Divergence of Tolman's Length in Polymer Solutions

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For decades the behavior of Tolman's length (a curvature-correction coefficient in the surface tension) has remained one of the most controversial issues in mesoscopic thermodynamics of fluids. It was commonly believed that Tolman's length played no significant role in practice. However, it has been recently shown that Tolman's length strongly diverges at the critical point of fluids; the amplitude of this divergence depends on the degree of asymmetry in fluid phase coexistence. In this paper we consider a curvature dependence of the interfacial tension in polymer solutions. We show that Tolman's length in asymmetric polymer systems may become as large as the thickness of the interface, thus playing a significant role in behavior of micro droplets and flow of polymer fluids in porous media.

INTRODUCTION

Surface tension is the most important physical property for a large number of processes in petroleum and chemical engineering, including nucleation and cluster formation, filtration through porous media, wetting and drying, *etc*. In the Gibbs theory of nucleation, the kinetic barrier is proportional to the third power of the surface tension. 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. A significant curvature-dependence of the surface tension would affect the description of nucleation phenomena and our understanding of the behavior of fluids in microcapillaries or nanopores. The rationale for neglecting the curvature dependence of the surface tension is twofold. First, some theoretical studies on Tolman's length often contradict each other and appear unconvincing. As a result, the curvature-dependence of the surface tension has remained one of the most controversial issues in mesoscopic thermodynamics for decades. Second, the predicted effects obtained by mean-field approaches are commonly believed to be very small, even for nanosized droplets.

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." Tolman's length (δ) is defined as a curvature-correction coefficient in the surface tension (σ) of a liquid or vapor droplet:

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

where R is the droplet radius, taken equal to the radius of the surface of tension, and σ_∞ is the surface tension for the planar interface.

The sign and the value of the correction is a subject of prolonged debate [2-9]. The controversy is even more seen when considering the behavior of Tolman's length for a smooth interface near the critical point. While square-gradient theories gave consistent results in mean-field approximation [6], the actual near-critical behavior of Tolman's length, affected by critical fluctuations, has not been not certain, either in sign or behavior. These studies vary greatly, predicting that at the critical point δ is either finite, logarithmically divergent, or algebraically divergent with different exponents [4-9]. It has been recognized that the difference between the equimolar surface and the surface of tension is phenomenologically associated with asymmetry in fluid phase coexistence [4,6,8]. In symmetric systems, such as the lattice-gas model and the regular-solution model, the difference between the equimolar surface and the surface of tension vanishes; therefore Tolman's length does not exist. Based on scaling arguments, Rowlinson [8] and Fisher and Wortis [9] predicted a very weak algebraic divergence of Tolman's length at the critical point with an exponent –0.065. Since the latter prediction was supported by an exact result obtained for the Widom-Rowlinson "penetrable-sphere model" [10], it became commonly accepted.

More recently, it has been shown that a proper treatment of asymmetry in fluid phase behavior, known as "complete scaling" [11], yields a much stronger algebraic divergence of Tolman's length at the critical point than previously believed, with an exponent –0.304. This is purely a fluctuation-induced effect which does not exist in any mean-field model, and its amplitude depends on the degree of asymmetry in fluid phase behavior. This result suggests that in highly asymmetric fluids and fluid mixtures, this divergence may significantly affect interfacial behavior.

SMOOTH INTERFACE AND TOLMAN'S LENGTH IN POLYMER SOLUTIONS

Smooth interfaces 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, or "thickness" of the interface, assumed to be directly proportional to the correlation length ξ [12]. Such interfaces are mesoscopic, extending from nanometers to microns; however, the droplet size cannot be smaller than the thickness of its interface. Simulation of a smooth interface (by using toolboxes in MATLAB developed in ref. [13]) of a fluid droplet near the critical point is presented in Fig. 1. Specifically, a polymer-rich droplet ($R \approx 200$ nm) in a solution of polystyrene (with a degree of polymerization $N \approx 2 \cdot 10^3$) in cyclohexane, near the critical point of liquid-liquid separation ($T_c \approx 296$K) [14] at $T - T_c \approx 1.3$K, would appear simlar to the image shown in Fig. 1 with the thickness of the interface $2\xi \approx 40$ nm. The surface tension of smooth interfaces is usually very low, vanishing at the critical point; hence the interface undergoes strong fluctuations.

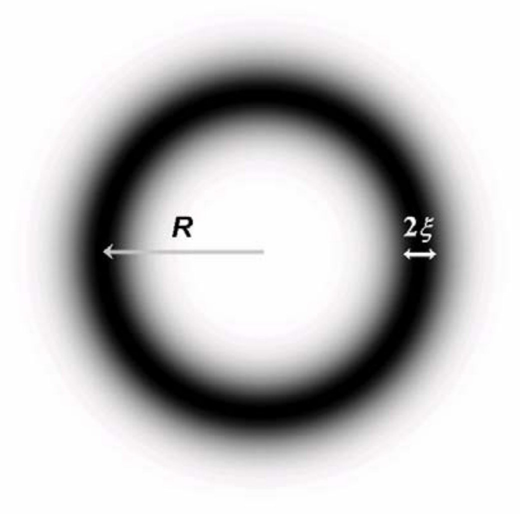

Figure 1. Simulation of a smooth interface for a droplet near the critical point of fluid-fluid separation. Intensity of shadowing indicates the value of the density/concentration gradient in the interfacial profile as predicted by renormalization-group theory [12]. The "thickness" of the interface, given by a characteristic decay-length of the profile, is indicated by 2ξ.

What would be the curvature effect for such an interface? A recent study [15] shows that there are two key elements that determine the correction to the surface tension of a smooth interface. First, there is an intrinsic system-dependent fluid-phase asymmetry caused by specific intermolecular interactions. Second, there is a universal modification of this asymmetry by critical fluctuations. Figure 2 schematically shows a typical asymmetric vapor-liquid phase diagram for fluids. Far away from the critical temperature, the mean of the vapor and liquid densities is represented in first approximation by a rectilinear diameter. However, close to the critical point, the critical fluctuations modify not only the shape of the coexistence boundary, but also the mean of the densities, making it "singular," with its temperature derivative diverging at the critical point [11].

It was suggested in ref. [15] that a ratio of the "excess density" ($\Delta\rho_{\mathrm{d}} = \left(\rho'' + \rho'\right)/2 - \rho_{\mathrm{c}}$) and the difference between the densities of the coexisting phases ($\rho'' - \rho'$) can be related to the ratio of Tolman length (δ) and the thickness of interface (2ξ) as

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

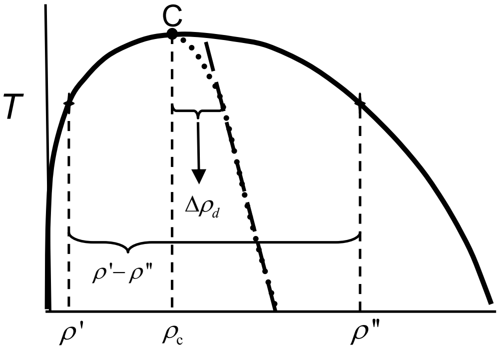

Figure 2. Schematic phase diagram for a fluid with asymmetric vapor-liquid coexistence showing singular diameter (dotted line) and mean-field extrapolation of rectilinear diameter (long dashed line).

Equation (2) unambiguously defines the sign of Tolman's length as negative for liquid droplets and positive for bubbles, provided that the slope of the "diameter" of the coexistence is negative. Since in the mean-field regime the ratio $\left(\rho'' - \rho'\right)/\Delta\rho_{\mathrm{d}}$ and the thickness of the interface depend on temperature near the critical point in the same manner [12], the mean-field Tolman length in simple fluids remains finite and microscopic [6]. However, when modified by fluctuations, the excess density splits into two diverging terms: one associated with a coupling between fluctuations of density and molecular volume and the other with a coupling between density and entropy fluctuations [11]. As follows from refs. [11] and [15],

$$\frac{\Delta\rho_{\mathrm{d}}}{\rho_{\mathrm{c}}} \approx a_{\mathrm{eff}} B_0^2 \left|\Delta\hat{T}\right|^{2\beta} - b_{\mathrm{eff}} \frac{A_0^-}{1-\alpha} \left|\Delta\hat{T}\right|^{1-\alpha} + \ldots, \ \text{(3a)} \quad \frac{\rho'' - \rho'}{2\rho_{\mathrm{c}}} \approx \pm B_0 \left|\Delta\hat{T}\right|^{\beta}, \ \text{(3b)} \quad \xi \approx \xi_0^- \left|\Delta T\right|^{-\nu}, \ \text{(3c)}$$

$$\delta \approx \mp\xi_0^- \left(a_{\mathrm{eff}} B_0 \left|\Delta\hat{T}\right|^{\beta-\nu} - b_{\mathrm{eff}} \frac{A_0^-}{B_0\left(1-\alpha\right)} \left|\Delta\hat{T}\right|^{1-\alpha-\beta-\nu} + \ldots \right). \tag{4}$$

Here, a_{eff} and b_{eff} are "effectife" asymmetry coefficients specific to a particular system [11b], ξ_0^- is the correlation-length amplitude below the critical point, and B_0 and A_0^- are critical amplitudes. The temperature variable is defined as $\Delta\hat{T} \equiv \left(T - T_{\mathrm{c}}\right)/T_{\mathrm{c}}$. The universal critical exponents are $\alpha \approx 0.109$, $\beta \approx 0.326$ and $\nu \approx 0.630$ [11]. The amplitudes of the divergence are system-dependent and may be evaluated from a mean-field equation of state. The second term in Eq. (4) diverges weakly and algebraically as a function of $\Delta\hat{T}$ with an exponent −0.065, a result well known from earlier studies [8,9]. The first term is new and diverges more strongly, with an exponent −0.304; it can be shown to be the only effect of practical significance for polymer solutions. It has not been proven that Eq. (2) is a rigorous thermodynamic relation, although it appears to satisfy both asymptotic scaling and mean-field regimes. However, this new relation provides a practical tool for evaluating Tolman's length from phase-coexistence data, even far beyond the critical region, where Eq. (4) is no longer valid.

A polymer solution is a remarkable example of a highly asymmetric fluid coexistence. A typical phase diagram of a polymer solution is shown in Fig. 3. In the “critical regime where $x \equiv \frac{1}{2} N^{1/2} \left|\Delta\hat{T}\right| << 1$ [16], the coexistence is described by Eq. (3) with the volume fraction ϕ replacing the density ρ and with $B_0 \approx (3/2) N^{\beta/2}$[17]. In the “polymer” regime where $x >> 1$, $\phi \approx (3/2) x$ [16,17]. We adopt a simple interpolation for crossover between these two regimes:

$$\frac{\phi'' - \phi'}{2\phi_{\mathrm{c}}} \approx \frac{3}{2} x^{\beta} \left(1 + x\right)^{1-\beta} . \qquad (5)$$

Equation (2) can be generalized for polymer solutions as

$$\frac{\delta}{2\xi} \approx -\frac{\Delta\phi_d}{\phi'' - \phi'} , \qquad (6)$$

which behaves very differently in “critical” and “polymer” regimes. We will now consider a droplet of polymer-rich phase, with concentration ϕ'', in a solution with concentration ϕ'. Simple scaling arguments suggest that in the “critical” regime, Tolman’s length should diverge when $\Delta\hat{T} \to 0$, in the same manner as in simple fluids but with an *N*-dependent amplitude, whereas in the “polymer” regime, Tolman’s length and the thickness of the interface should not depend on *N*.

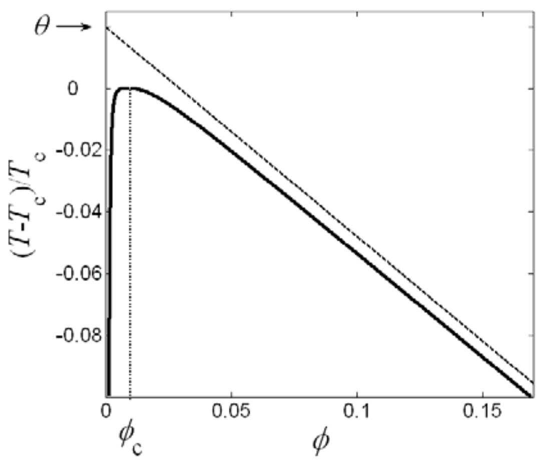

Figure 3. Asymmetric coexistence curve for a polymer solution with a degree of polymerization $N = 10^4$ near the critical point as follows from Flory theory modified by critical fluctuations [17]. The solid line represents the phase separation curve interpolated between the critical regime and theta-point regime by Eq.(7). The dashed line represents the Flory-Huggins phase behavior at an infinite degree of polymerization [16,17].

Consider, first, the critical regime. In this regime, all critical amplitudes depend on the degree of polymerization. The asymmetry coefficient a_{eff}, as evaluated from the Flory-Huggins model by the method developed in ref. [11b], quickly reaches a finite value of 3/5 in the limit $N \to \infty$. Thus, one obtains from Eq. (6) by accounting for the leading term in $\Delta\phi_{\mathrm{d}}$ from Eq. (3a) and using Eq. (3b) for $\phi'' - \phi'$:

$$\frac{\delta}{\xi} \approx -x^{\beta} . \qquad (7)$$

As first shown by de Gennes [18] and confirmed by experiment [14], the correlation length in the critical regime scales with *N* as

$$\xi \approx \xi_0^- \left|\Delta\hat{T}\right|^{-\nu} \approx r_0 N^{(1-\nu)/2} \left|\Delta\hat{T}\right|^{-\nu} \approx R_g \left(N^{1/2} \left|\Delta\hat{T}\right|\right)^{-\nu} = R_g x^{-\nu} , \qquad (8)$$

where $R_g \approx r_0 N^{1/2}$ is the radius of gyration for an ideal (random-walk) polymer chain with r_0 being of the order of monomer size. Therefore, since $\beta \approx 0.326$ and $\nu \approx 0.63$, Tolman’s length in the “critical” regime behaves as

$$\delta \approx -R_g x^{\beta-\nu} \approx -r_0 N^{0.348} \left|\Delta\hat{T}\right|^{-0.304} . \tag{9}$$

In the "polymer" regime, when $x \to \infty$ since $N \to \infty$ at any given $\Delta\hat{T}$, similar arguments [19,20] yield

$$\xi \approx \frac{R_g}{x} \to 2r_0 \left|\Delta\hat{T}\right|^{-1} . \tag{10}$$

In this regime, all properties are independent of the degree of polymerization (since $N \to \infty$) and, as obvious from Fig. 3, the ratio $\Delta\phi_{\mathrm{d}} / \left(\phi'' - \phi'\right)$ approaches 1/2. Therefore,

$$\frac{\delta}{\xi} \approx -1 \tag{11}$$

and

$$\delta \approx -R_g x^{-1} . \tag{12}$$

In the mean-field approximation $\left(\beta = \nu = 1/2\right)$ in the "critical" regime, as follows from Eq. (9), Tolman's length does not depend on temperature $\left(\delta \approx -R_g\right)$, while in the "polymer" regime, which is proven to be mean-field-like [14,19,20], it remains unchanged $\left(\delta \approx -\xi \approx -2r_0 \Delta\hat{T}^{-1}\right)$.

Crossover between the "critical" and "polymer" regimes for the thickness of the interface can be approximated by a simple interpolation as

$$\xi \approx \frac{R_g x^{-\nu}}{\left(1+x\right)^{1-\nu}} , \tag{13}$$

$$\frac{\delta}{\xi} \approx -\frac{x^{\beta}}{\left(1+x\right)^{\beta}} , \tag{14}$$

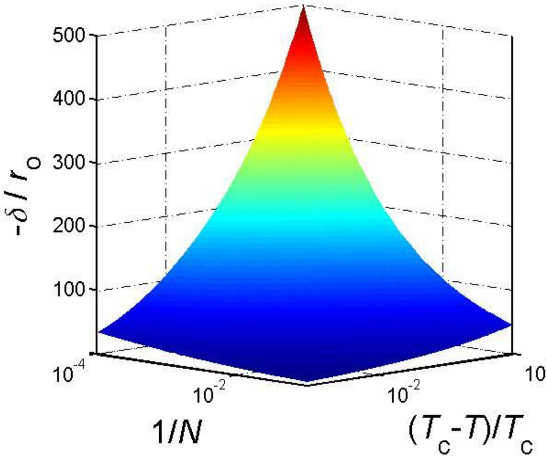

Figure 4. Universal behavior of dimensionless Tolman's length with respect to degree of polymerization and temperature distance to phase separation for a polymer-rich droplet, calculated with Eq. (15).

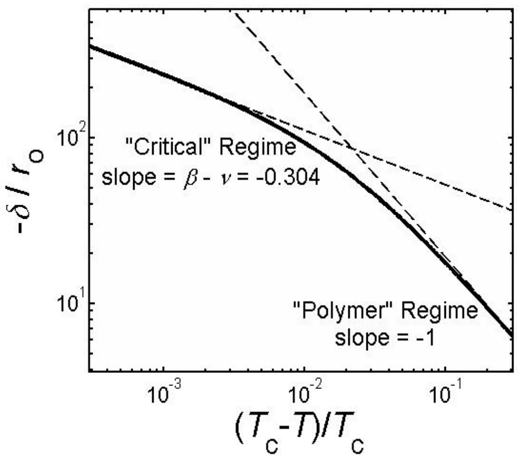

Figure 5. Dimensionless Tolman's length exhibiting crossover between the "critical" and "polymer" regimes for a polymer-rich droplet with $N = 10^4$, calculated with Eq. (15).

$$\delta \approx -\frac{R_g x^{\beta-\nu}}{\left(1+x\right)^{1+\beta-\nu}} . \tag{15}$$

Figure 4 shows the universal Tolman's length behavior predicted for polymer solutions calculated from the crossover expression (15). For $r_0 \approx 0.1$ nm, the Tolman length reaches 50 nm at $\left|\Delta\hat{T}\right| = 10^{-4}$ and $N = 10^4$. Figure 5 illustrates the crossover temperature dependence of Tolman's length between "critical" and "polymer" regimes.

CONCLUSIONS

The curvature effects on the surface tension in polymer solutions are significant: the Tolman length becomes mesoscopic, diverging with $N \to \infty$ 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 degree-of-polymerization ratio.

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