Behavior of the Widom Line in Critical Phenomena

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Using linear scaling theory, we study the behavior of response functions extrema in the vicinity of the critical point. We investigate how the speed of convergence of the loci of response function extrema to the Widom line depends on the parameters of the linear scaling theory. We find that when the slope of the coexistence line is near zero, the line of specific heat maxima does not follow the Widom line but instead follows the coexistence line. This has relevance for the detection of liquid-liquid critical points, which can exhibit a near-horizontal coexistence line. Our theoretical predictions are confirmed by computer simulations of a family of spherically symmetric potentials.

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A wide variety of physical systems exhibit critical phenomena [1–4]. According to scaling theory, asymptotically near the critical point all response functions can be expressed in terms of the correlation length [5–7]. The response functions diverge at the critical point and display maxima in the one-phase region either along constant-pressure (P) paths or constant-temperature (T) paths [8–11]. Near the critical point, the loci of response function extrema converge into a single line, the Widom line, which is defined as the line of zero ordering field [12–15]. Thus, the Widom line can be used to locate the critical point. In practice, the Widom line itself is difficult to find, and therefore response function maxima are regularly used to estimate its location. This raises two important questions that are often ignored: (i) to what extent do the loci of response function maxima deviate from the Widom line, and (ii) do all maxima always follow the Widom line?

Theoretical studies and computer simulations predict a liquid-liquid phase transition (LLPT) between a low density liquid (LDL) and a high density liquid (HDL) in several systems, such as water, silicon, and germanium [16–21]. In all these systems the LLPT ends in a liquid-liquid critical point (LLCP) which is deeply buried in a metastable supercooled region, making the traditional experimental way of detecting the LLCP as the terminal point of the coexistence line difficult. Thus, studies of the Widom line in the supercritical region [10] give an alternative way of locating LLCP. For instance, Liu *et al.* used the convergence of the dynamic crossover line into the Widom line to experimentally locate the LLCP in confined water [22].

Because the slope of the LLPT coexistence line in the PT plane is different for each system (can be either positive or negative), the behavior of the Widom line may also differ. To get a complete picture of the critical phenomena near LLCP we study, using linear scaling theory and molecular dynamics simulations, the behavior of the Widom line in terms of the response functions when the slope of the coexistence line is positive, negative, and horizontal.

In the general scaling theory of critical phenomena [6], the field-dependent thermodynamic potential ψ is considered a homogeneous function of two scaling fields: the ordering field h_1 and the thermal field h_2. Near the critical point, ψ can be written as $\psi \simeq |h_2|^{2-\alpha} f(h_1/|h_2|^{\beta+\gamma})$, where f is an analytical scaling function, and α, β, and $\gamma = 2-\alpha-2\beta$ are the critical exponents. Following Refs. [12–15] we assume that for a LLPT the critical exponents have the values of the three-dimensional Ising universality class: $\alpha \approx 0.110$, $\beta \approx 0.3265$, and $\gamma \approx 1.237$. The scaling fields can be written as linear combinations of the physical fields P and T [23]. A similar approach was used by Anisimov *et al.* in order to explain the crossover between vapor-liquid and liquid-liquid critical phenomena in binary fluids [24]. Here we introduce the tuning parameters φ (slope of the coexistence line) and φ' (slope of the ordering field axis), both defined via

$$h_1 = \Delta\hat{P}\cos\varphi - \Delta\hat{T}\sin\varphi,$$
$$h_2 = \Delta\hat{T}\cos\varphi' + \Delta\hat{P}\sin\varphi', \qquad (1)$$

where $\Delta\hat{P} \equiv \hat{P} - \hat{P}_c = (P-P_c)/(\rho_c R T_c)$ and $\Delta\hat{T} \equiv \hat{T} - 1 = (T-T_c)/T_c$, with ρ the number density, R the universal gas constant, and subscript c indicating the values of P, T, and ρ at the critical point. The dimensionless slope of the coexistence line is $d\hat{P}/d\hat{T} = \tan\varphi$. The first order derivatives of the thermodynamic potential ψ are the "ordering parameter" ϕ_1 and "thermal density" ϕ_2,

$$\phi_1 \equiv -\left(\frac{\partial\psi}{\partial h_1}\right)_{h_2}, \qquad \phi_2 \equiv -\left(\frac{\partial\psi}{\partial h_2}\right)_{h_1}. \qquad (2)$$

The second derivatives define three susceptibilities,

$$\chi_1 \equiv \left(\frac{\partial \phi_1}{\partial h_1}\right)_{h_2}, \qquad \chi_2 \equiv \left(\frac{\partial \phi_2}{\partial h_2}\right)_{h_1}$$
$$\chi_{12} \equiv \left(\frac{\partial \phi_1}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \phi_2}{\partial h_1}\right)_{h_2}. \tag{3}$$

If ψ is the scaled Gibbs free energy, then the scaled volume and entropy are $\hat{V} = (\partial\psi/\partial\hat{P})_T$ and $\hat{S} = -(\partial\psi/\partial\hat{T})_P$, respectively. The critical (fluctuation-induced) parts of the dimensionless response functions, isothermal compressibility $\hat{K}_T = -(\partial\hat{V}/\partial\hat{P})_T/\hat{V}$, isobaric specific heat $\hat{C}_P = \hat{T}(\partial\hat{S}/\partial\hat{T})_P$, and isobaric thermal expansion $\hat{\alpha}_P = (\partial\hat{V}/\partial\hat{T})_P/\hat{V}$, can be expressed as the scaling susceptibilities using Eqs. (1), (2), and (3),

$$\hat{K}_T = (\chi_1\cos^2\varphi + \chi_{12}\sin 2\varphi + \chi_2\sin^2\varphi)/\hat{V},$$
$$\hat{C}_P = \hat{T}(\chi_1\sin^2\varphi - \chi_{12}\sin 2\varphi + \chi_2\cos^2\varphi),$$
$$\hat{\alpha}_P = ((\chi_1 - \chi_2)\sin 2\varphi - 2\chi_{12}\cos 2\varphi)/(2\hat{V}). \tag{4}$$

For simplicity we assume here that $\varphi' = \varphi$.

Linear scaling theory, developed by Schofield *et al.* [25,26], presents the scaling fields and susceptibilities as functions of "polar" variables r and $\theta \in [-1, 1]$. Near the critical point, the thermodynamic potential is written as $\psi = r^{2-\alpha}p(\theta)$, where $p(\theta)$ is an analytical function of θ, and the fields are

$$h_1 = ar^{\beta+\gamma}\theta(1-\theta^2), \qquad h_2 = r(1-b^2\theta^2), \tag{5}$$

with $b^2 = (\gamma - 2\beta)/\gamma(1-2\beta) \approx 1.36$. In coordinates r and θ, the Widom line corresponds to $\theta = 0$, and the coexistence line corresponds to $\theta = \pm 1$. According to Refs. [25,26], the ordering parameter for liquid-gas phase transitions and magnetic systems can be approximated by $\phi_1 = kr^\beta\theta$, i.e., a *linear* function of θ. Here, both a and k are system-dependent fitting parameters. The susceptibilities can then be written as

$$\chi_1 = \frac{k}{a}r^{-\gamma}c_1(\theta), \qquad \chi_2 = akr^{-\alpha}c_2(\theta),$$
$$\chi_{12} = kr^{\beta-1}c_{12}(\theta), \tag{6}$$

where $c_1(\theta)$, $c_{12}(\theta)$, $c_2(\theta)$ are rational functions of θ [12–15] which do not have singularities in the interval $[-1, 1]$. Moreover, $c_1(\theta)$ and $c_2(\theta)$ are even functions of θ, while $c_{12}(\theta)$ is an odd function and negative for $\theta > 0$.

Combining Eqs. (1) and Eqs. (5), we find the positions of the maxima of the response functions as functions of $\Delta\hat{T}$ at constant $\Delta\hat{P}$. Clearly these positions do not depend on k, which is a proportionality coefficient of the χ_i. If $\varphi \neq 0$ and $\Delta\hat{P} \to 0$, the leading term in $r(\Delta\hat{P})$ becomes $r = \Delta\hat{P}/[(1-b^2\theta^2)\sin\phi]$ since $\beta + \gamma > 1$. Thus, χ_1 becomes the dominant term in the response functions

$$\hat{K}_T = \cos^2\varphi(\Delta\hat{P})^{-\gamma}f_1(\theta, \Delta\hat{P})/\hat{V}_c,$$
$$\hat{C}_P = \hat{T}_c\sin^2\varphi(\Delta\hat{P})^{-\gamma}f_2(\theta, \Delta\hat{P}),$$
$$\hat{\alpha}_P = \sin\varphi\cos\varphi(\Delta\hat{P})^{-\gamma}f_3(\theta, \Delta\hat{P})/\hat{V}_c, \tag{7}$$

where $\hat{V}_c \approx \hat{T}_c \approx 1$ near the LLCP, and

$$f_i(\theta, \Delta\hat{P}) = ka^{-1}c_1(\theta)[(1-b^2\theta^2)\sin\varphi]^\gamma \times [1 + ad_i(\theta)(\Delta\hat{P})^{\beta+\gamma-1} + o(\Delta\hat{P}^{\beta+\gamma-1})], \tag{8}$$

with $d_i(\theta)$ as odd functions of θ satisfying $d_i(0) = 0$ and $0 < d_1'(0) < d_3'(0) < d_2'(0)$. Since $c_1(\theta)$ is an even function of θ, the loci of the maxima of all response functions coincide for $\Delta\hat{P} \to 0$ along the Widom line ($\theta = 0$), which projects onto a PT plane as a line emanating from the critical point with a slope $\tan\varphi$ (Fig. 1). The larger

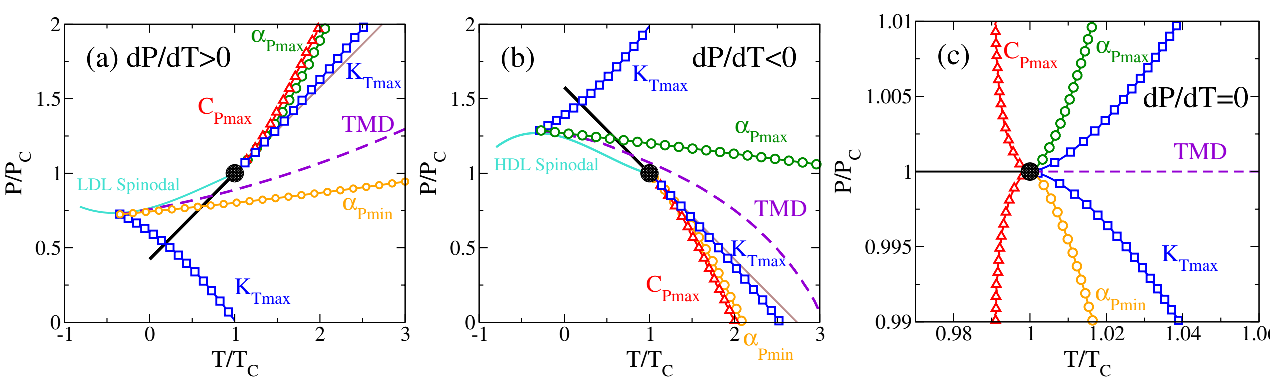

FIG. 1 (color online). The behavior of the Widom line in systems with different coexistence line slopes according to linear scaling theory. (a) Positively sloped coexistence line; C_P (upper triangle), α_P (opened circle), and K_T (square) maxima loci converge into the Widom line close to the LLCP. (b) Negatively sloped coexistence line; similar to the mirror image of (a). (c) Horizontal coexistence line; symmetric loci of C_P, $|\alpha_P|$, and K_T maxima above and below P_c, all approach the LLCP horizontally, with the C_P maximum line from $T < T_c$ and the other two from $T > T_c$. Graphs are constructed from numerical solutions of linear scaling theory, taking $\varphi' = \varphi$ for simplicity, and with $\phi = 30°$, $-30°$, and 0, respectively. The spinodals are drawn as interpolation between the critical point and the extrapolated crossing point of the TMD ($\alpha_P = 0$) line and the K_T maxima line beyond the coexistence line where the spinodal must be horizontal. The Widom line is indicated with a thin brown line in (a) and (b), and overlaps with the TMD line in (c).

the value of a, the faster the deviation of these loci from the Widom line as $\Delta\hat{P}$ increases. Since $d_1'(0) < d_3'(0) < d_2'(0)$, the deviation of the locus for $\hat{C}_P$ is greater than the deviation for $\hat{\alpha}_P$, which is greater than the deviation of $\hat{K}_T$. The latter follows the Widom line for the longest range (Fig. 1).

In contrast, if $\varphi = 0$, then $r = (\Delta\hat{P}/[a\theta(1-\theta^2)])^{1/(\beta+\gamma)}$ and

$$\hat{K}_T = \frac{k}{a}\frac{1}{\hat{V}}\left(\frac{a\theta(1-\theta^2)}{\Delta\hat{P}}\right)^{\gamma/(\beta+\gamma)} c_1(\theta),$$
$$\hat{C}_P = \hat{T}ka\left(\frac{a\theta(1-\theta^2)}{\Delta\hat{P}}\right)^{\alpha/(\beta+\gamma)} c_2(\theta),$$
$$\hat{\alpha}_P = -k\frac{1}{\hat{V}}\left(\frac{a\theta(1-\theta^2)}{\Delta\hat{P}}\right)^{(1-\beta)/(\beta+\gamma)} c_{12}(\theta). \tag{9}$$

The $\hat{K}_T$, $\hat{\alpha}_P$, and $\hat{C}_P$ given by Eq. (9) are functions of θ that have maxima at $\theta_1 = \pm 0.525638$, $\theta_{12} = \pm 0.746766$, and $\theta_2 = \pm 0.925073$, respectively. Note that for $\varphi = 0$, $\Delta\hat{T}$ coincides with h_2; thus,

$$\Delta\hat{T} = \left(\frac{\Delta\hat{P}}{a\theta_i(1-\theta_i^2)}\right)^{1/(\beta+\gamma)} (1 - b^2\theta_i^2) \tag{10}$$

gives the equation of the loci of K_T, C_P, and α_P, for each θ_i [Fig. 1(c)]. These loci have two symmetric branches for $\Delta\hat{P} > 0$, $\theta_i > 0$ and $\Delta\hat{P} < 0$, $\theta_i < 0$. Since $c_{12}(\theta)$ is an odd function, $\hat{\alpha}_P < 0$ for $\Delta\hat{P} < 0$; therefore, the lower branch of the $\hat{\alpha}_P$ extrema is a line of $\hat{\alpha}_P$ minima, which lies entirely in the density anomaly region. Since $1/(\beta+\gamma) < 1$, all the loci are tangential to the Widom or coexistence line at the LLCP. Since $0 < |\theta_1| < |\theta_{12}| < 1/b < |\theta_2| < 1$ and $\theta = 1/b$ corresponds to the line $\Delta\hat{T} = 0$, the loci of the $\hat{K}_T$ and $\hat{\alpha}_P$ extrema emanate from the critical point in the direction $\Delta\hat{T} > 0$, but the $\hat{\alpha}_P$ extrema line deviates from the Widom line much faster than the $\hat{K}_T$ maxima line. In contrast, the $\hat{C}_P$ maxima line emanates in the direction $\Delta\hat{T} < 0$, i.e., along the coexistence line. Therefore, the heat capacity maximum will be difficult to observe for small φ in the supercritical region $T > T_c$, and for $\varphi = 0$ it will be buried below T_c.

Figure 1 shows the behavior of the loci of extrema of response functions computed using Eqs. (4) and (6). It is in perfect agreement with the asymptotic behavior described by Eq. (7) for $\varphi \neq 0$ and Eq. (9) for $\varphi = 0$. When the slope of the coexistence line is nonzero [Figs. 1(a) and 1(b)], there is only one locus of C_P maxima, two loci of α_P extrema (separated by a temperature of maximal density (TMD) line where $\alpha_P = 0$), and two loci of K_T maxima. When $dP/dT > 0$ [Fig. 1(a)], the locus of C_P maxima, α_P maxima, and the locus corresponding to the largest values of K_T all originate from the LLCP and extend into the one-phase region as a continuation of the coexistence line. Close to the LLCP, these response function maxima converge to a single Widom line, but separate as the pressure is increased above the critical value. This happens such that the locus of C_P maxima has the lowest temperature, the locus of K_T maxima has the highest temperature, and the locus of α_P maxima lies between the two.

When $dP/dT < 0$ [Fig. 1(b)], the situation mirrors the case $dP/dT > 0$, but with the locus of α_P maxima replaced by the locus of α_P minima. The other locus of α_P extrema and the K_T maxima of smaller magnitude both approach the limits of liquid stability (spinodals): the LDL spinodal for $dP/dT > 0$ and the HDL spinodal for $dP/dT < 0$.

When the coexistence line is horizontal [Fig. 1(c)], we must zoom in to find the C_P maxima. We see two symmetric C_P maxima lines emerge, but near the LLCP they bend below the critical temperature T_c and approach the LLCP horizontally from $T < T_c$. Both loci of α_P extrema and the two loci of K_T maxima are symmetric with respect to $P = P_c$, have equal magnitude, correspond to the critical fluctuations, and approach the LLCP horizontally from $T > T_c$. Thus, in the case of a coexistence line with zero slope, the three response function maxima do not converge upon approaching the LLCP.

Using molecular dynamics simulations, we test our results on a family of Jagla potentials with repulsive and attractive ramps [27–31] that show a LLPT. In this model, particles interact with a spherically symmetrical pair potential given by

$$U(r) = \begin{cases} \infty & r < a \\ \frac{b-r}{b-a}(U_R + U_0) - U_0 & a \le r < b \\ -\frac{c-r}{c-b}U_0 & b \le r < c \\ 0 & r \ge c \end{cases}, \tag{11}$$

where a is the hard-core distance, b the soft-core distance, and c the long-distance cutoff. The potential has a minimum $-U_0$ at $r = b$. At the top of the repulsive ramp, at $r = a$, the potential is U_R. By tuning the parameters of the model, one can change the slope of the liquid-liquid coexistence line [30]. The slope is positive for $b = 1.72a$, $c = 3a$, $U_R = 3.478U_0$, and zero for $b = 1.59a$, $c = 2.59a$, $U_R = 2.547U_0$. If $b/a < 1.59$ the LLCP disappears below the line of homogeneous nucleation, and the slope of the LLPT can no longer be measured [30].

When the slope of the coexistence line is positive, the simulation results match the linear scaling theory (Fig. 2). When the coexistence line is horizontal, both K_T maxima lines are observed and the α_P extrema lines are approximately vertical. C_P increases until the system either crystallizes or enters a glassy state, so no C_P maximum is observed in the liquid phase. Note that a third locus of K_T' maxima (K_T as a function of P at constant T) becomes

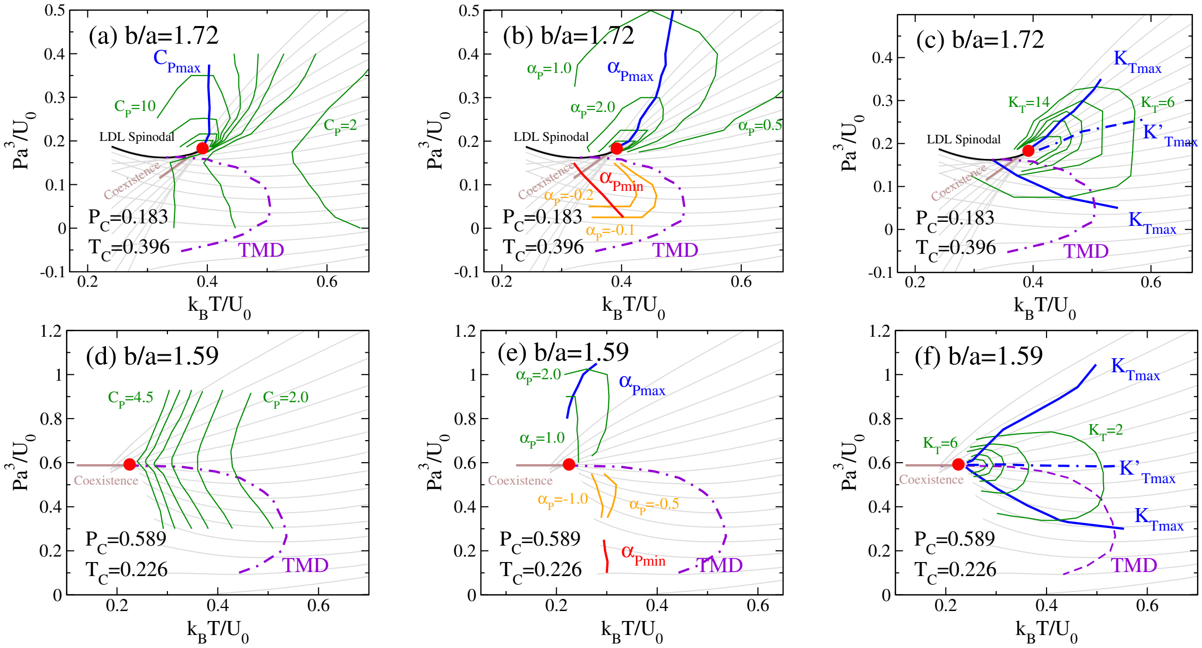

FIG. 2 (color online). Phase diagram with C_P, α_P, and K_T from molecular dynamics simulations of the Jagla potential, with (a),(b), (c) the positively sloped coexistence line case, and (d),(e),(f) the horizontal coexistence line case. Isochores (solid gray), TMD line (dashed purple), and LLCP (solid circle) are shown. The loci of the response function maxima cross the lines for a constant value of the corresponding response function at the extreme points of pressure. In the vicinity of the LLCP, all three loci merge into a single line—the Widom line. The loci of α_P minima and loci of K_T maxima converge at the minimum of the LDL spinodal. For $b/a = 1.59$, there is no $C_{P,\max}$ observed in the equilibrium region. Both $K_{T,\max}$ are symmetric, but the third locus of K'_T maxima (the K_T maximum as function of P at constant T) peaks at P_c for all $T > T_c$.

approximately horizontal, showing maxima near P_c for all $T > T_c$ [Fig. 2(f)]. In linear scaling theory, this third locus K'_T corresponds to $\theta = 0$.

In summary, we find that linear scaling theory not only predicts that the loci of response function extrema converge into the Widom line, but it also quantifies how far these extrema deviate from the true Widom line as we move away from the critical point. For a given class of universality, there are only two system-dependent parameters in the linear scaling theory: a and k. The k parameter does not affect the location of the extrema, but the a parameter does. The larger the value of a, the faster the deviation from the Widom line as $\hat{P} - \hat{P}_c$ increases [see Eq. (8)]. From the three response functions considered, the compressibility K_T deviates the least and the isobaric specific heat C_P deviates the most. This deviant behavior of C_P is exaggerated when the slope of the coexistence line is small and, in the extreme case of $\varphi = 0$, the locus of the C_P maxima leaves the Widom line altogether and follows the coexistence line [Fig. 1(c)]. Thus when the coexistence line is approximately horizontal we can no longer identify the Widom line by tracing the C_P maxima [32]. Studies of C_P maxima or α_P extrema are best reserved for systems in which the slope of the coexistence line is strongly positive or negative. However, the response function maxima in terms of volume fluctuations are still well defined; thus, the loci of K_T maxima can still be used to identify the Widom line. We expect that these results remain valid in the limit $T_c \to 0$ known as the singularity free scenario. In this case, the slope of the Widom line can be found by studying the K_T maxima as a function of pressure at constant temperature, and we do not expect to find C_P maxima above the glass transition.

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