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Thermodynamic geometry, phase transitions, and the Widom line

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A microscopic characterization, based on the thermodynamic curvature R, is proposed for first-order liquid-gas phase transitions. Near the critical point, where R is proportional to the correlation volume ξ^3, we propose that R takes the same value in the coexisting phases. This proposal allows a determination of the liquid-gas coexistence curve with no use of the problematic Maxwell equal area construction. Furthermore, $|R| \sim \xi^3$ allows a direct determination of the Widom line in the supercritical regime. We illustrate with input from the van der Waals model and the National Institute of Standards and Technology Chemistry WebBook.

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Macroscopic properties of matter undergo discontinuous changes across a first-order liquid-gas coexistence curve that culminates in a second-order critical point [1]. This curve is extendable into the supercritical region as the Widom line [2–4], which serves as a line of sharp crossover for dynamical fluid properties and is characterized by the locus of points with maximum correlation length ξ. Historically, liquid-gas coexistence curves were modeled by the van der Waals (vdW) equation augmented by the Maxwell "equal area" construction. This approach lies at the foundation of the modern thermodynamic picture characterizing coexisting phases through equal molar Gibbs free energies. However, the vdW-Maxwell theory suffers from several unresolved conceptual drawbacks [5,6]. Here, inspired by the microscopic approach of Widom, we devise a novel construction to characterize liquid-gas phase transitions based on the continuity of ξ between the phases, with the Riemannian geometric thermodynamic scalar curvature $|R| \sim \xi^3$ [7]. The idea that the correlation lengths of the coexisting phases are equal, and its computational realization through $|R|$, provides a method for predicting the phase coexistence curve when used in conjunction with any equation of state or experimental data. Further, our method allows an analytic prediction of the Widom line from the condition that it represents a locus of maximum correlation length without recourse to any ad hoc response function. We illustrate this issue here with the vdW equation. We also determine the location of the Widom line for several fluids, both with the vdW equation and with data from the National Institute of Standards and Technology (NIST) Chemistry WebBook [8].

The key physical idea in our coexistence curve analysis originates from Widom's microscopic perspective of phase transitions [9]. In this framework, spontaneous density fluctuations cause the local density $\rho(\vec{r})$ in a single phase fluid to deviate from the overall mean density ρ_0 in some complex, time-dependent manner. Mathematically, $\rho(\vec{r}) = \rho_0$ corresponds to an intricate contour surface that separates two sides with local mean densities $\rho > \rho_0$ and $\rho < \rho_0$. A straight line through the fluid intersects this surface at points spaced an average distance ξ apart. ξ is generally small in a disorganized system like an ideal gas, but diverges at the critical point for real fluids. When a single-phase fluid is very near a first-order phase transition, a small amount of a second, minority phase will begin to form. A reference point in this single phase fluid typically has local density close to that of either of the two incipient coexisting phases. The typical density difference $|\Delta\rho|$ across the contour surface $\rho(\vec{r}) = \rho_0$ thus equals that of the two phases. Reversing the role of the majority and minority phases leaves this argument unchanged, with the same $|\Delta\rho|$. ξ in the single phase plays a similar role in anticipating the properties in the two phases since ξ is the thickness of the interface between the two phases [9]. This anticipated interface thickness must be the same approaching the phase transition, with either of the two phases being the majority phase, and the correlation length ξ should thus be the same in the two coexisting phases, the condition at the heart of our approach.

Our approach is a means of accommodating phase coexistence (and hence density inhomogeneity) into the mean-field vdW equation of state, which otherwise models fluids with spatially uniform density. Of course this is only an approximation. Issues like capillary waves, curvature of the interface, etc., are not factoring in. Our focus here is to exploit the geometric invariant R to obtain phase coexistence.

For experimental predictability, we need an estimate of ξ, allowing a thermodynamic expression for the equality of the correlation lengths at the interface. This can be realized using the Riemannian geometry of the equilibrium thermodynamic state space of the system with metric elements:

$$g_{\alpha\beta} = -\frac{1}{k_B}\frac{\partial^2 s}{\partial a^\alpha \partial a^\beta}. \tag{1}$$

Here (α, β = 1, 2), k_B is Boltzmann's constant, and $s = s(a^1,a^2)$, a^1, and a^2 denote the entropy, energy, and particle number, respectively, each per unit volume [7]. Let (a^1,a^2) specify the state of an open subsystem of an infinite environment. The probability of fluctuations Δa^α of this state away from the equilibrium state corresponding to maximum entropy is given by Einstein's famous formula: probability $\propto \exp[-V(\Delta\ell)^2/2]$. Here, $(\Delta\ell)^2 = g_{\alpha\beta}\Delta a^\alpha \Delta a^\beta$ denotes the invariant, positive-definite thermodynamic entropy metric [7], where the $g_{\alpha\beta}$'s are evaluated in the equilibrium state. The

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thermodynamic Riemannian curvature scalar $R = R(a^1,a^2)$ of this metric is an invariant scalar quantity independent of what coordinates we calculate in. For a diagonal metric, R is given by the simple expression $[g \equiv \det(g_{\alpha\beta})]$

$$R = \frac{1}{\sqrt{g}}\left[\frac{\partial}{\partial a^1}\left(\frac{1}{\sqrt{g}}\frac{\partial g_{22}}{\partial a^1}\right) + \frac{\partial}{\partial a^2}\left(\frac{1}{\sqrt{g}}\frac{\partial g_{11}}{\partial a^2}\right)\right], \qquad (2)$$

with a more complicated but standard expression for nondiagonal metrics, which we omit here for brevity. For the ideal gas $R = 0$, and near the critical point $|R| \sim \xi^3$, the desired connection between R and ξ [7]. Experimental predictions for the coexistence curves of first-order phase transitions can thus be obtained from the equality of $|R|$ calculated in the two coexisting phases. We call this the R-crossing method. In the supercritical region beyond the critical point, the locus of the maximum of $|R|$, via $|R| \sim \xi^3$, provides a direct theoretical prediction for the Widom line. As mentioned, R is a scalar, i.e, a geometric invariant, and hence our method is independent of transformations of the coordinates (a^1,a^2) that characterize the manifold of equilibrium thermodynamic states.

As a direct test of our proposal, we calculate R for hydrogen in both phases using the NIST Chemistry WebBook [8,10] and its program REFPROP. These provide data based on phenomenological equations of state, with fit parameters determined by matching to experimental fluid data. Results are shown in Fig. 1, where agreement between the R's in the two phases is better than 1% in the range $0.96 < T/T_c < 1$. Here, T_c is the critical temperature. By contrast, at $T/T_c = 0.96$, the molar densities of the coexisting liquid and gas phases differ from each other by a factor of ~3. To be sure, it would be premature to ascribe undue significance to this finding, since the fitting formulas in the NIST Chemistry WebBook do not contain the scaled equations of state appropriate to critical phenomena. However, the NIST Chemistry WebBook certainly offers a necessary first place to look, and results are encouraging.

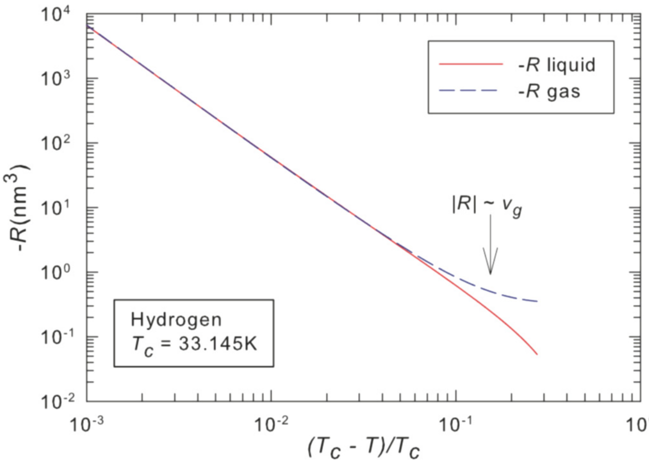

FIG. 1. (Color online) $-R$ for the coexisting liquid and gas phases vs $(T_c - T)/T_c$ for normal hydrogen calculated with the NIST Chemistry WebBook. We see strong agreement between the values of R in the liquid and gas phases. The arrow indicates the temperature where $|R| \sim v_g$, with v_g the molecular volume in the gas phase. Below this value of $|R|$, its interpretation as the correlation length loses significance.

Figure 1 shows superior agreement between the coexisting liquid and gas R's in the asymptotic critical region than Widom's qualitative argument might lead one to suspect. This very close agreement originates from a commensurate R theorem, with proof based on the Rehr-Mermin asymptotic scaling description of fluid criticality [11], which specifically incorporates asymmetry between the phases. Here, the pressure is written as

$$P(T,\mu) = P_0(T,\mu) + |\tau|^{2-\alpha}\, Y_\pm\left(\frac{\zeta}{|\tau|^{\beta\delta}}\right), \qquad (3)$$

where μ is the chemical potential, with critical point value μ_c, $\tau \equiv T - T_c + c_1(\mu - \mu_c)$, $\zeta \equiv \mu - \mu_c + c_2(T - T_c)$, c_1 and c_2 are two constants, $P_0(T,\mu)$ is the regular part of the pressure, the term containing the function $Y_\pm$ is the singular part of the pressure, and α, β, and δ are critical exponents. $Y_\pm$ is assumed to be symmetric in its argument, and has two branches ($\pm$) depending on the sign of τ [11]. These branches join smoothly along the curve $\tau = 0$, except at the critical point $\{\tau,\zeta\} = \{0,0\}$. We take $Y_+'(0) = 0$, but $Y_-'(0_+) = -Y_-'(0_-) \neq 0$, modeling a first-order phase transition at $\zeta = 0$, and distinct phases depending on whether ζ goes to zero from a positive value or a negative value. If $\alpha > 0$ and $c_1 c_2 < 1$, which translates into the coexistence curve not being too asymmetric, a straightforward calculation shows that the value of R is the same in the coexisting phases, $R_-(\tau,0_-) = R_-(\tau,0_+)$. For a detailed proof, see Ref. [12].

Our proof assumes that along the coexistence curve $\mu = \mu(T)$ is analytic as we approach the critical point. However, this assumption has been questioned in the context of the Yang-Yang anomaly where the second derivative $\mu''(T)$ diverges at the critical point. There is some experimental basis for this possibility [13], which, if correct, would require a revision of our proof, and possibly our theorem. We add that Evans *et al.* [14] showed with density functional theory and a short range intermolecular fluid potential that the character of the density decay (including the correlation length) at the interface matches that in the bulk, lending further support to the Widom argument.

Our R-crossing method complements the canonical macroscopic rule for first-order phase transitions, namely, the equality of the molar Gibb's free energies $\mathcal{G}$ of the coexisting phases [1]. Applied to the vdW equation, however, there are unresolved conceptual issues in the realization of this macroscopic rule. Finding states with equal $\mathcal{G}$'s involves contentious issues of integration along a reversible path through a thermodynamically unstable region in the Maxwell construction, or through the critical point in Kahl's approach [15]. Such conceptual difficulties are bypassed in our construction.

As a simple theoretical example, we apply the R-crossing method to the universal vdW equation in its reduced form,

$$p_r = \frac{8t_r}{3v_r - 1} - \frac{3}{v_r^2}, \qquad (4)$$

where $p_r = P/P_c$, $t_r = T/T_c$, $v_r = v/v_c$, and P and v are the pressure and molar volume, with the subscript c denoting their critical values. The critical quantities are known to be related to the vdW constants a and b by $P_c = a/(27b^2)$, $T_c = 8a/(27k_B b)$, and $v_c = 3b$. The Maxwell equal-area construction yields the limiting slope of the coexistence curve $dp_r/dt_r = 4$, independent of the fluid and its heat capacity.

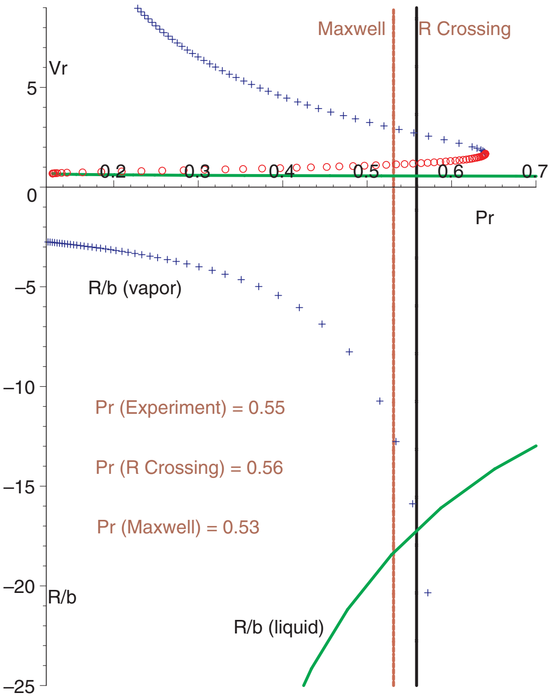

FIG. 2. (Color online) R/b vs p_r along an isotherm of Helium with $t_r = 0.86$ in the lower half, and v_r vs p_r along the same t_r in the upper half. The blue curve marked with crosses, and the solid green curve represents the two stable branches, while the red curve marked with open circles is the unstable branch. The black vertical line to the right, labeled "R-crossing" denotes the p_r where the R's of the liquid and gas phases become equal. The orange vertical line to the left, labeled "Maxwell," represents the corresponding p_r from Maxwell's construction.

Our R-crossing method inherits the same limiting slope here. This number is closely followed only by helium and hydrogen, for which this example is expected to be maximally effective. R can be calculated here as a function of the variables (p_r, v_r) via the thermodynamic metric using standard formulas, and gives [7] $R = A \cdot B$, where

$$A = -\frac{b}{3}\frac{3v_r - 1}{c_v\left(p_r v_r^3 - 3v_r + 2\right)^2} \tag{5}$$

and

$$\begin{aligned} B = {} & c_v\left(p_r^2 v_r^5 - 9p_r v_r^4 + 12p_r v_r^3 - 27v_r^2 - p_r v_r^2 + 27v_r - 3\right) \\ & + 18v_r\left(p_r v_r^3 + 1\right), \end{aligned} \tag{6}$$

where c_v is the dimensionless molecular specific heat at constant volume (assumed constant, though possibly different in the liquid and gas phases) and b plays no role in our subsequent analysis.

For vdW isotherms with given p_r and given $t_r < 1$, substituting p_r from Eq. (4) into Eqs. (5) and (6) results in two physical branches for R, corresponding to the liquid and gas phases, with R diverging at the end points; see the color-coded Fig. 2. The value of p_r where the R values are equal (i.e., they cross) is interpreted as the reduced saturation pressure corresponding to t_r. For the cases we consider here, c_v on the gas side is taken as 1.5, the ideal gas value. On the liquid side, we have chosen the average value $c_v = 1.2$ determined from NIST Chemistry WebBook [8] over the range of temperatures that we are interested in. Equivalently, for vdW isobars, the R-crossing method can be used to predict the saturation temperature.

In the supercritical region, isobaric $|R|$ exhibits a local maximum with respect to t_r, whose locus is naturally interpreted as the Widom line, signifying a crossover for certain dynamical fluid properties from gaslike on the low pressure side to liquidlike on the high pressure side [2–4]. We can calculate the Widom line as per its definition through $|R| \sim \xi^3$, free from the theoretical difficulty of characterizing it via the maximum of the specific heat c_p as is conventional in the literature [3].

A natural estimate for the validity of our analysis for vdW is offered by the dimensionless quantity $|R|/v_g$, where v_g is

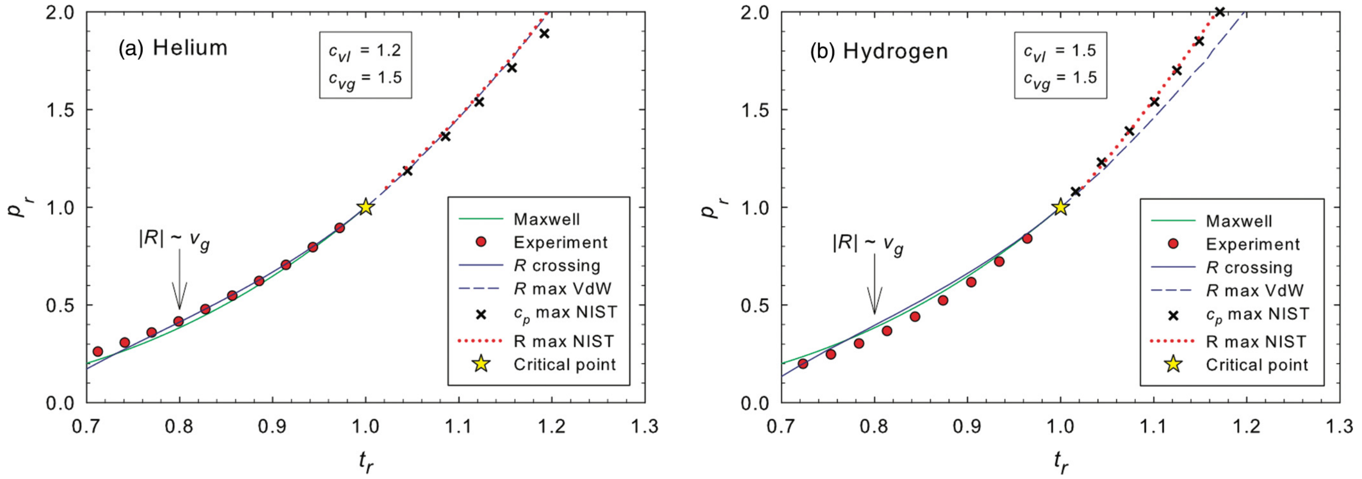

FIG. 3. (Color online) Phase coexistence and the Widom line for (a) helium ($T_c = 5.19$K, $P_c = 2.26$ bars), and (b) hydrogen ($T_c = 33.19$ K, $P_c = 13.30$ bars). The coexistence curve is calculated from vdW with the Maxwell equal-area construction and with R crossing, and compared with experimental data from NIST Chemistry WebBook [8]. The Widom line is calculated by finding the locus of maximum values along isobars of $|R|$ both with vdW and from NIST Chemistry WebBook. We compare with the maximum values along isobars of c_p from experimental data (NIST). The liquid and gas heat capacities c_{vl} and c_{vg} are indicated for vdW. In the supercritical region, we use c_{vg}.

the coexistence molecular volume in the gas phase. $|R| \gtrsim v_g$ implies that ξ^3 is greater than a molecular volume, and we are in a regime where our analysis is reasonable. We find that for vdW, this restricts us to $t_r \gtrsim 0.8$ along the coexistence curve, and to $p_r \lesssim 10$, in the supercritical region. May and Mausbach have found similar lower volume limits on implementing this method in the Lennard Jones fluid [16].

Figure 3 summarizes our results for helium and hydrogen. Table I supplements these for neon and argon. From Fig. 3, it can be seen that the R-crossing method, in conjunction with vdW, predicts excellent results within its range of applicability. Away from criticality, deviation from data is also due to the mean-field nature of the vdW equation of state. Direct application of the R-maximization method using the NIST Chemistry WebBook for the Widom line in the supercritical regime shows striking agreement with experimental c_p maximum values in the scaling region, and as expected, deviates marginally outside this region.

In conclusion, we have constructed a novel geometrical technique to characterize liquid-gas phase transitions from a microscopic perspective, through the thermodynamic scalar curvature R. Our method, which is independent of coordinate transformations in the manifold of equilibrium thermodynamic states, is distinct from (local) metric-component based approaches [17]. When applied in conjunction with the vdW equation, our procedure bypasses theoretical issues with the Maxwell equal area construction and its variants. Our technique generalizes to any phenomenological equation of state, including those obtained as multiparameter fits to experimental data. This analysis further provides the first direct theoretical construction for the Widom line, without using any ad hoc thermodynamic response function.

Our method unifies concepts in Riemannian geometry, thermodynamics, phase transitions, and critical and supercritical phenomena. Although we have primarily applied our technique to liquid-gas phase transitions, the method should be universally applicable to any first-order phase transition terminating in a critical point. This makes it of crucial significance to a diverse range of disciplines in physical, chemical and biological sciences, and engineering. It further generalizes even to gravitational systems like anti–de Sitter black holes, which also appear to exhibit liquid-gas–like first-order phase transitions [18].

TABLE I. Saturation temperatures on the left and Widom line temperatures on the right (in Kelvins) for neon ($T_c = 44.49$ K, $P_c = 26.79$ bars) on the upper part and argon ($T_c = 150.69$ K, $P_c = 48.63$ bars) on the lower part. T_R^{sat}(vdW) is the prediction of the saturation temperature from the R-crossing method, using the vdW equation, and is compared with experimental values from the NIST Chemistry WebBook. Corresponding values of $|R|/v_g$ are also shown to indicate the validity of our method. Widom line predictions from the R-maximization method are obtained both from vdW with $c_v = 1.5$ [T_R^W(vdW)] and from NIST [T_R^W(NIST)]. We have also shown the prediction of the Widom line obtained from maximizing c_p as T_{ex}^W.

P/P_c	T_R^{sat}(vdW)	$T_{\text{ex}}^{\text{sat}}$	$\|R\|/v_g$
0.4	36.04	37.97	0.60
0.5	37.68	39.41	1.16
0.6	39.24	40.66	2.36
0.8	42.09	42.76	15.35
0.9	43.33	43.66	76.48
0.4	122.89	129.16	0.57
0.5	128.19	133.93	1.11
0.6	133.34	138.07	2.23
0.8	142.70	145.00	14.29
0.9	146.85	147.98	72.49
P/P_c	T_R^W(vdW)	T_R^W(NIST)	T_{ex}^W
1.1	45.56	45.25	45.26
1.2	46.57	45.95	46.01
1.4	48.43	47.26	47.39
1.6	50.15	48.50	48.64
2.0	53.26	50.83	50.79
1.1	154.32	153.15	153.21
1.2	157.74	155.47	155.60
1.4	164.04	159.72	160.00
1.6	169.84	163.69	163.89
2.0	180.41	170.96	170.49

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