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.

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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 h1 and the thermal field h2. Near the critical point, ψ can be written as $ψ ≈ [h_2]^{\alpha−\beta} f(h_1/h_2)^{\gamma}$, where f is an analytical scaling function, and α, β, and γ = 2 − α − 2β 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: $α ≈ 0.110$, $β ≈ 0.3265$, and $γ ≈ 1.237$. 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 q (slope of the coexistence line) and $q'$ (slope of the ordering field axis), both defined via

$$h_1 = \Delta P \cos q - \Delta T \sin q,$$

$$h_2 = \Delta T \cos q' + \Delta P \sin q',$$

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

$$φ_1 \equiv -\left(\frac{∂ψ}{∂h_1}\right)_{h_2}, \quad φ_2 \equiv -\left(\frac{∂ψ}{∂h_2}\right)_{h_1}. \quad (2)$$

The second derivatives define three susceptibilities,
The critical (fluctuation-induced) parts of the dimensionless response functions, isothermal compressibility $\hat{K}_T = (\partial V/\partial P)_T/\hat{V}$, isobaric specific heat $\hat{C}_P = \hat{T}(\partial S/\partial T)_p$, and isobaric thermal expansion $\hat{\alpha}_P = (\partial V/\partial T)_p/\hat{V}$, can be expressed as the scaling susceptibilities using Eqs. (1), (2), and (3),

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

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 $\psi = r^2 - p(\theta)$, where $p(\theta)$ is an analytical function of $\theta$, and the fields are

$$h_1 = ar^{b+1}(1-\theta^2), \quad h_2 = r(1-b^2\theta^2),$$

with $b^2 = (r-2)/(r(1-2\theta)) \approx 1.36$. In coordinates $r$ and $\theta$, 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 $\phi_1 = kr^\theta$, i.e., a linear function of $\theta$. Here, both $a$ and $k$ are system-dependent fitting parameters. The susceptibilities can then be written as

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

where $c_1(\theta)$, $c_{12}(\theta)$, $c_{2}(\theta)$ are rational functions of $\theta$ [12-15] which do not have singularities in the interval $[-1, 1]$. Moreover, $c_1(\theta)$ and $c_2(\theta)$ are even functions of $\theta$, 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 $\Delta T$ at constant $\Delta \hat{P}$. Clearly these positions do not depend on $k$, which is a proportionality coefficient of the $\chi_i$. If $q \neq 0$ 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, $\chi_1$ becomes the dominant term in the response functions

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

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

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

with $d_i(\theta)$ as odd functions of $\theta$ satisfying $d_i(0) = 0$ and $0 < d_i'(0) < d_i'(0) < d_i'(0)$. Since $c_1(\theta)$ is an even function of $\theta$, 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
the value of $a$, the faster the deviation of these loci from the Widom line as $\Delta \dot{P}$ increases. Since $d_1'(0) < d_2'(0) < d_4'(0)$, the deviation of the locus for $C_P$ 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 $r = (\Delta \dot{P}/[a \theta (1 - \theta^2)])^{1/(\beta + \gamma)}$ and

$$
\hat{K}_T = \frac{k}{a V} \left( \frac{a \theta (1 - \theta^2)}{\Delta \dot{P}} \right)^{\gamma/(\beta + \gamma)} c_1(\theta),
$$

$$
\hat{C}_P = \frac{\hat{T} k a}{a \theta (1 - \theta^2)} \left( \frac{a \theta (1 - \theta^2)}{\Delta \dot{P}} \right)^{\alpha/(\beta + \gamma)} c_2(\theta),
$$

$$
\hat{\alpha}_P = -k \frac{1}{V} \left( \frac{a \theta (1 - \theta^2)}{\Delta \dot{P}} \right)^{(1-\beta)/(\beta + \gamma)} c_{12}(\theta). \quad (9)
$$

The $\hat{K}_T$, $\hat{\alpha}_P$, and $\hat{C}_P$ given by Eq. (9) are functions of $\theta$ 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,

$$
\Delta \hat{T} = \left( \frac{\Delta \dot{P}}{a \theta_1 (1 - \theta_1^2)} \right)^{1/(\beta + \gamma)} (1 - b^2 \theta_1^2) \quad (10)
$$

gives the equation of the loci of $\dot{K}_T$, $\dot{C}_P$, and $\dot{\alpha}_P$, for each $\theta_i$ [Fig. 1(c)]. These loci have two symmetric branches for $\Delta \dot{P} > 0$, $\theta_i > 0$ and $\Delta \dot{P} < 0$, $\theta_i < 0$. Since $c_{12}(\theta)$ is an odd function, $\hat{\alpha}_P < 0$ for $\Delta \dot{P} < 0$; therefore, the lower branch of the $\hat{\alpha}_P$ extrema is a line of $\alpha_P$ 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 $\hat{C}_P$ 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 $\varphi$ 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 $\alpha_P$ 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, $\alpha_P$ 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 $\alpha_P$ 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 $\alpha_P$ maxima replaced by the locus of $\alpha_P$ minima. The other locus of $\alpha_P$ extrema and the $K_T$ maxima of smaller magnitude both approach the limits of liquid stability (spindaloids): 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 $\alpha_P$ 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

$$
U(r) = \begin{cases} 
\infty & r < a \\
\frac{b-r}{b-a} (U_R + U_0) - U_0 & a \leq r < b \\
-\frac{c-r}{c-a} U_0 & b \leq r < c \\
0 & r \geq c
\end{cases} \quad (11)
$$

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 $\alpha_P$ 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 (as $K_T$ as a function of $P$ at constant $T$) becomes
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 \( \dot{P} - \dot{P}_c \) 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 \( C_p \) 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 \( \alpha_p \) 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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