Beyond the Pair-Potential Model of Fluids at the Liquid-Vapor Critical Point

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Evidence is presented that many-body interactions in fluids have important consequences at the liquid-vapor critical point. In particular, three-body interactions in lattice-gas models are shown to lead to revised scaling variables and to a singularity in the coexistence-curve diameter with an amplitude proportional to the molecular polarizability. This is confirmed in experiments reported here. A companion van der Waals theory explains several other observed correlations between nonuniversal critical amplitudes.

Experimental and theoretical results are reported here which indicate that the pair-potential model of fluids is insufficient in the critical region. From an analysis of lattice models, we show that the scaling variables which describe the critical behavior become "revised"[1] in the presence of triplet interactions: The thermal scaling field acquires a dependence on the bare chemical potential μ, and this *field mixing* leads to a singularity in the coexistence-curve diameter $\rho_d \equiv (\rho_l + \rho_v)/2\rho_c$, with ρ_l, ρ_v, and ρ_c, respectively, the coexisting liquid and vapor densities, and the critical density. With $t = (T_c - T)/T_c$ the reduced temperature, then as $t \to 0$ the diameter varies as

$$\rho_d = 1 + A_{1-\alpha} t^{1-\alpha} + A_1 t + \cdots, \qquad (1)$$

where the exponent $\alpha (\approx 0.11)$ is that of the specific heat at $\rho = \rho_c$. The linear term is a background contribution universally observed in all fluids.

The century-old law of the rectilinear diameter[2] asserts that ρ_d is instead an *analytic* function of temperature, with $A_{1-\alpha} = 0$. The nonanalyticity in (1) has been predicted by a variety of continuum[3] and lattice models,[4,5] and by renormalization-group calculations.[6] Yet, its experimental verification in insulating fluids has proven exceedingly difficult, leaving unresolved the fundamental issue of the relation between the scaling fields at the liquid-vapor critical point and the reduced temperature and external field at the Curie point of the Ising model (lattice gas), for which $A_{1-\alpha} = 0$ by the symmetry of the Hamiltonian.

In metals such as cesium and rubidium, it is suggested[7] that many-body effects related to electronic screening lead to the remarkably large-amplitude singularities found recently.[8] Here, we relate the amplitudes of field mixing in insulating fluids directly to the *molecular polarizability*, and experimental results reported below lend strong support to the analysis. Systematic trends in other *nonuniversal* critical amplitudes are also reported, and can be directly attributed to three-body forces.

The most important of the many-body interactions in fluids is the Axilrod-Teller[9] interaction coupling triplets of particles. With θ_i the interior angles and r_{ij} the leg lengths of the triangle formed by a trio, this potential is $V_{AT} = \frac{9}{16} I \alpha_p^3 f(\{\theta_i\})/r_{12}^3 r_{13}^3 r_{23}^3$, where α_p is the molecular polarizability, I the ionization energy, and f a function of angles which makes V_{AT} primarily repulsive. In comparison, the attractive part of the dominant two-body interaction is $V_2(r) = -\frac{3}{4} I \alpha_p^2 / r^6$. With ρ_c proportional to the typical value of $1/r_{ij}^3$ in the critical region, a dimensionless measure of the relative importance of V_{AT} and V_2 is the *critical polarizability product* $\alpha_p \rho_c$. Since the critical temperature scales with V_2, it follows that $\alpha_p \rho_c \sim T_c^{1/2}$: *Triplet interactions are relatively more important in highly polarizable fluids with correspondingly higher critical temperatures.*

Figure 1 shows the diameters of Ne, N_2, C_2H_6, and SF_6. The data on Ne and N_2 were obtained by dielectric constant measurements, described previously,[10] and for ethane[11] and ethylene[12] (not shown, but similar to ethane) from measurements of the index of refraction in the two phases. The diameter of SF_6, one of the few examples until now to exhibit an anomaly, is from dielectric measurements of Weiner, Langley, and Ford.[13] A full description of the new data and its analysis is given elsewhere.[14]

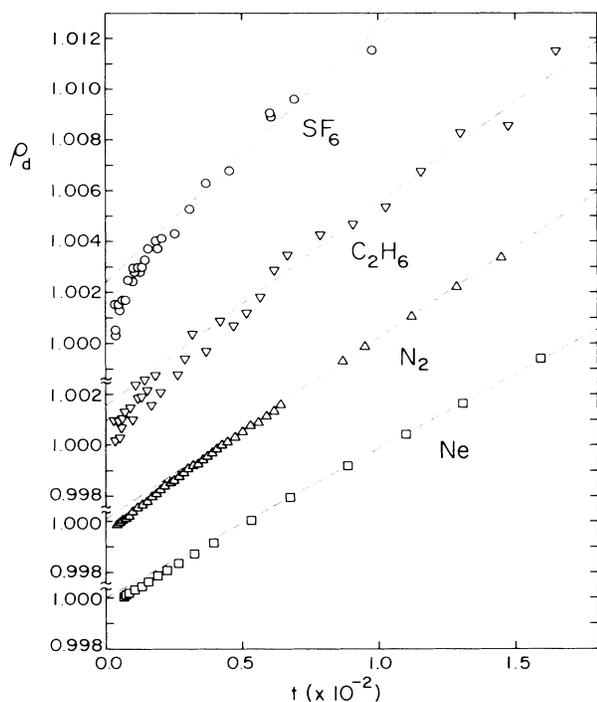Two trends in the data are immediately clear: First,

FIG. 1. Coexistence-curve diameters vs reduced temperature, with linear fits (dashed lines) determined at large t.

FIG. 2. Deviations of diameters from the linear fits. Inset: Deviations normalized by the critical polarizability product $\alpha_p \rho_c$.

as has been noted before,[15] the slope of the diameter far from T_c systematically *increases* with the critical temperature of the fluid [$T_c = 44.48$ (Ne), 126.21 (N_2), 282.38 (C_2H_4), 305.27 (C_2H_6), and 318.71 K (SF_6)]. (The dashed lines in the figure are least-squares fits of the data to a functional form of $\rho_d = A_0 + A_1 t$ over the temperature range $8 \times 10^{-3} < t < 2 \times 10^{-2}$.) Second, the deviations from the linear behavior which appear at smaller t also increase in the same order. For Ne, N_2, and SF_6, those deviations are shown for clarity in Fig. 2. Detailed analysis[14] shows that *all* of the diameters are consistent with the functional form implied by Eq. (1). The inset shows the deviations normalized by $\alpha_p \rho_c$, and from the near common collapse of the data, it is clear that the magnitudes of the anomalies are essentially proportional to $\alpha_p \rho_c$.

The five fluids also exhibit a linear variation of the diameter slope A_1, determined at large t, and of the critical compressibility factor $Z_c \equiv P_c/\rho_c k_B T_c$ with $\alpha_p \rho_c$ [Fig. 3(a)]. Combining the present data with those of other fluids[5] we see [Fig. 3(b)], that there exists a monotonic relationship between A_1 and A_β, the amplitude of the order-parameter variation; $(\rho_l - \rho_v)/2\rho_c \sim A_\beta t^\beta$. The offset of older data (solid dots) from the present results (open circles) is due to different apparent values of β and different temperature ranges studied in the analysis.

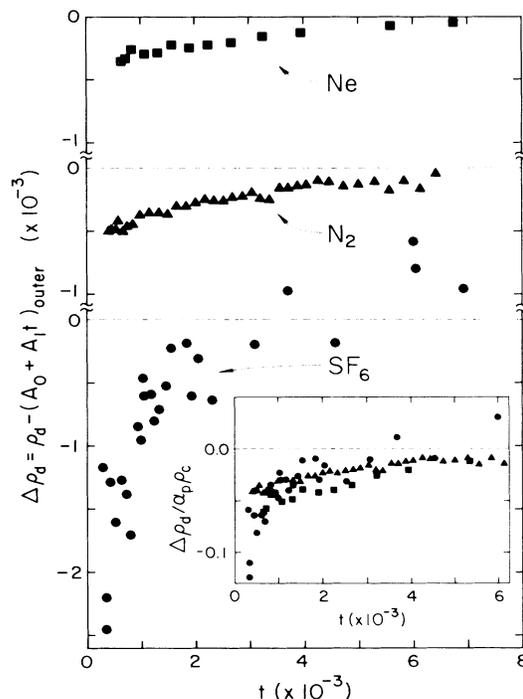To account for the data in Fig. 3, consider the van der

Waals free energy of a fluid of N particles interacting with a pair potential V_2 *and* a triplet potential V_3;

$$F = Nk_B T \ln \left[\frac{N \Lambda^3}{e(V - Nb)} \right] - aN \left[\frac{N}{V} \right] + qN \left[\frac{N}{V} \right]^2,$$

(2)

with Λ the thermal wavelength and b the excluded volume. Here, $a = -\frac{1}{2} \int d\mathbf{r} V_2(\mathbf{r})$, $q = \frac{1}{6} \int\int d\mathbf{r} d\mathbf{r}' V_3(\mathbf{r}, \mathbf{r}', \mathbf{r} - \mathbf{r}')$, the integrals being over the regions of the potentials outside a hard core. For weak V_3, a Maxwell construction yields amplitudes $A_\beta = 2 + \frac{2}{3} x + \ldots$ (with $\beta = \frac{1}{2}$), $A_1 = \frac{2}{5} + \frac{22}{15} x + \ldots$, and $Z_c = \frac{3}{8} - \frac{1}{8} x + \ldots$, where $x = q/ab$ is proportional to $\alpha_p \rho_c$. We thus find the *parameter-independent* relation $A_\beta = \frac{20}{11} + \frac{5}{11} A_1$, shown as the dashed line in Fig. 3(b), whose slope is in excellent agreement with the data. That the mean-field values of A_β are larger than those from experiment is again due to the nonclassical value of $\beta (\approx \frac{1}{3})$ in real fluids. Further evidence for the presence of three-body interactions comes from the ratio of slopes of the two curves shown in Fig. 3(a), which theory predicts is $A_1'(\alpha_p \rho_c)/Z_c'(\alpha_p \rho_c) = -\frac{176}{15} \approx -11.7$. The experimental value of -8.7 ± 0.5 is in good agreement in magnitude and in sign.

Turning now to the deviations from analyticity shown in Figs. 1 and 2, we note that if a fluid with triplet in-
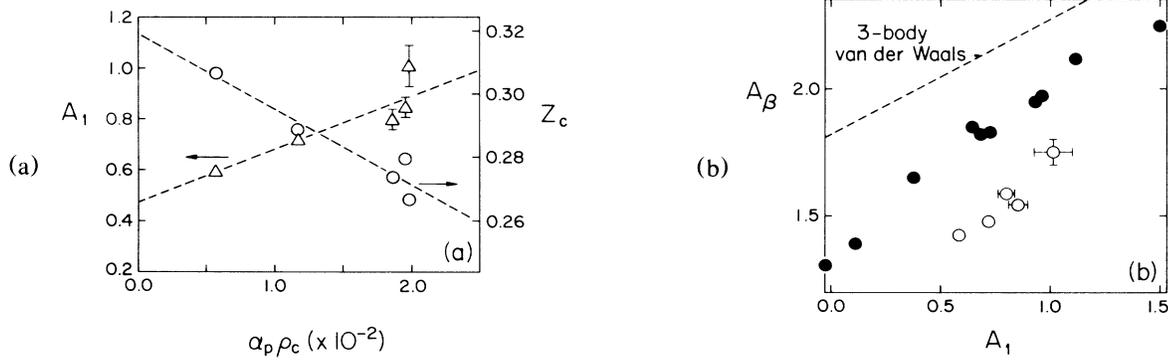
FIG. 3. (a) Diameter slope A_1 and compressibility factor Z_c vs critical polarizability product for Ne, N_2, C_2H_6, C_2H_4, and SF_6 (left to right), along with linear fits (dashed lines). (b) Order-parameter amplitude A_β vs diameter slope A_1 for (solid dots, left to right) ^3He, ^4He, H_2, Ar, O_2, Xe, N_2O, CO_2, NH_3, and H_2O, from Ref. 5. Open circles (left to right) are Ne, N_2, C_2H_6, C_2H_4, and SF_6.

teractions is in the same universality class as one without, then they share a common scaling function for the singular part of the free energy in the critical region, and an analytic map must exist which relates the scaling fields of the two systems. We have constructed such maps[16] for two- and three-dimensional lattice gases with weak triplet interactions,[17] and report here the result for the simplest system, the honeycomb lattice gas.

Consider a honeycomb lattice site labeled "1" and its three nearest neighbors, A, B, and C, with a nearest-neighbor interaction K, and three-spin interactions L coupling sequential triplets (e.g., $1AB$) and M coupling equilateral trios (e.g., ABC). For L and M small, and with a total number of sites (volume) N, the grand free energy per particle $\omega = \Omega/N$ can be related to that with L and M zero (the "reference system") by first-order thermodynamic perturbation theory;

$$\omega(z,K,L,M) \simeq \omega_0(z,K) + \frac{1}{3!N}\sum_{1,A,B}{}' L\rho_0^{(3)}(1,A,B) + \frac{1}{3!N}\sum_{A,B,C}{}'' M\rho_0^{(3)}(A,B,C) + \ldots , \tag{3}$$

where $\omega_0(z,K) = \omega(z,K,L=0,M=0)$, the $\rho_0^{(3)}(ijk)$ are the reference-system three-body distribution functions, $z = \exp(\beta\mu)$ is the fugacity, μ being the chemical potential, and the primes restrict the sums to triads of the appropriate geometry. The Kirkwood-Salsburg[18] identities allow us to express these particular $\rho_0^{(3)}$'s in terms of the density $\rho^{(1)}(1)$ and the correlation function $\rho^{(2)}(1,A)$;

$$\rho^{(3)}(1,A,B) = S_0^{(1AB)} + S_1^{(1AB)}\rho^{(1)}(1) + S_{1A}^{(1AB)}\rho^{(2)}(1,A), \tag{4}$$

and similarly for $\rho_0^{(3)}(A,B,C)$. At the critical point, the S's are simple analytic functions of z and K. Given (4), Eq. (3) can be compared with the leading-order term in an expansion of ω_0 under small shifts in the fugacity and nearest-neighbor coupling, i.e,

$$\omega_0(z+\Delta z, K+\Delta K) \approx \omega_0(z,K) - k_BT\frac{\Delta z}{z}\rho_0^{(1)}(1) + \tfrac{3}{2}\Delta K\rho_0^{(2)}(1,A).$$

We thus identify Δz and ΔK in terms of the expansion coefficients $S_0^{(1AB)}$, and obtain the desired map in a form identical to the continuum[3] and lattice models,[4,5] namely, $\omega(z,K,L,M) \simeq \omega_0(z',K') + \omega_b(z,K,L,M)$, where $K'=K+\Delta K$, and $z'=z+\Delta z$, and ω_b is an analytic background contribution.

The thermodynamic density, $\rho^{(1)}(z,K,L,M) = -(z/k_BT)(\partial\omega/\partial z)$, is therefore

$$\rho^{(1)} = -\frac{z}{k_BT}\frac{\partial\omega_b}{\partial z} + \frac{z}{z'}\frac{\partial z'}{\partial z}\rho_0^{(1)}(z',K') - \frac{3}{2}\frac{z}{k_BT}\frac{\partial K'}{\partial z}\rho_0^{(2)}(z',K'). \tag{5}$$

With minor modifications, this form of $\rho^{(1)}$ holds in other two- and three-dimensional models.[17] From the exact solution of the honeycomb Ising model, it is known[19] that on the coexistence curve, the even-parity part of $\rho_0^{(2)}$ has a critical anomaly like that of the energy density, of the form $t^{1-\alpha}$ ($t\ln t$ in two dimensions, with $\alpha=0$). The amplitude of the anomaly is governed by the field-mixing derivative $\partial K'/\partial z$, which is given completely in terms of the expansion coefficients in Eq. (4). The diameter singularity can be shown to scale with L/K (and hence like the polarizability in a

fluid), and for a repulsive potential like that in insulating fluids, to have a sign in agreement with that exhibited by the data reported here.

To summarize, we suggest that there is now clear evidence that many-body interactions have important consequences in the critical region of fluids, in particular, introducing a revision of the scaling variables that pertain in the simple lattice-gas model.

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