droplet growth has been experimentally confirmed [5,6] (see, e.g., Fig. 3 of Ref. [5]). From the volume conservation under the constraint of constant h, we obtain the relation $hR_S dR_S/dt \sim Q$, where R_S is the radius of a wetting droplet. Using Siggia's growth law for the bulk tubes, $a \propto (\sigma/\eta)t$, we obtain the relation

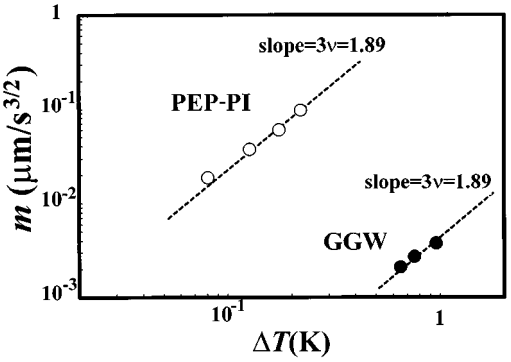

FIG. 2. Dependence of the prefactor m on the quench depth ΔT for two mixtures, PEP-PI and GGW. The dashed lines have a slope of $3\nu = 1.89$, where ν is the critical exponent of the correlation length and $\nu = 0.63$ for the 3D Ising universality class.

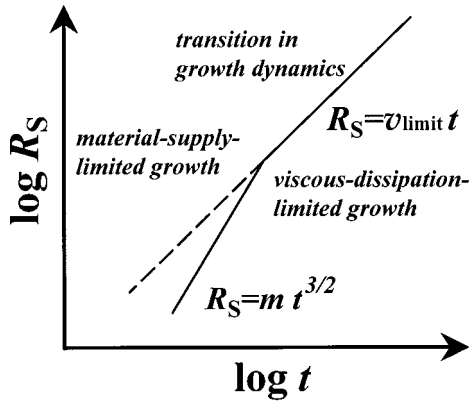

FIG. 3. Schematic figure of dynamic turnover from material-supply-limited growth to viscous-dissipation-limited growth.

$R_S \sim h^{-1/2}[(\sigma/\eta)t]^{3/2}$. This explains the fast mode naturally. Under weak wettability, on the other hand, the wetting droplet shape cannot be purely two-dimensional and likely becomes more hemispherical (3D) since the interface tension dominates the shape of a wetting droplet instead of the wetting force. For an exactly 3D droplet growth, for instance, we obtain $R_S^2 dR_S/dt \sim Q$. Including both the above coarsening laws for 2D and 3D wetting droplets, we obtain the following general relation:

$$R_S \sim [(\sigma/\eta)t]^{3/D}, \tag{1}$$

where D is the spatial dimensionality of a wetting droplet. This model can explain the exponent range from 3/2 to 1, which has been experimentally observed for the fast mode [7,8].

The remaining questions are (i) why the bulk hydrodynamic growth mode of $a \sim t$ has not been reported [5–7] and (ii) how the bulk domains continuously grow as $a \sim t$ with supplying fluid to wetting droplets. On question (i), we believe that the bulk mode is hidden in the scattering function because of the following reason: The tube structure in bulk can be directly seen, overlapped with wetting droplets, in Fig. 11 of Ref. [6], Fig. 4 of Ref. [7], and Fig. 8 of Ref. [8] only in the early stage where the fast growth mode does exist. At the time when the fast growth mode loses its scattering intensity, the bulk tube structure has already disappeared and only fine droplets produced by double phase separation can be seen in bulk. It should be noted that there is not much difference in peak wave numbers between the mode of $t^{3/2}$ and that of t (less than a factor of 2) in the limited lifetime of the fast mode. On question (ii), the growth law of tubes ($a \sim t$) is confirmed experimentally by the cross-sectional observation of the bulk tube structure in a 1D capillary [15]. We believe that there is no essential difference between 1D and 2D capillaries on the dynamics of the supply of fluid into wetting droplets via bulk tubes [15]: In both cases, wetting droplets (layers) are formed by the hydrodynamic flow via bulk bicontinuous tubes [this also supports the conclusion about question (i)]. The velocity fields in bulk tubes connected to wetting droplets could be composed of the background, rather steady velocity fields directed from bulk to wetting droplets whose magnitude is $\sim \sigma/\eta$ and the weaker fluctuating velocity fields caused by capillary instability of bulk tubes themselves. We speculate that the unidirectional background flow stabilizes selectively a pumping tube near the wall, while the local flow driven by local curvature gradients causes the coarsening of tubes ($a \sim t$). Further theoretical studies are highly desirable for understanding the physical mechanism.

B. Comparison with the experimental results

Next we discuss the prefactor m defined by $R_S = m t^{3/2}$. The dependence of the prefactor m on ΔT is shown in Fig. 2. The values of m for the mixture of poly(ethylene-propylene) and polyisoprene (PEP-PI) and the mixture of guiaiacol and glycerol-water (GGW) are obtained from Fig. 1 of Ref. [5] and Fig. 2 of Ref. [7], respectively. The dashed lines in Fig. 2 have a slope of 3ν (~ 1.89). According to our model, $m \propto h^{-1/2}(\sigma/\eta)^{3/2} = h^{-1/2}(0.2 k_B T/\eta\xi^2)^{3/2} = h^{-1/2}(0.2 k_B T)^{3/2}(\Delta T/T_c)^{3\nu}/(\eta^{1/2}\xi_0)^3$. This relation, $m \propto (\Delta T)^{3\nu}$, is quite consistent with the experimental results (see Fig. 2). The difference in the amplitude of m between PEP-PI and GGW can also be explained by our prediction that $m \propto \eta^{-3/2}\xi_0^{-3}$: The bare correlation length ξ_0 is more than several times larger for PEP-PI [22] than for GGW [23], reflecting the molecular size difference. The value of viscosity η is about 4 poise for PEP-PI [6] and 3.5 poise for GGW [8]. These values of η and ξ_0 lead to the amplitude ratio of several hundreds, which is comparable to the ratio of ~ 400 obtained from Fig. 2. Thus, our model can explain not only the time exponent of the fast mode, but also the behavior of the prefactor of the power law [24].

C. Dynamic turnover of the exponent

1. Viscous dissipation

Next we discuss the dynamic turnover of the growth mode of 3/2 to linear growth in the final stage, which has recently been experimentally found by Harrison *et al.* [8]. This transition from a nonsteady to a steady state can probably be explained by the existence of two dynamic stages of droplet spreading (see Fig. 3): (i) an initial stage where the supply of fluid is the limiting process and the velocity grows as $v = dR_S/dt \sim t^{3/2}$ and (ii) a late stage where the growth speed is bound by a limiting interface velocity $v_{\rm limit} \sim \sigma/\eta$ determined by the viscous dissipation. In other words, this turnover is a result of the transition from a regime of constant h to that of $h \sim R_S(t)$.

Since the energy dissipation due to viscosity associated with the hydrodynamic domain growth steeply increases with an increase in the speed of domain growth, there should be the maximum limiting speed to be allowed, as pointed out by Marko [10]. Under strong wettability, a wetting droplet has a 2D disklike shape with the largest energy gain due to the wetting. However, this configuration costs the largest energy dissipation from the velocity gradient required to satisfy the boundary condition at the solid surface. Thus, the balance among the rate of fluid supply from bulk, the viscous dissipation upon spreading, and the wetting power would select the wetting domain morphology including the thickness h.

2. Difference in bulk and surface hydrodynamic growth

Finally, we consider why the spreading droplet can grow much faster than the bulk tube, even though both grow essentially by the same mechanism of hydrodynamic coarsening.

Note that the prefactor k of the relation $R \sim k(\sigma/\eta)t$ is different between the surface wetting domains and bulk domains. For a bulk symmetric mixture, it is well known that the phase separation proceeds by the hydrodynamics unique to the bicontinuous pattern and the pattern coarsens as $R \propto (\sigma/\eta)t$ in the late stage [1,14]. For bicontinuous phase separation, the tube flow is essentially caused by the fluctuation of tube size. Siggia estimated $k = k_b$ as 0.1 on the basis that the pressure difference along the tube is $\sim \sigma/R$ [14]. As he pointed out [14], this pressure difference is probably overestimated for the tube-radius fluctuation. Thus k_b is likely smaller than k_w. Wong and Knobler [25] estimated k_b as 0.001 from their experimental results. San Miguel *et al.* [26] theoretically reestimated k_b on the basis of the capillary instability and they obtained the relation $k_b \sim 0.04$ for the two-phase fluids having similar viscosity. The recent experiments by Guenoun *et al.* [27] and by Bates and Wiltzius [28] supported this evaluation ($k_b \sim 0.04$). For surface wetting droplets, on the other hand, the tube flow is caused deterministically by a difference in the curvature between the tube and the wetting droplet; and, thus, $k = k_w$ is likely the order of unity.

This difference between k_w and k_b naturally explains why the spreading droplet is wider than the tube which is supplying it with material, even though both coarsen by the same mechanism of hydrodynamic coarsening. The viscous dissipation limit of the velocity is likely given by $k\sigma/\eta$, where k is likely the order of unity.

IV. THE BEHAVIOR OF SCATTERING FUNCTIONS: CORRELATION EFFECTS

Finally, we discuss the evolution of the scattering pattern originating from individual growth of wetting droplets. The fact that the scattering intensity of the fast mode stems from wetting droplets on a 2D solid surface is confirmed by Wiltzius and Cumming *et al.* [5,6]. This is also confirmed by the recent experiment by Harrison *et al.* [8], which shows that the Fourier transform of a 2D image of wetting droplets gives the scattering function of the fast mode. Wiltzius and Cumming *et al.* also reported that the scattering intensity of the fast growth mode initially increases, then decreases, and eventually disappears (see Fig. 12 of Ref. [6] and Fig. 1 in Ref. [5]). This fact can be explained by the violation of the local conservation law on the 2D solid surface: In the initial stage, the surface coverage (Φ_S) of the wetting domains is negligible. In the final stage, on the other hand, the solid surface is completely covered by the complete wetting layer ($\Phi_S = 1$). The surface coverage changes with time because of the supply of the more wettable fluid from bulk. Such a temporal change in the surface coverage can be seen in Fig. 4 of Ref. [5], Fig. 4 of Ref. [7], and Fig. 8 of Ref. [8].

To understand the above behavior experimentally observed, we have made a simple simulation on the evolution of the structure factor $S(q)$ for growing 2D droplets. We generate 50 white droplets with a value of 1 on a 2D black surface with a value of 0 (size 256×256). The radii of droplets are increased as $R_S \propto t^{3/2}$. Then we calculate the power spectrum of 2D Fourier transformation of an image and obtain the structure factor $S(q)$ by circularly averaging the 2D power spectrum $S(\vec{q})$. The spatial correlation effect is a prerequisite to producing a peak in $S(q)$ [6]. The spatial correlation of wetting droplets likely stems from the periodicity of bulk phase-separation patterns. Here, this coherent effect is artificially introduced by imposing the linear q-dependence of $S(q)$ for small q. This q-dependence produces a nearly Gaussian shape of $S(q)$ experimentally observed [5,7,8]. We also calculate $\Phi_S(1-\Phi_S)$ by using the surface coverage Φ_S of white droplets measured from an image. The temporal change in $S(q)$ is shown in Fig. 4(a), and those in $q_{\max}$, $S(q_{\max})$, and $\Phi_S(1-\Phi_S)$ are plotted in Fig. 4(b). The peak wave number $q_{\max}$ decreases as $t^{-3/2}$ and the peak intensity $S(q_{\max})$ exhibits maximum, as expected. $S(q_{\max})$ behaves similarly with $\Phi_S(1-\Phi_S)$ and has the maximum at $\Phi_S = 1/2$. All the behavior is quite consistent with the experimentally observed behavior [5,6].

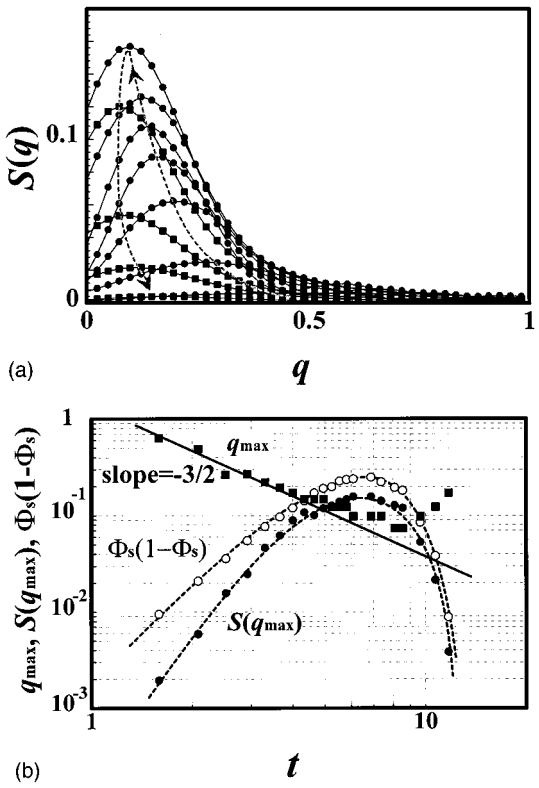

FIG. 4. (a) Temporal change in $S(q)$ obtained by the simulation. The dashed curve with arrows indicates the change in the peak position with time. Filled circles, growing process; filled squares, decaying process. (b) Temporal changes in $q_{\max}$, $S(q_{\max})$, and $\Phi_S(1-\Phi_S)$. Solid line has a slope of $-3/2$ and dashed curves are guides for the eye.

V. REMAINING PROBLEMS OF OUR MODEL

Although our hydrodynamic model intuitively explains many features of fast surface domain growth, the theory is quite qualitative and there are some remaining unsolved problems.

The most crucial one is the question of why the 2D droplet thickness h is constant with time during the growth and what physical factors determine h. We speculate that the

balance among the rate of fluid supply from bulk, the viscous dissipation upon spreading, and the wetting power select the wetting domain morphology including the thickness h. At this point, we think that h is determined mainly by the kinetic factors and h is not strongly affected by the thermodynamic factors such as the interface thickness ξ. If h is strongly dependent upon the quench depth, however, the dependence of the prefactor m on the quench depth ΔT can be altered. These problems about the wetting droplet thickness seem to be most difficult to solve and further theoretical studies are highly desirable.

Our model simply treats the bulk and surface pattern evolution independently and assumes that a bulk bicontinuous tube increases its radius as $R \sim t$. We need to explain how the pumping mechanism of a single tube continues to work with hydrodynamic coarsening. Although this has been confirmed experimentally [15,16], the development of a more analytical theory including both coarsening processes in a self-consistent way is highly desirable.

We also need to clarify the number density of tubes connected to a solid surface before the pumping mechanism starts to work. Another question relating to this problem is the spatial correlation between wetting domains. The spatial correlation is a prerequisite for producing a peak in the scattering function. The spatial distribution of wetting droplets is probably dominated by the initial configuration of tubes perpendicularly connected to the wall before the beginning of hydrodynamic coarsening. Thus, we speculate that the correlation originates from the correlation in the original bulk phase-separated structure, but there is no firm basis on this speculation and this point also needs to be clarified.

VI. CONCLUSION

In summary, we have proposed a possible model explaining the fast mode of wetting droplet growth observed in a phase-separating symmetric fluid mixture confined in a 2D capillary. Our model is based on the hydrodynamic tube instability, and essentially differs from the model based on diffusion [9]. Dependences of the time exponent on the quench depth and the phase-separation time can also be explained by our model. We believe that the fast mode should be observed only in a symmetric fluid mixture, and neither in asymmetric fluid phase separation having a droplet pattern nor in solid phase separation. The universality of the phenomenon found so far [7,8] is consistent with this prediction.

Simulation is another promising way to study this fast mode. Relating to this, it should be noted that hydrodynamic tube instability only exists in 3D, but not in 2D [26]. This likely explains why the fast mode has not been observed in 2D fluid simulations [11]. Simulation of phase separation in a 3D fluid mixture under a surface field is probably required to see this effect.

The study of liquid spreading dynamics has so far been limited to isolated droplets [3]. Further theoretical studies are highly desirable for the deep understanding of the spreading kinetics of a droplet under the supply of fluid from its outside.

ACKNOWLEDGMENTS

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[1] J.D. Gunton, M. San Miguel, and P. Sahni, in *Phase Separation and Critical Phenomena*, edited by C. Domb and J.H. Lebowitz (Academic, London, 1983), Vol. 8.
[2] J.W. Cahn, J. Chem. Phys. **66**, 3667 (1977).
[3] See, e.g., P.G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).
[4] See, e.g., G. Krausch, Mater. Sci. Eng. **R14**, 1 (1995).
[5] P. Wiltzius and A. Cumming, Phys. Rev. Lett. **66**, 3000 (1991).
[6] A. Cumming, P. Wiltzius, F.S. Bates, and J.H. Rosedale, Phys. Rev. A **45**, 885 (1992).
[7] B.Q. Shi, C. Harrison, and A. Cumming, Phys. Rev. Lett. **70**, 206 (1993).
[8] C. Harrison, W. Rippard, and A. Cumming, Phys. Rev. E **52**, 723 (1995).
[9] S.M. Troian, Phys. Rev. Lett. **71**, 1399 (1993); **72**, 3739 (1994).
[10] J.F. Marko, Phys. Rev. E **48**, 2861 (1993).
[11] P. Keblinski, W.J. Ma, A. Maritan, J. Koplik, and J. Banavar, Phys. Rev. E **47**, R2265 (1993); Phys. Rev. Lett. **72**, 3738 (1994).
[12] T.M. Rogers, K.R. Elder, and R.C. Desai, Phys. Rev. A **38**, 5303 (1988).
[13] H. Tanaka, Phys. Rev. Lett. **72**, 3690 (1994); Phys. Rev. E **51**, 1313 (1995).
[14] E.D. Siggia, Phys. Rev. A **20**, 595 (1979).
[15] H. Tanaka, Phys. Rev. Lett. **70**, 53 (1993).
[16] H. Tanaka, Phys. Rev. Lett. **70**, 2770 (1993).
[17] P. Guenoun, D. Beysens, and M. Robert, Phys. Rev. Lett. **65**, 2406 (1990).
[18] J. Bodensohn and W.I. Goldburg, Phys. Rev. A **46**, 5084 (1992).
[19] H. Tanaka, Europhys. Lett. **24**, 665 (1993).
[20] A.J. Liu, D.J. Durian, E. Herbolzheimer, and S.A. Safran, Phys. Rev. Lett. **65**, 1897 (1990).
[21] We assume here, for simplicity, that a single tube supplies fluid to a wetting droplet. We think that during the growth of a wetting droplet the number of tubes connected to it can be regarded approximately as constant, since the spreading of a droplet causes strong flow fields along its interface, which prevents other tubes from being connected. Thus, the spatial distribution of wetting droplets is largely dominated by the initial configuration of tubes perpendicularly connected to the wall before the beginning of hydrodynamic coarsening. The number of tubes perpendicular to the wall is probably not large since in the initial diffusion regime there is a tendency that tubes or layers are formed along the wall [4,10].
[22] P. Stepanek, T.P. Lodge, C. Kedrowski, and F.S. Bates, J. Chem. Phys. **94**, 8289 (1991).

[23] R.G. Johnston, N.A. Clark, P. Wiltzius, and D.S. Cannell, Phys. Rev. Lett. **54**, 49 (1985).

[24] It should be noted that we assume that the value of h is about the same for all the cases. We point out that the values of h reported [6,8] are likely overestimated since they are inconsistent with the experimental evidence of the 2D nature of droplets [5,6].

[25] N.C. Wong and C.M. Knobler, J. Chem. Phys. **69**, 725 (1978).

[26] M. San Miguel, M. Grant, and J.D. Gunton, Phys. Rev. A **31**, 1001 (1985).

[27] P. Guenoun, R. Gastaud, F. Perrot, and D. Beysens, Phys. Rev. A **36**, 4876 (1987).

[28] F.S. Bates and P. Wiltzius, J. Chem. Phys. **91**, 3258 (1989).