A droplet near the critical point: the divergence of Tolman’s length

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Abstract
Application of “complete scaling” [Kim et al., Phys. Rev. E 67, 061506 (2003); Anisimov and Wang, Phys. Rev. Lett. 97, 25703 (2006)] to the interfacial behavior of fluids shows that Tolman’s length, a curvature correction to the surface tension, diverges at the critical point of fluids much more strongly than is commonly believed. The amplitude of the divergence depends on the degree of asymmetry in fluid phase coexistence. A new universal amplitude ratio, which involves this asymmetry, is introduced. In highly asymmetric fluids and fluid mixtures the Tolman length may become large enough near criticality to be detected in precise experiments with microcapillaries and in simulations.
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For decades the behavior of Tolman’s length has remained one of the most controversial issues in mesoscopic thermodynamics. The Tolman length ($\delta$) is defined as a curvature-correction coefficient in the surface tension ($\sigma$) of a liquid or vapor droplet [1]:

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

where $R$ is the droplet radius, taken equal to the radius of the surface of tension $[2, 3]$, and $\sigma_\infty$ is the surface tension for the planar interface. The physical origin of the curvature correction is a difference between the equimolar surface and the surface of tension; the difference is phenomenologically associated with asymmetry in fluid phase coexistence. 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 and the Tolman length does not exist [3][4]. The curvature dependence of the surface tension is important for the description of nucleation phenomena and fluids in microcapillaries or nanopores. However, while square-gradient theories gave consistent results in mean-field
approximation \[1\] [5] [6], the actual critical behavior of Tolman’s length is not certain, either in sign or in behavior [7] [6]. Fisher and Wortis [4] and Rowlinson [8] have predicted a very weak algebraic divergence at the critical point with an exponent \(-0.065\). Since this prediction is supported by an exact expression [8] obtained for the Widom-Rowlinson ”penetrable-sphere model” [9], it has become commonly accepted.

In this Letter, I show that the application of “complete scaling” [10] [11], which properly describes vapor-liquid asymmetry, to the problem of Tolman’s length yields a much stronger algebraic divergence at the critical point, with an exponent \(-0.304\). The amplitude of this divergence depends on the degree of asymmetry in fluid phase behavior. In highly asymmetric fluids and fluid mixtures this divergence may be strong enough to be detected in accurate experiments and simulations.

The generalized Laplace-Tolman equation reads [2] [3].

\[
P_\alpha - P_\beta = \frac{2\sigma_\infty}{\rho} \left(1 - \frac{2\delta}{R} + \ldots\right) ,
\]

(2)

where \(P_\alpha - P_\beta\) is the difference between the pressure inside the droplet (phase \(\alpha\)) and outside (phase \(\beta\)). The difference \(P_\alpha - P_\beta\) in Eq. (2) can be separated into two parts, namely, a symmetric part, which does not depend on which fluid phase is inside or outside the droplet, and an asymmetric part, i.e.,

\[
(P_\alpha - P_\beta) = (P_\alpha - P_\beta)_\text{sym} + (P_\alpha - P_\beta)_\text{asym} .
\]

Since Tolman’s length is associated with the asymmetric part only, one can conclude that

\[
\frac{2\sigma_\infty}{\rho} \approx \frac{2\delta}{R} \frac{(P_\alpha - P_\beta)_\text{asym}}{(P_\alpha - P_\beta)_\text{sym}} .
\]

(3)

In scaling theory [2] the surface tension in a three-dimensional system can be estimated as a product of the ”critical part” \(\Delta P_{\text{cr}}\) of the grand potential per unit volume \((\Omega/V = -\Delta P)\), which scales as \(\Delta P_{\text{cr}} \sim \xi^{-3}\), and the characteristic ”thickness” of the interface, the correlation length of density fluctuations \(\xi\). The correlation length diverges asymptotically as \(\xi \approx \xi_0 |\Delta T|^{-\nu}\) with the universal critical exponent \(\nu \approx 0.630\) and the amplitude (below the critical point) \(\xi_0\), while the surface tension vanishes at the critical point as \(\sigma_\infty \approx \sigma_0 |\Delta T|^{2\nu} \propto \xi^{-2}\).

Here and below, the circumflex indicates dimensionless variables, such as \(\Delta \hat{T} = (T - T_c)/T_c\), \(\Delta \hat{P} = (P - P_c)/\rho_c k_B T_c\), \(\Delta \hat{\mu} = (\mu - \mu_c)/k_B T_c\), and \(\Delta \hat{\rho} = (\rho - \rho_c)/\rho_c\), with \(k_B\) being Boltzmann’s constant, while the subscript \(c\) indicates the critical value of temperature, pressure, chemical potential, and molecular density, correspondingly.

The function \(\Delta P_{\text{cr}}\) can also be separated into symmetric and asymmetric parts. For a planar interface, \(\sigma_\infty/\Delta P_{\text{cr}} \approx c_\sigma\), where \(c_\sigma \approx 3.79\) is a universal constant. The mean-field value of \(c_\sigma\) is 16/3 [13]. Therefore, \((P_\alpha - P_\beta)_\text{sym} R^2\) scales as \((\Delta P_{\text{cr}})_\text{sym} \xi\) and \((P_\alpha - P_\beta)_\text{asym} R^2\) scales as \((\Delta P_{\text{cr}})_\text{asym} \xi^2\).

Hence, it follows from Eq. (4) that

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where $c_3$ is another universal constant. As shown below, the mean-field value of $c_3$ is $5/6$, while the scaling-theory value is estimated as $\sim 0.6 - 0.7$.

Close to the critical point, $\Delta P_{cr}$ can be approximated as $\Delta P_{cr} \approx \chi (\Delta \mu)^2$, where the derivative $\chi = \frac{\partial \rho}{\partial \mu}$, $T$ is the derivative with respect to density fluctuations, is taken for liquid or vapor phase (depending on which would be considered as $\alpha$-phase) at the corresponding phase boundary. The susceptibility $\chi$ becomes asymptotically symmetric close to the critical point but exhibits growing asymmetry upon departure from the critical point, containing two terms, symmetric $\chi_{sym}$ (equal for both phases) and asymmetric $\chi_{asym}$ (having opposite signs for the different phases). Since $(\Delta P_{cr})_{sym} \approx \chi_{sym} (\Delta \mu)^2$ and $(\Delta P_{cr})_{asym} \approx \chi_{asym} (\Delta \mu)^2$, Eq. (4) becomes

$$\frac{2\delta}{\xi} \approx -c_3 \frac{\chi_{asym}}{\chi_{sym}}, \quad (5)$$

The vapor-liquid asymmetry in fluid criticality is most appropriately treated by so-called "complete scaling", originally introduced by Fisher and Orkoulas [14] and further elaborated by Kim et al. [10] and by Anisimov and Wang [11]. Specifically, it was shown [11] that with an appropriate choice of the critical value of the entropy, $\rho c = \frac{dP}{dT}_{cxc}$, where the subscript cxc means vapor-liquid coexistence, the asymmetry in fluid criticality is governed in first approximation by only two coefficients, $a_3$ and $b_2$, in the linear mixing of three physical fields (pressure, temperature, and chemical potential) into two independent scaling fields, the "ordering" field $h_1$ and the "thermal" field $h_2$ according to

$$h_1 = \Delta \mu + a_3 \left[ \Delta \hat{P} - \left( \frac{d\hat{P}}{dT} \right)_{cxc} \Delta \hat{T} \right], \quad (6)$$

$$h_2 = \Delta \hat{T} + b_2 \Delta \hat{\mu}, \quad (7)$$

where the derivative $\left( \frac{d\hat{P}}{dT} \right)_{cxc}$ is taken at the critical point. The corresponding field-dependent thermodynamic potential $h_3 (h_1, h_2)$ is also a linear combination of the physical fields. In traditional ("incomplete") scaling for fluids, the nontrivial coefficient $a_3$, responsible for the pressure mixing into the ordering field, is assumed to be zero [15, 16].

The total susceptibility $\chi = \chi_{sym} + \chi_{asym}$ is, in general, a combination of three symmetric scaling susceptibilities: strong $\chi_1 = \left( \frac{\partial^2 h_3}{\partial h_1^2} \right)$, weak $\chi_2 = \left( \frac{\partial^2 h_3}{\partial h_2^2} \right)$, and cross $\chi_{12} = \left( \frac{\partial^2 h_3}{\partial h_1 \partial h_2} \right)$ [10, 16]. A detailed derivation of the susceptibility, based on "complete-scaling", has been made by Kim et al. [10]. As a lower-order approximation of the result given in ref. [10], one can
obtain
\[
\hat{\chi} = \left( \frac{\partial \hat{\mu}}{\partial \hat{T}} \right)_{\hat{T}} = \hat{\chi}_{\text{sym}} + \hat{\chi}_{\text{asym}} \\
(1 + a_3)^2 \left( 1 + \frac{3a_3}{1 + a_3} \Delta \rho \right) \chi_1 + b_2^2 \chi_2 + 2(1 + a_3)b_2 \chi_{12}.
\]
(8)

When \(a_3 = 0\) (traditional “incomplete” scaling), Eq. (8) becomes identical to the result obtained in ref. [10].

By using expressions for the scaling susceptibilities along the vapor-liquid coexistence (\(h_1 = 0\)) obtained in refs. [10] [16], one can derive from Eq. (8)
\[
\hat{\chi}_{\text{sym}} \approx \Gamma_0^{-} |\Delta \hat{T}|^{-\gamma} \left( 1 + \Gamma_1^{-} |\Delta \hat{T}|^{\theta} + \ldots \right)
\]
(9)

and
\[
\hat{\chi}_{\text{asym}} \approx \pm \Gamma_0^{-} |\Delta \hat{T}|^{-\gamma} \left[ \frac{3a_3}{1 + a_3} B_0 |\Delta \hat{T}|^{\beta} - 2b_2 \frac{\beta B_0}{\Gamma_0} |\Delta \hat{T}|^{1-\alpha-\beta} + \ldots \right],
\]
(10)

where \(\Gamma_0^{-}\) is the asymptotic critical amplitude of the susceptibility, \(B_0\) is the asymptotic amplitude in the expression \(\Delta \hat{\rho} \approx \pm B_0 |\Delta \hat{T}|^{\beta}\), \(\gamma \approx 1.239\), \(\beta \approx 0.326\), and \(\alpha \approx 0.109\) are universal “Ising” critical exponents; \(\Gamma_1^{-}\) is the first symmetric (“Wegner”) correction amplitude, and \(\theta \approx 0.5\) is the “Wegner” correction exponent; \(\pm\) corresponds to liquid and vapor densities, respectively.

By expanding the ratio \(2\delta / \xi \approx -c_8 (\hat{\chi}_{\text{asym}} / \hat{\chi}_{\text{sym}})\), one obtains
\[
\frac{2\delta}{\xi} \approx \mp c_8 \left( \frac{3a_3}{1 + a_3} B_0 |\Delta \hat{T}|^{\beta} - 2b_2 \frac{\beta B_0}{\Gamma_0} |\Delta \hat{T}|^{1-\alpha-\beta} + \ldots \right) \left( 1 - \Gamma_1^{-} |\Delta \hat{T}|^{\theta} + \ldots \right).
\]
(11)

Hence, Tolman’s length contains two diverging terms, namely,
\[
\delta \approx \mp \xi_0^{-} c_8 \left[ \frac{3a_3}{2(1 + a_3)} B_0 |\Delta \hat{T}|^{\beta - \nu} - b_2 \frac{\beta B_0}{\Gamma_0} |\Delta \hat{T}|^{1-\alpha-\beta-\nu} + \ldots \right],
\]
(12)

where \(\mp\) corresponds to a liquid droplet or a bubble of vapor, respectively.

The behavior of Tolman’s length, given by Eq. (12), differs in an essential way from the results obtained by previous investigators [3] [4] [8]: a new term, \(\propto |\Delta \hat{T}|^{\beta - \nu}\), emerges from the complete-scaling analysis. The first term in Eq. (14) diverges more strongly, since \(\beta - \nu \approx -0.304\), whereas \(1 - \alpha - \beta - \nu \approx -0.065\). In “incomplete scaling”, when \(a_3 = 0\), Tolman’s length diverges very weakly, namely as \(|\Delta \hat{T}|^{1-\alpha-\beta-\nu} = |\Delta \hat{T}|^{-0.065}\) [4] [8]. However, the “incomplete scaling” result may be valid for some specific systems, such as the “penetrable sphere model” [3] [9], since that model has an exact symmetry axis on which the chemical potential is an analytic function of temperature [17].

Equation (12) can be further re-expressed as
\[
\delta \approx \mp c_3 \left[ \frac{3a_3}{2(1 + a_3)} \Delta \rho + cb_2 \frac{\Delta (\bar{\rho} \hat{S})}{\Delta \rho} \right] \xi, 
\]

with use of the universal ratio \( c = \beta B_0^2 / T_0 A_0^2 \approx 1.58 \) [18] and by introducing \( \Delta (\bar{\rho} \hat{S}) = \int (C_V)_{cr} dT / k_B T \approx - \left( A_0 / (1 - \alpha) \right) |\Delta T|^{1-\alpha} - B_{cr} |\Delta T| \), the dimensional entropy (per unit volume) deviation from its critical value; \( A_0^2 \) is the amplitude of the critical (fluctuation-induced) part of the isochoric heat capacity \( (C_V)_{cr} \) in the two-phase region [11]. The higher-order term \( B_{cr} |\Delta T| \), known as the "fluctuation-induced critical background", does not contribute to the divergence of Tolman’s length, since \( 1 - \beta - \nu \approx 0.44 \). However, this term is needed to satisfy crossover to the mean-field regime [11]; moreover its contribution is of lower order than that from the "Wegner" correction \( (\beta + \theta - \nu \approx 0.2) \).

In mean-field approximation, where \( c = 2, \beta = 1/2, \alpha = 0, \) and \( \nu = 1/2, \) Tolman’s length remains finite:

\[
\delta \approx \mp \tilde{\xi}_0 \tilde{c}_3 \left[ \frac{3a_3}{2(1 + a_3)} \tilde{B}_0 - 2b_2 \frac{\Delta \tilde{C}_V}{k_B \tilde{B}_0} \right] = \mp \tilde{\xi}_0 \tilde{c}_3 \left[ \frac{3a_3}{2(1 + a_3)} \left( \frac{6\hat{\mu}_{11}}{\hat{\mu}_{30}} \right)^{1/2} - 2b_2 \frac{3\hat{\mu}_{11}^2}{\hat{\mu}_{30}} \left( \frac{\hat{\mu}_{30}}{6\hat{\mu}_{11}} \right)^{1/2} \right],
\]

where \( \tilde{\xi}_0^- \) is the mean-field amplitude of the correlation length and \( \tilde{c}_3 \) is the mean-field value of the constant \( c_3; \hat{\mu}_{ij} = \partial^{i+j} \hat{\rho} / \partial \hat{\rho}^i \partial \hat{T}^j \) are the derivatives of the dimensionless chemical potential, \( \tilde{B}_0 = (\hat{\mu}_{30} / 6\hat{\mu}_{11})^{1/2} \) is the mean-field amplitude of the density coexistence curve, and \( \Delta \tilde{C}_V / k_B = 3\hat{\mu}_{11}^2 / \hat{\mu}_{30} \) is the mean-field heat-capacity discontinuity [19]. The leading asymmetry coefficients, which are assumed to be unaffected by fluctuations, can also be expressed through the derivatives \( \hat{\mu}_{ij} \) [11] as

\[
\frac{a_3}{1 + a_3} = \frac{2}{3} \frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{1}{5} \frac{\hat{\mu}_{40}}{\hat{\mu}_{30}}, \quad b_2 = \frac{1}{\hat{\mu}_{11}} \left( \frac{\hat{\mu}_{21}}{\hat{\mu}_{11}} - \frac{1}{5} \frac{\hat{\mu}_{40}}{\hat{\mu}_{30}} \right). \]

Substituting Eqs. (15) into Eq. (14), one obtains the compact result

\[
\frac{\delta}{\tilde{\xi}_0^-} = \pm \frac{\tilde{c}_3}{10} \tilde{B}_0 \hat{\mu}_{40} / \hat{\mu}_{30} = \pm \frac{\tilde{c}_3}{10} \left( \frac{6\hat{\mu}_{11}}{\hat{\mu}_{30}} \right)^{1/2} \frac{\hat{\mu}_{40}}{\hat{\mu}_{30}}. \]

By comparing this with the mean-field result of Fisher and Wortis [1] and Giessen et al. [5], namely, \( \delta / \tilde{\xi}_0^- = \pm \tilde{B}_0 \hat{\mu}_{40} / 12 \hat{\mu}_{30} = \pm (6\hat{\mu}_{11} \hat{\mu}_{30})^{1/2} \hat{\mu}_{40} / 12 \hat{\mu}_{30} \), one obtains the mean-field value \( \tilde{c}_3 = 5/6 \). For the (mean-field) van der Waals fluid, where \( a_3 = 1/4, b_2 = 4/45, \hat{\mu}_{21} = 0, \hat{\mu}_{11} = 9/4, \hat{\mu}_{40} = -\hat{\mu}_{30} = -27/8, \) and \( \tilde{B}_0 = 2 \) [11], one obtains \( \delta = \mp \tilde{\xi}_0^- / 6 \). If one adopts \( \tilde{c}_3 = 1, \delta = \mp \tilde{\xi}_0^- / 5 \). Hence, Tolman’s length in the van der Waals fluid is negative for a drop of liquid and
positive for a bubble of vapor, in agreement with the conclusions of Fisher and Wortis [4] and Blokhuis and Kuipers [6]. The same sign is anticipated for real asymmetric fluids when \( a_3 \) is large and positive [11].

It is also interesting that \( \hat{\mu}_{21} \) does not enter in the mean-field result for Tolman’s length, which depends only on one asymmetry amplitude \( \hat{\mu}_{40} \), the fifth-order coefficient in the expansion of the Helmholtz energy per unit volume in powers of density. When \( a_3 = 0 \), Eq. (15) gives \( b_2 = \hat{\mu}_{40}/10\hat{\mu}_{30}\hat{\mu}_{11} \) and the mean-field result for Tolman’s length given by Eq. (16) remains unchanged. However, in the scaling regime this asymmetry term, renormalized by fluctuations, produces two different singularities, namely, \( \propto 1/\Delta T \) and \( \propto \Delta T \). A renormalization-group treatment of the fifth-order term in the initial Hamiltonian, with this fifth-order term regarded as a “non-Ising asymmetry”, produces a new critical exponent \( \theta_5 \cong 1.3 \) [20] and results in a nondivergent contribution to Tolman’s length, \( \propto \Delta T \left| \beta_{\text{non}} \right| \sim \Delta T^{0.7} \) [4]. Actually, the fifth-order term in the initial Hamiltonian also generates a singularity, \( \propto \Delta T^{\beta_{\text{non}} - \nu} \), making a special treatment of “non-Ising asymmetry” practically irrelevant.

In order to obtain an estimate for the universal constant \( c_\delta \) in the scaling regime, one can consider an approximate square-gradient-theory expression for Tolman’s length \( \delta \), namely,

\[
\delta \approx -\frac{\sigma_{\infty}}{(\rho_\alpha - \rho_\beta)^2} \left( \frac{\chi_\alpha - \chi_\beta}{\sigma_\infty} \right). \tag{17}
\]

By calculating the difference of the susceptibilities via Eqs. (9) and (10), and by using \( (\rho_\alpha - \rho_\beta)^2 \approx 4B_0 \Delta T^{\beta_{\text{non}}} \), \( \sigma_{\infty} \approx \sigma_0 \Delta T^{2\nu} \) and the universal ratios \( \sigma_0/k_B T_c \rho_c \xi_0 A_0^{-1} \approx 2.25 \) [13], \( \Gamma_0 A_0^3/B_0^2 \approx 0.21 \) [15], one obtains \( c_\delta \approx 0.47 \). Since in mean-field approximation Eq. (17) gives \( \tau_0 = 2/3 \) instead of the “exact” value \( \tau_0 = 5/6 \) [4, 16] or instead of (also plausible) \( \tau_0 = 1 \), the \( c_\delta \) value must be corrected at least by a factor of 5/4, yielding \( c_\delta \approx 0.6 \) or by 3/2, yielding \( c_\delta \approx 0.7 \).

One can also notice that Tolman’s length can be thermodynamically expressed through the amount of excess adsorption, \( \Gamma_s \), at the surface of tension as \( \delta = \Gamma_s/(\rho_\alpha - \rho_\beta) \) [11, 5]. Assuming that the excess (asymmetric part) density at the surface of tension is associated with the “singular diameter” (the deviation of the mean density from the critical isochore), \( \hat{\rho}_d - 1 \equiv (\rho_\alpha + \rho_\beta)/2\rho_c - 1 \approx a_3/(1 + a_3)(\Delta \hat{\rho})^2 + b_2\Delta \left( \hat{\rho}^\delta \right) \) [11], in such a way that \( \Gamma_s \approx -\xi \rho_c (\hat{\rho}_d - 1) \), one obtains \( \delta \approx -\xi (\hat{\rho}_d - 1)/(\rho_\alpha - \rho_\beta) \). If one adopts \( c_\delta = 2/3 \), this estimate asymptotically agrees with Eq. (13). For the van der Waals fluid such an assumption yields \( \delta/\xi_0 \equiv \mp D/B_0 = \mp 1/5 \), where \( D = (\hat{\rho}_d - 1)/\Delta T = -(3/5)\hat{\mu}_{11}\hat{\mu}_{40}/\hat{\mu}_{30}^2 = 2/5 \) is the mean-field rectilinear
diameter of the coexistence densities \[19\], in agreement with Eq. (16) if $\tau_3 = 1$. The exponent combination $\beta - \nu$, which is responsible for the leading divergence of the Tolman’s length, arises in several contexts in surface thermodynamics \[21\]. In particular, the total adsorption $\Gamma \sim \xi (\rho_\alpha - \rho_\beta)$ diverges at the critical point as $|\Delta \hat{T}|^{\beta - \nu}$. Interestingly, in mean-field approximation, where, formally, $\beta - \nu = 0$, the adsorption, instead of being finite, becomes logarithmically divergent \[2, 21\]. Whether a similar logarithmic divergence may also persist in the mean-field approximation for Tolman’s length in the critical region remains unclear.

A straightforward application of the present results to the problem of Tolman’s length in asymmetric binary fluids can be made by a generalization of ”complete scaling” \[22\] with use of the ”isomorphism principle” \[16\]. In particular, one can use the expression for Tolman’s length given by Eq. (13) for ”incompressible” liquid mixtures replacing $\Delta \hat{\rho}$ by $\Delta \hat{x} = (x - x_c) / x_c$, the deviation of the molar fraction $x$ from its critical value $x_c$.

The divergence of Tolman’s length may be large enough to be detected in well designed accurate experiments with microcapillaries and in simulations. Predictions for Tolman’s length in several fluids exhibiting strong vapor-liquid asymmetry are shown in Fig. 1. In less asymmetric fluids with small-size molecules, such as nitrogen or methane, the coefficient $a_3$ is too small \[11\] to make Tolman’s length growing to a nanoscale in any reasonable proximity to the critical point. However, in highly asymmetric fluids and fluid mixtures, such as high-molecular-weight hydrocarbons and their mixtures with small-molecular-volume species, or in ionic fluids, the Tolman’s length can easily reach a nanoscale. From Eq. (13) with $c_3 = 2/3$, for the liquid mixture n-hexadecane+nitrobenzene, one obtains $-2\delta \simeq 5$ nm at $|\Delta \hat{T}| = 10^{-4}$, while $\xi \approx \xi_0 |\Delta T|^{-0.63} \simeq 60$ nm. For the so-called ”restricted primitive model” (RPM) of a electrolyte, which exhibits a vapor-liquid phase transition in a system of oppositely charged spherical ions of the same size, the Tolman’s length is predicted to be twice as large. The correlation length must be sufficiently smaller than the size of the drop, allowing a thermodynamic approach while retaining the concept of the droplet interface. Therefore, in these systems, for a micron-size drop, which at $|\Delta \hat{T}| = 10^{-4}$ is still much larger than the correlation length/thickness of the interface, the curvature correction to the surface tension is about 1-2%. Faraway from the critical point, Tolman’s length is only a small fraction of the molecular size and, in order to obtain a 1-2% correction to the surface tension, one needs a nanosize drop.

In conclusion, let me emphasize the principal result given by Eq. (13) and presented in Fig. 1. Tolman’s length diverges at the critical point much more strongly than is commonly believed. In fluids exhibiting strong asymmetry of phase coexistence, Tolman’s length may become mesoscopic near criticality, thus noticeably affecting the surface tension of curved interfaces.

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[12] In symmetric systems, along the phase coexistence, \( \Delta \hat{P}_{cr} = \left( \Delta \hat{P}_{cr} \right)_{sym} \approx A_0^{-2} \xi^{-3} \), where \( 2 - \alpha = 3\nu \) and \( A_0^{-2} \) is the asymptotic amplitude of the isochoric heat capacity in the two-phase region.

[13] Universal ratios that involve the surface tension near the critical point are well established and can be represented in various ways. A study of Ising lattices gives \( \sigma_0 / k_B T_c \approx 0.37 \) [S.-Y. Zinn and M. E. Fisher, Physica A 226, 168 (1996)] in agreement with the most reliable experiments on fluids [H. Chaar, M. R. Moldover, and J. W. Schmidt, J. Chem. Phys. 85, 418 (1986)]. Two-scale-factor universality, \( A_0^{2} \xi_0^{3} \approx 0.172 \) with \( A_0^{2} \approx 0.523 A_0^{-} \) and \( \xi_0^{+} \approx 1.96 \xi_0^{-} \) [M. E. Fisher and S.-Y. Zinn, J. Phys. A 418 (1986)], yields \( \sigma_0 / k_B T_c \xi_0^{-} A_0^{-} \approx 2.25 \) and \( \sigma_\infty / (\Delta \hat{P}_{cr})_{sym} \xi \approx \sigma_0 (2 - \alpha) / k_B T_c \xi_0^{-} A_0^{-} = c_\sigma \approx 3.79 \). The corresponding mean-field value is \( 2\sigma_0 / k_B T_c \xi_0^{-} (\Delta C_V / k_B) = 16/3 \), where \( \Delta C_V \) is the mean-field discontinuity of the isochoric heat capacity; see more details in ref. [2].

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The value of $c$ is calculated through the "Ising" universal ratios: $A_0^-/A_0^- \simeq 0.523$, $\Gamma_0^+/\Gamma_0^- \simeq 4.95$, and $\alpha A_0^+ \Gamma_0^+/B_0^2 \simeq 0.0581$ [M. E. Fisher and S.-Y. Zinn, J. Phys. A 31, L629 (1998)].

Fig. 1. Tolman’s length (multiplied by factor of 2), calculated from Eq. (13) with $c_4 = 2/3$, as a function of distance to the critical temperature. The solid curves represent $n$-heptane ($\xi^- \simeq 0.11$ nm, $a_3 \simeq 0.37$, $b_2 \simeq 0.09$, $B_0 \simeq 1.84$, $A_0^- \simeq 22.6$, and $B_{cr} \simeq 18.4$ [11, 23]), $n$-hexadecane+nitrobenzene (C16-NB) ($\xi^- \simeq 0.18$ nm, $a_3 \simeq 0.48$, $b_2 \simeq 0$, and $B_0 \simeq 2.4$, [22, 23]), and the restricted primitive model (RPM) ($\xi^- \simeq 0.18$ nm for the 0.5 nm ion diameter, $a_3 \simeq 0.14$, $b_2 \simeq -0.48$, $B_0 \simeq 3.64$, $A_0^- \simeq 11.6$, and $B_{cr} \simeq 4.9$ [11, 23]). The dotted curve represents the positive contribution to $-2\delta$ for $n$-heptane, diverging as $|\Delta T|^{1-\alpha-\beta-\nu}$, while the dashed curve is the negative contribution, diverging as $|\Delta T|^{\beta-\nu}$. 

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Fig. 1

\[-2\delta (\text{nm})\]

\[\frac{(T_c - T)}{T_c}\]

RPM

C16–NB

n-heptane