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Diverging curvature correction to the interfacial tension in polymer solutions

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Application of polymer scaling to the problem of Tolman's length, a curvature correction coefficient in the interfacial tension, shows that Tolman's length in polymer solutions may become as large as half of the thickness of the interface. Tolman's length depends on the degree of polymerization N and the distance to the critical point of phase separation, $\Delta\hat{T}$. In the "critical" regime ($N^{1/2}|\Delta\hat{T}|\ll 1$) Tolman's length diverges upon approach to the critical temperature as $\sim N^{0.348}|\Delta\hat{T}|^{-0.304}$. In the "polymer" regime ($N^{1/2}|\Delta\hat{T}|\gg 1$) Tolman's length does not depend on N, but diverges more strongly, as $\sim|\Delta\hat{T}|^{-1}$, proportional to the thickness of the interface.

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I. INTRODUCTION

The surface tension of a curved interface is different from that of a planar interface, a fact recognized by theoretical scientists but commonly ignored in practice. The curvature correction to the surface tension was first introduced by Tolman [1]. A key parameter in Tolman's work is the distance between the equimolar dividing surface and the surface of tension, known as "Tolman's length." The Tolman length, δ, defines the first curvature-correction coefficient in the surface tension, σ, of a liquid droplet or a vapor bubble:

$$\sigma(R) \simeq \sigma_\infty\left(1 - \frac{2\delta}{R} + \cdots\right), \tag{1}$$

where R is the droplet radius, taken equal to the radius of the surface of tension [2], and σ_∞ is the surface tension for the planar interface. Therefore the generalized Laplace-Tolman equation reads [2,3]

$$P'' - P' \simeq \frac{2\sigma_\infty}{R}\left(1 - \frac{2\delta}{R} + \cdots\right), \tag{2}$$

where $P''-P'$ is the difference between the pressure inside the droplet/bubble and the pressure outside.

Although the sign and the value of the correction $2\delta/R$ in Eq. (1) has been a subject of prolonged debate [3–13], square-gradient theories give consistent results in the mean-field approximation [8–10]. It has also been recognized that the difference between the equimolar surface and the surface of tension is phenomenologically associated with asymmetry in fluid-phase coexistence [2,3]. In symmetric systems, such as the lattice-gas (Ising) model and the regular-solution model, the difference between the equimolar surface and the surface of tension is absent; therefore Tolman's length vanishes. The interfacial tension for a droplet of a symmetric fluid does not depend on which phase is inside the droplet. Even for asymmetric phase equilibria, mean-field theories predict a very small Tolman's length: a small fraction of molecular size. Moreover, if the first curvature correction is very small, higher-order terms of the expansion in powers of $1/R$ in Eq. (1) become important, thus making the detection of Tolman's length by experiment or by simulation virtually impossible.

The situation may become very different for smooth interfaces, which are ubiquitous in soft matter. Examples include near-critical vapor-liquid and liquid-liquid interfaces in simple and complex fluids, interfaces in polymer solutions and polymer blends, liquid membranes, and vesicles. A smooth near-critical interface is characterized by the interfacial density/concentration profile with a characteristic length scale ξ; thus the "thickness" of the interface may be defined as 2ξ [2]. The length ξ turns out to be the same as the correlation length of the critical fluctuations of density/concentration in the two-phase region:

$$\xi \approx \xi_0|\Delta\hat{T}|^{-\nu}, \tag{3}$$

where $\Delta\hat{T}\equiv(T-T_c)/T_c$ (T is the temperature and T_c is the critical temperature), $\nu\simeq 0.630$ is the universal (three-dimensional Ising) critical exponent, and ξ_0 a system-dependent amplitude for the two-phase region [14]. Here and below $\approx$ means asymptotically equal, while $\simeq$ means approximately equal. Such interfaces are mesoscopic, extending from nanometers to microns; however, the droplet size, by definition, cannot be smaller than the thickness of its interface. The surface tension of smooth interfaces is usually very low, vanishing at the critical point; hence the interface undergoes large fluctuations.

An image of a smooth interface for a fluid droplet near the critical point is presented in Fig. 1. Specifically, a polymer-rich droplet of the radius $R\simeq 500$ nm (0.5 μm) with the thickness of the interface $2\xi\simeq 100$ nm in a solution of polystyrene in cyclohexane for a degree of polymerization $N \simeq 2\times 10^3$ (molecular weight about 200 000, radius of gyration $R_g\simeq 10$ nm) near the critical point of liquid-liquid separation at $T_c-T\simeq 0.1$ K [17] would appear similar to the image shown in Fig. 1.

What would be the curvature effect on such an interface? A recent study [18] shows that there are two key elements that determine the first correction to the surface tension of a smooth interface. First, there is an intrinsic system-

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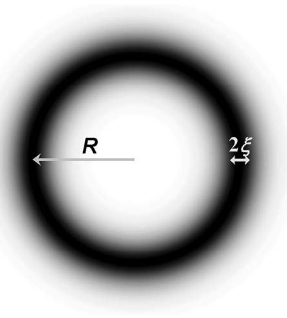

FIG. 1. Simulation of a smooth interface (by using toolboxes in MATLAB [15]) for a droplet near the critical point of fluid-fluid separation. Intensity of shadowing indicates the value of the density/concentration gradient in the interfacial profile [16]. The "thickness" of the interface, given by a characteristic decay length of the profile, is indicated by 2ξ.

dependent fluid-phase asymmetry caused by specific intermolecular interactions. This intrinsic asymmetry can be evaluated from a mean-field equation of state. Second, there is a universal modification of this asymmetry by critical fluctuations. It has been shown [18] that a proper treatment of asymmetry in fluid phase behavior, known as "complete scaling" [19–21], yields an algebraic divergence of Tolman's length upon approaching the critical point as a function of $\Delta\hat{T}$ with an exponent -0.304—much stronger than previously believed [3,12,13]. This is purely a fluctuation-induced effect which does not exist in any mean-field model.

It was proposed [18] that a ratio of the "excess density," defined as the deviation of the mean density from the critical density, $\Delta\rho_{\mathrm{d}} \equiv (\rho'' + \rho')/2 - \rho_{\mathrm{c}}$, and the difference between the densities of the liquid/vapor coexisting phases, $\rho'' - \rho'$, can be phenomenologically related to the ratio of Tolman length and the thickness of interface as [22]

$$\frac{\delta}{2\xi} \simeq \mp \frac{\Delta\rho_{\mathrm{d}}}{\rho'' - \rho'}. \tag{4}$$

Equation (4) unambiguously defines the sign of Tolman's length as being negative for liquid droplets and positive for bubbles, provided that the slope of the "diameter" of the phase coexistence is negative [23]. Since in the mean-field approximation for the critical region the ratio $(\rho'' - \rho')/\Delta\rho_{\mathrm{d}} \sim |\Delta\hat{T}|^{-1/2}$ and the thickness of the interface $2\xi \sim |\Delta\hat{T}|^{-1/2}$ depend on $|\Delta\hat{T}|$ in the same manner [2], the mean-field Tolman length in simple fluids at the critical points remains finite and microscopic [8–10].

In real fluids, being modified by fluctuations, the excess density splits into two nonanalytic terms [19–21]:

$$\frac{\Delta\rho_{\mathrm{d}}}{\rho_{\mathrm{c}}} \simeq a_{\mathrm{eff}}\hat{B}_0^2|\Delta\hat{T}|^{2\beta} - b_{\mathrm{eff}}\frac{\hat{A}_0^-}{1-\alpha}|\Delta\hat{T}|^{1-\alpha} + \cdots, \tag{5}$$

where a_{eff} and b_{eff} are system-dependent asymmetry coefficients (to be evaluated from a mean-field equation of state), $\beta \simeq 0.326$ and $\alpha \simeq 0.109$ are universal critical exponents, and $\hat{B}_0$ and $\hat{A}_0^-$ are system-dependent critical amplitudes. Since, asymptotically,

$$\frac{\rho'' - \rho'}{2\rho_{\mathrm{c}}} \approx \hat{B}_0|\Delta\hat{T}|^{\beta}, \tag{6}$$

one can obtain the Tolman length from Eqs. (3)–(6):

$$\delta \simeq \mp \xi_0\left[a_{\mathrm{eff}}\hat{B}_0|\Delta\hat{T}|^{\beta-\nu} - b_{\mathrm{eff}}\frac{\hat{A}_0^-}{\hat{B}_0(1-\alpha)}|\Delta\hat{T}|^{1-\alpha-\beta-\nu} + \cdots\right]. \tag{7}$$

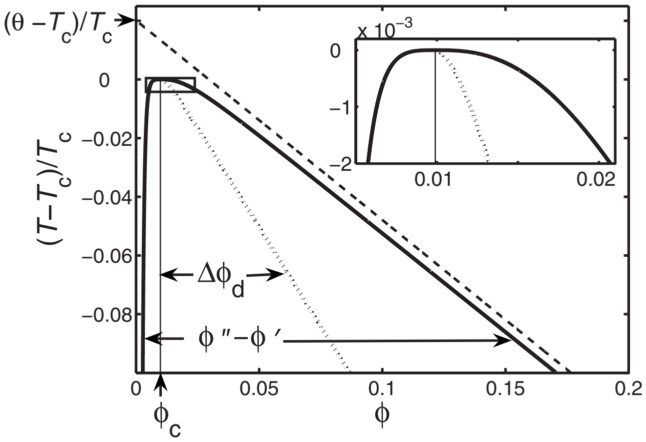

FIG. 2. Asymmetric coexistence curve for a polymer solution with a degree of polymerization $N = 10^4$ near the critical point as follows from Flory theory modified by critical fluctuations [25]. The solid line represents the phase separation curve interpolated between the critical regime and theta-point regime by Eq. (10). The dashed line represents the Flory-Huggins phase behavior for infinite degree of polymerization [24,25]. The crossover "diameter" of the coexistence is interpolated as $\Delta\hat{\phi}_{\mathrm{d}} \equiv (\phi'' + \phi')/2\phi_{\mathrm{c}} - 1 \simeq Bx^{\beta}[(1+x)^{1-\beta} - (1+Bx^{\beta})^{-1}]$ and shown by the dotted curve (plotted with $B = 3/2$). In the critical regime (enlarged in inset) the coexistence curve is asymptotically described by Eq. (8), while the "diameter" recovers singular behavior $\sim B^2x^{2\beta}$.

The second term in Eq. (7) diverges weakly with the small exponent $1 - \alpha - \beta - \nu \simeq -0.065$, a result well-known from earlier studies [3,12,13]. The first term is new and diverges more strongly, with the exponent $\beta - \nu \simeq -0.304$; we will show this term to be the only effect of practical significance for near-critical polymer solutions. It has not been proven that Eq. (4) is a rigorous thermodynamic relation, although it appears to satisfy both asymptotic scaling and mean-field regimes [30]. However, this relation provides a practical tool for evaluating Tolman's length from phase-coexistence data, even far beyond the critical region, where Eq. (7) is no longer valid.

II. DIVERGENCE OF TOLMAN'S LENGTH IN POLYMER SOLUTIONS

A polymer solution is a remarkable example of highly asymmetric fluid coexistence. Equations (1) and (2) are still valid for the liquid-liquid interface in polymer solutions, where $P'' - P'$ will be the difference between the osmotic pressures inside and outside the droplet. A typical phase diagram of a polymer solution is shown in Fig. 2. To be specific, we have plotted the phase diagram for the Flory-Huggins free energy modified by fluctuations in the critical region [25]. There are two regimes in polymer solutions, the "critical" regime and the "polymer" regime, in which the solution phase behavior differs dramatically. These two regimes are separated by the Widom variable $x \equiv (1/2)N^{1/2}|\Delta\hat{T}|$ [24]. In the critical regime, where $x \ll 1$ (with $|\Delta\hat{T}|$ small enough for any given $N \gg 1$), the liquid-liquid coexistence is described by Eqs. (5) and (6) with the polymer volume fraction ϕ replacing the density ρ and ϕ_c replacing ρ_c. Since for $N \gg 1$, $\hat{B}_0 \simeq \hat{B}_{0,N=1}N^{\beta/2}$ and $\phi_c \simeq 1/\sqrt{N}$ [17,25], one obtains the polymer-solution phase coexistence in the critical regime as a function of x:

$$\frac{\phi'' - \phi'}{2\phi_c} \approx B_{cr}x^{\beta}, \tag{8}$$

where $B_{cr} = 2^{\beta}\hat{B}_{0,N=1}$. For the symmetric lattice (Ising) model ($N=1$) in the mean-field approximation $\hat{B}_{0,N=1} = \sqrt{3} \simeq 1.7$ [25,27]; however, this value is affected by the critical fluctuations and becomes smaller in the scaling regime ($\hat{B}_{0,N=1} \simeq 1$ for the 3d Ising model with short-range interactions [27]).

In the polymer regime, where $x \gg 1$ (satisfied by sufficiently large N at any given $|\Delta\hat{T}| \ll 1$), the phase coexistence becomes anglelike [17,24]:

$$\frac{\phi'' - \phi'}{2\phi_c} \approx \frac{\phi''}{2\phi_c} \approx B_p x. \tag{9}$$

In the Flory-Huggins model $B_p = 3/2$ [17,24,25]. When $N \to \infty$, the critical temperature tends to the *theta* temperature (Θ), thus $\Delta\hat{T} \to (T-\Theta)/\Theta$. Renormalization-group theory [26] predicts almost mean-field tricritical behavior in the polymer regime, with some detectable logarithmic corrections induced by fluctuations [17], which, however, do not significantly affect the interfacial behavior and are ignored in this work. For the sake of simplicity, we adopt $B_p = B_{cr} = B$. Therefore we suggest a simple interpolation for crossover between the critical and polymer regimes in the fluctuation-modified Flory-Huggins model:

$$\frac{\phi'' - \phi'}{2\phi_c} \simeq Bx^{\beta}(1+x)^{1-\beta}, \tag{10}$$

shown in Fig. 2 by the solid curve.

Equation (4) can be adopted for polymer solutions in the form

$$\frac{\delta}{2\xi} \simeq \mp \frac{\Delta\phi_d}{\phi'' - \phi'}. \tag{11}$$

This ratio behaves very differently in the critical and polymer regimes. Consider a droplet of polymer-rich phase, with concentration ϕ'', in coexistence with solution with concentration ϕ'. In this particular case the sign of Eq. (11) will be negative. Scaling arguments suggest that in the critical regime (when $\Delta\hat{T} \to 0$) Tolman's length should diverge, in the same manner as in simple fluids, but with an N-dependent amplitude; whereas in the polymer regime (when $N \to \infty$) Tolman's length and the thickness of the interface should not depend on N.

Consider, first, the critical regime, where all critical amplitudes depend on the degree of polymerization. The asymmetry coefficient a_{eff}, as explicitly evaluated through the derivatives of the Flory-Huggins free energy by the method developed in Refs. [20,21],

$$a_{\text{eff}} = \frac{3}{5}\frac{N-1}{N+\sqrt{N}}, \tag{12}$$

quickly reaches a finite value of 3/5 in the limit $N \to \infty$ and vanishes in the "symmetric" limit $N=1$. The second asymmetry coefficient,

$$b_{\text{eff}} = a_{\text{eff}}\frac{N\sqrt{N}}{N+\sqrt{N}}, \tag{13}$$

behaves asymptotically as $b_{\text{eff}} \approx (3/5)\sqrt{N}$. Thus we obtain from Eq. (11) by adopting Eq. (5) for $\Delta\phi_d/\phi_c$ and by using Eq. (8)

$$\frac{\delta}{\xi} \simeq -(c_1 x^{\beta} - c_2 x^{1-\alpha-\beta}). \tag{14}$$

The prefactors c_1 and c_2 are both order of unity: $c_1 = 2^{\beta}(3/5)\hat{B}_{0,N=1} \simeq 1$ and $c_2 = 2^{(1-\alpha-\beta)}(3/5)\hat{A}^-_{0,N=1}/(1-\alpha)\hat{B}_{0,N=1} \simeq 1$ [28]. We may further simplify Eq. (14) by adopting $c_1 = c_2$. Moreover, the second term becomes negligible at $x \ll 1$ since the ratio of the second term to the first one vanishes as $x^{1-\alpha-2\beta}$ when $x \to 0$.

As first shown by de Gennes [29] and confirmed experimentally [17], the correlation length in the critical regime scales with N as

$$\xi \simeq \xi_0^-|\Delta\hat{T}|^{-\nu} \simeq \xi^-_{0,N=1}N^{(1-\nu)/2}|\Delta\hat{T}|^{-\nu} \simeq c_0 R_g\left(\frac{1}{2}N^{1/2}|\Delta\hat{T}|\right)^{-\nu}$$

$$\simeq c_0 R_g x^{-\nu}, \tag{15}$$

where $R_g \simeq r_0 N^{1/2}$ is the radius of gyration for an ideal (random-walk) polymer chain with r_0 being of the order of monomer size, $\xi^-_{0,N=1}$ is the amplitude of the correlation length in the two-phase region for $N=1$, and $c_0 = 2^{-\nu}\xi^-_{0,N=1}/r_0 \lesssim 1$ [30]. Adopting $c_0 \simeq 1$, for the sake of simplicity, we finally obtain

$$\xi \simeq R_g x^{-\nu}. \tag{16}$$

Keeping only the leading term in Eq. (14) and using Eq. (16), we obtain the Tolman length in the "critical" regime:

$$\delta \simeq R_g x^{\beta-\nu}. \tag{17}$$

Since $\beta \simeq 0.326$ and $\nu \simeq 0.630$, the Tolman length diverges at the critical point with an amplitude increasing with the degree of polymerization: $\delta \simeq r_0 N^{0.348}|\Delta\hat{T}|^{-0.304}$.

In the polymer regime, when $x \gg 1$, the correlation length of concentration fluctuations becomes the mean-field correlation length $\bar{\xi} \simeq R_g x^{-1/2}$ [17], being infinite at any given $\Delta\hat{T}$ when $N \to \infty$ and $\phi_c = 0$. This is essentially a tricritical mean-field regime (with some fluctuation-induced logarithmic corrections) [26]. The thickness of the interface, which does not

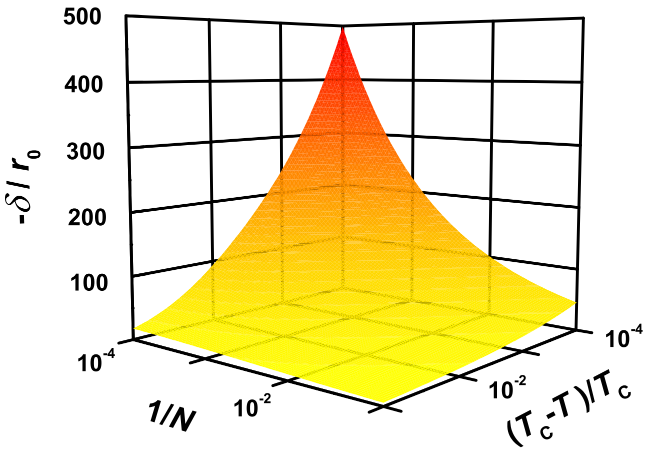

FIG. 3. (Color online) Universal behavior of dimensionless Tolman's length with respect to degree of polymerization and temperature distance to phase separation for a polymer-rich droplet, calculated with Eq. (23).

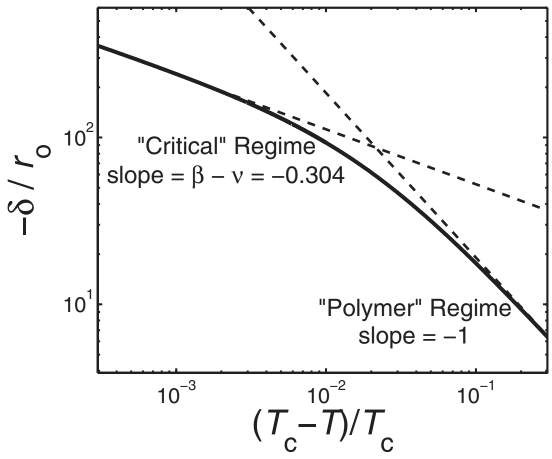

FIG. 4. Dimensionless Tolman's length exhibiting crossover between the critical and polymer regimes for a polymer-rich droplet with $N=10^4$, calculated with Eq. (23).

depend on the degree of polymerization in this regime, is no longer determined by the correlation length of concentration fluctuations. Instead, the other correlation length, associated with the behavior of the infinitely long polymer chain, will determine the thickness of the interface and the interfacial concentration profile. The concentration profile will be extremely asymmetric with the thickness of the interface diverging at the *theta* point [31]. A scaling analysis for the thickness of the interface yields [26,31]

$$\xi \simeq 2r_0|\Delta\hat{T}|^{-1} \simeq \frac{R_g}{x}. \tag{18}$$

In the "polymer" regime, the ratio $\Delta\phi_d/(\phi''-\phi')$ approaches 1/2, as obvious from Fig. 3. Therefore

$$\frac{\delta}{\xi} \simeq -1 \tag{19}$$

and

$$\delta \simeq -\frac{R_g}{x}. \tag{20}$$

In the mean-field approximation for the critical regime $\beta=\nu=1/2$, thus as follows from Eq. (17), the mean-field Tolman length would not depend on temperature ($\delta \simeq -R_g$), while in the polymer regime, which near the *theta* point is proven to be the mean-field tricriticality [17,26], the result remains unchanged: $\delta \simeq -\xi \simeq -2r_0|\Delta\hat{T}|^{-1}$.

III. CROSSOVER BETWEEN THE CRITICAL AND POLYMER REGIMES

Crossover between the critical and polymer regimes for the thickness of the interface and Tolman's length can be approximated with a simple interpolation as

$$\xi \simeq \frac{R_g x^{-\nu}}{(1+x)^{1-\nu}}, \tag{21}$$

$$\frac{\delta}{\xi} \simeq -\frac{x^{\beta}}{(1+x)^{\beta}}, \tag{22}$$

$$\delta \simeq -\frac{R_g x^{\beta-\nu}}{(1+x)^{\beta-\nu+1}}. \tag{23}$$

A more rigorous approach to crossover between the polymer and critical regimes [17] shows that the variable x itself changes from $\sim N^{1/2}|\Delta\hat{T}|$ in the polymer regime to $\sim N^{1/2}|\Delta\hat{T}|^{2\nu}$ in the critical regime. This feature makes crossover expressions implicit. However, this complication does not significantly change the shape of the crossover function from that suggested by the simple interpolations (21)–(23). In the mean-field approximation, where $\nu=1/2$, the crossover variable x remains unchanged for both the critical and polymer regimes.

Figure 3 shows the universal Tolman's length behavior in polymer solutions calculated from crossover expression (23). For $r_0 \simeq 0.25$ nm and $N \simeq 10^4$, the Tolman length at $|\Delta\hat{T}| \simeq 10^{-4}$ reaches the value about -100 nm with the radius of gyration about 25 nm and the thickness of the interface about a micron. Even more remarkably, in the polymer regime, relatively far away from the tricritical phase separation (e.g., about 3 K away from the *theta* temperature, $|\Delta\hat{T}| \simeq 10^{-2}$), the Tolman length for the polystyrene-cyclohexane solution is mesoscopic, being about -50 nm with the thickness of the interface about 100 nm. Hence as follows from Eq. (1), for a polymer-rich droplet with $R \simeq 0.5$ μm the first correction to the interfacial tension in such a solution is expected to be positive and about 20%. Figure 4 illustrates the crossover behavior of Tolman's length between the critical and polymer regimes for $N \simeq 10^4$. The two asymptotic behaviors cross each other at $x \simeq 1$ which reflects the assumption that the characteristic microscopic length scale r_0 represents both the size of the monomer and the range of interactions [30].

IV. CONCLUSIONS

Our study shows that the first curvature correction to the interfacial tension for polymer solutions is significant: the

Tolman length becomes mesoscopic in a broad range of phase separation temperatures, diverging at $N \to \infty$ and $\Delta\hat{T} \to 0$. In particular, in the polymer regime ($N \to \infty$), Tolman's length is predicted to be as large as half of the thickness of the interface. A similar effect is expected in asymmetric polymer blends with a large difference in degree of polymerization.

A more dramatic effect of the divergence of Tolman's length is predicted for two-dimensional phase separation. Since in two dimensions the Ising critical exponents are $\beta = 1/8$ and $\nu = 1$ [32], Tolman's length will diverge very strongly as $\sim |\Delta\hat{T}|^{\beta-\nu} = |\Delta\hat{T}|^{-0.875}$ with an amplitude determined by the level of asymmetry in the two-dimensional phase coexistence.

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