Acc. Chem. Res. 1989, 22, 77–82

Liquid–Vapor Asymmetry at the Critical Point

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Received January 22, 1988 (Revised Manuscript Received November 1, 1988)

I. Introduction

Much of our present understanding of the nature of the liquid–vapor critical point is based on the deep correspondence between second-order phase transitions in fluids and those in magnetic systems as exemplified by the Curie points of ferromagnets. As stressed first by Lee and Yang,[1] and later reinterpreted as the principle of universality,[2] the relation between these systems rests on the isotropy and short-range nature of the interparticle potentials, the scalar character of their order parameters, and the spatial dimensionality. The experimental verification of universality among fluids and ferromagnets is by now nearly unquestionable with regard to the most directly measurable types of quantities, the exponents characterizing mathematical anomalies in densities and response functions and ratios of the amplitudes of those anomalies.[3]

Yet, there has remained over the years a fundamental unresolved problem lying at the heart of the fluid–magnet correspondence, centering on the validity of certain symmetry relations between thermodynamic properties in coexisting liquid and vapor phases close to the critical point. These relationships are rigorously present in the spin-$^1/_2$ Ising ferromagnet as a consequence of the symmetries of its Hamiltonian, but no such exact relations exist in the Hamiltonian of a fluid. The study of this aspect of the thermodynamics of liquids dates back in some sense to the last century, but until very recently, there has been a large gap between theoretical predictions and experimental observations.

This Account reviews recent work[4–9] which we believe has shed new light on the fluid–magnet correspondence. These theoretical results arise from a proposed *synthesis* of approaches ranging from those of the classical van der Waals type to lattice-model calculations and field-theoretic methods and provide a consistent description of new high-precision experimental data. Together, they suggest a possible basis for a fully quantitative microscopic theory of liquid–vapor critical phenomena in fluids.

II. The Experiments

It is now just over a century since the classic experiments of Cailletet and Mathias[10] demonstrated that as the liquid–vapor critical temperature T_c is approached along the saturated vapor pressure curve, the so-called *diameter*, the mean of the densities ρ_l and ρ_v of coexisting liquid and vapor phases, appears to deviate from the critical density ρ_c as a *linear* function of reduced temperature $t \equiv (T_c - T)/T_c$, as shown by the dashed line in the schematic Figure 1. This appears to occur despite the fact that the two branches of the coexistence curve each have power-law singularities,

$$\frac{\rho_{l,v}}{\rho_c} \simeq 1 \pm A_\beta t^\beta + A_1 t + ... \quad (2.1)$$

where the exponent $\beta \simeq {}^1/_3$, A_β is the amplitude of the asymptotic order parameter variation, $(\rho_l - \rho_v)/2\rho_c \simeq A_\beta t^\beta$, and A_1 characterizes the diameter $\rho_d \equiv (\rho_l + \rho_v)/2\rho_c$,

$$\rho_d - 1 \simeq A_1 t + ... \quad (2.2)$$

In contrast to the *universal* critical exponents like β, the amplitudes A_1 and A_β are *nonuniversal*; they depend on details of the molecular interactions. Universality would hold, however, for systems that possess pairwise additive conformal potentials and hence rigorously obey a "law of corresponding states" in the sense described by Guggenheim.[11]

The analyticity of $\rho_d(t)$ in eq 2.2, known as the "law of the rectilinear diameter", follows from any equation of state for which the free energy has an analytic expansion in t and $\rho - \rho_c$ near the critical point. Such models predict $\beta = {}^1/_2$, contrary to the nonclassical value seen in modern experiments and theory. Nevertheless, for decades, a linear diameter was observed in essentially all fluids studied, even at the level of precision at which nonclassical exponents are plainly apparent for the order parameter, specific heat, compressibility, etc. The apparent analyticity of the diameter is therefore distinct from the issue of the validity of mean field theory.

Beginning in the early 1970s, interest in this aspect of the critical behavior of fluids grew in the wake of a number of theoretical studies[12–14] suggesting that the

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(1) Lee, T. D.; Yang, C. N. *Phys. Rev.* **1952**, *87*, 410.
(2) See, e.g.: Fisher, M. E. In *Critical Phenomena*; Hahne, F. G. W., Ed.; Lecture Notes in Physics No. 186; Springer-Verlag: 1983.
(3) Sengers, J. V.; Levelt Sengers, J. M. H. *Annu. Rev. Phys. Chem.* **1986**, *37*, 189.
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(11) Guggenheim, E. A. *J. Chem. Phys.* **1945**, *13*, 253.
(12) Widom, B.; Rowlinson, J. S. *J. Chem. Phys.* **1970**, *52*, 1670. For a review, see: Rowlinson, J. S. *Adv. Chem. Phys.* **1980**, *41*, 1.
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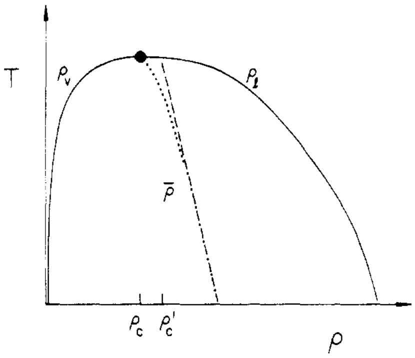

Figure 1. Schematic illustration of the temperature–density diagram of a one-component fluid, showing the coexisting liquid and vapor densities ρ_l and ρ_v and the mean density $\bar{\rho}$. Analytic (dashed) and nonanalytic (dotted) diameters are shown.

lack of perfect symmetry between liquid and vapor should modify the classical results (eq 2.1 and 2.2) to include a new *singular* term,

$$\rho_d - 1 \simeq A_{1-\alpha}t^{1-\alpha} + A_1 t + \ldots \quad (2.3)$$

Here, α ($\simeq$0.11) is the exponent characterizing the power-law divergence of the specific heat C along the critical isochore; $C \sim t^{-\alpha}$. Equation 2.3 implies a critical density ρ_c which differs from ρ_c', that estimated by a linear extrapolation from large reduced temperatures (see Figure 1), and it implies that the diameter itself actually has a *horizontal tangent* in the $\rho - T$ plane. The closeness of $1 - \alpha$ to unity makes the singularity very difficult to detect, but an early experiment by Weiner, Langley, and Ford[15] in 1974 on SF_6 found rather convincing evidence of its existence. Many subsequent experiments on other pure fluids and mixtures failed to detect any anomaly, though, leaving the field in an awkward state, with theory providing no microscopic explanation of the factors that control the magnitude of symmetry breaking.

The entire subject has had two rebirths in recent years: first, in 1985, with remarkable experiments by Jüngst, Knuth, and Hensel[4] on the liquid–vapor equilibria of the metals cesium and rubidium, and then, in 1987, with high-precision experiments[6,8] on neon and nitrogen by Pestak and Chan, and on ethane and ethylene by de Bruyn and Balzarini. These experiments finally revealed that singularities with the predicted critical exponent $1-\alpha$ do indeed exist. Here, we concentrate on the results and interpretation of the experiments on classical insulating fluids, for which the contact between theory and experiment is closest.

Perhaps the most important aspect of the experiments[6,8] on insulating fluids is the discovery that *various critical amplitudes exhibit a strong correlation with the molecular polarizability*, or, equivalently (see below), with the critical temperature. Examples of these trends are shown in Figures 2–4. Figure 2a displays the coexistence curves of several insulating fluids in the critical region on a reduced scale. In order of increasing critical temperature, from ^3He (T_c = 3.31 K) through N_2 (126.2 K) to SF_6 (318.7 K), it is clear that the breadth of the coexistence curve, and hence the amplitude A_β, systematically increases. This is in marked contrast with the apparently universal behavior suggested by the less precise data in Guggenheim's famous 1945 plot (Figure 2b). The diameters of some of the fluids in Figure 2a are arranged in order of increasing T_c in Figure 3, and again certain properties vary systematically. The diameter slope A_1 determined far from T_c increases with the critical temperature of the fluid, as does the amplitude $A_{1-\alpha}$ of the anomaly (the "hook" in the data) near t = 0. Note also that the singularity always has the same sign; $A_{1-\alpha} > 0$.

We have suggested that these observations are the key to understanding liquid–vapor asymmetries and have argued[6-9] that the above trends arise from the existence of a *new energy scale* in these systems, one different from that of the critical point itself, k_BT_c. That new energy scale is proposed to arise from three-body Axilrod–Teller[16] (AT) interactions. While there are other microscopic origins of deviations from a law of corresponding states, such as variations in the detailed form of two-body potentials, quantum effects, and so on, we find that liquid–vapor symmetry appears to be particularly sensitive to three-body forces.

We begin by recalling that in the simplest "one-level" approximation to the frequency-dependent atomic polarizability $\alpha(\omega)$ of an atom, namely, $\alpha(\omega) = \alpha(0)\Delta^2/(\Delta^2 - \omega^2)$, the long-range part of the attractive two-body dispersion force between atoms is $\phi_1(r) = -(^3/_4)\hbar\Delta\cdot\alpha(0)^2/r^6$. The classical or van der Waals theory of the critical point embodies the essential result that the thermal energy at the critical point scales with the Fourier transform of ϕ_1 at zero momentum, $k_BT_c \sim \hat{\phi}_1(0)/\sigma^3 \sim \hbar\Delta\alpha(0)^2/\sigma^6$, with the critical density varying as $\rho_c \sim \sigma^{-3}$, σ being a short-distance cutoff of the potential ϕ_1. The same approximation to $\alpha(\omega)$ yields the AT potential for three particles at positions $(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, forming a triangle with vertex angles θ_i, as

$$\psi_{AT}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \frac{9}{16}\alpha(0)^3\hbar\Delta\frac{3\cos\theta_1\cos\theta_2\cos\theta_3 + 1}{r_{12}{}^3 r_{13}{}^3 r_{23}{}^3} \quad (2.4)$$

The two most important characteristics of this interaction are (i) that its amplitude scales with (static polarizability)^3 and (ii) that it is repulsive for the majority of the configurations of the triad. Our analysis relates (i) to the existence of a new energy scale and (ii) to the *sign* of the diameter anomaly. On purely dimensional grounds, we can see that the *relative* importance of triplet to pair interactions, ψ_{AT}/ϕ_1, is given by the dimensionless "critical polarizability product"[6] $\alpha(0)\rho_c$, itself proportional to $T_c^{1/2}$. That is, *systems with higher critical temperatures have relatively more important many-body interactions.* The significance of this quantity as a perturbation parameter is demonstrated in Figure 4, where it is seen that the values of $A_{1-\alpha}$ estimated from experiment vary linearly with $\alpha(0)\rho_c$. With these experimental observations in mind, let us now review the original theoretical predictions of diameter anomalies.

III. Theoretical Background

The Penetrable-Sphere Model and Decorated-Lattice Models. Introduced by Widom and Rowlinson[12] in 1970, the penetrable-sphere model was the first to suggest the presence of a singular diameter and shares a common mathematical mechanism with the

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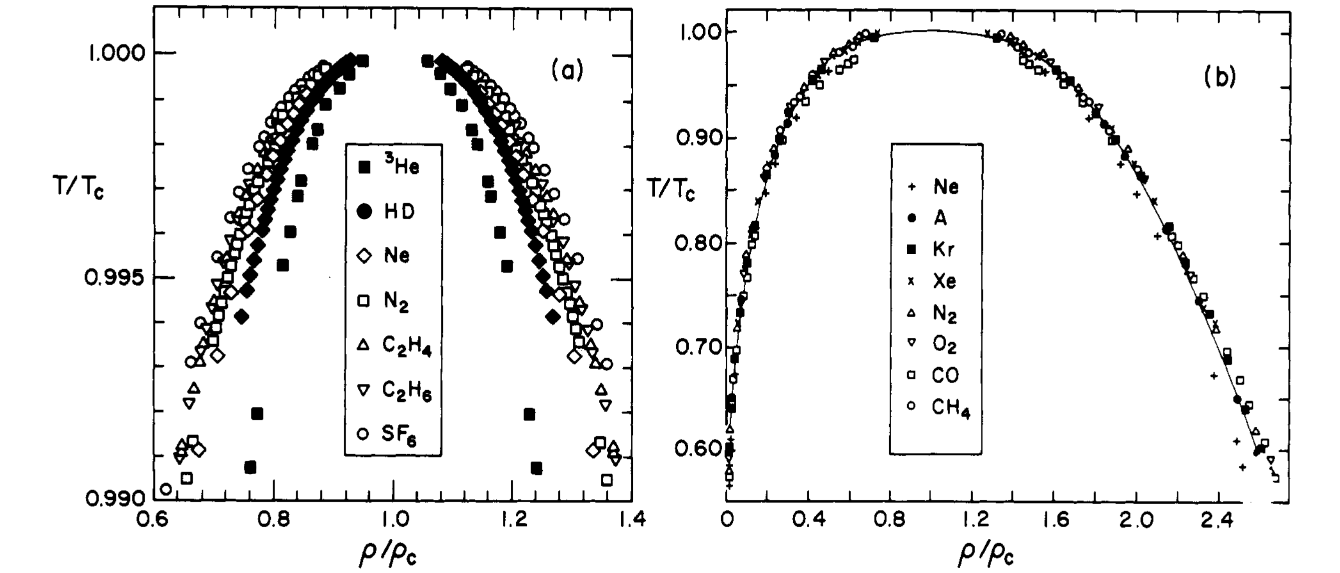

Figure 2. Coexistence curves of several simple fluids in the critical region. Data in part a are from ref 8. Part b represents Guggenheim's corresponding-states plot, adapted from ref 11. Note the different scales in parts a and b.

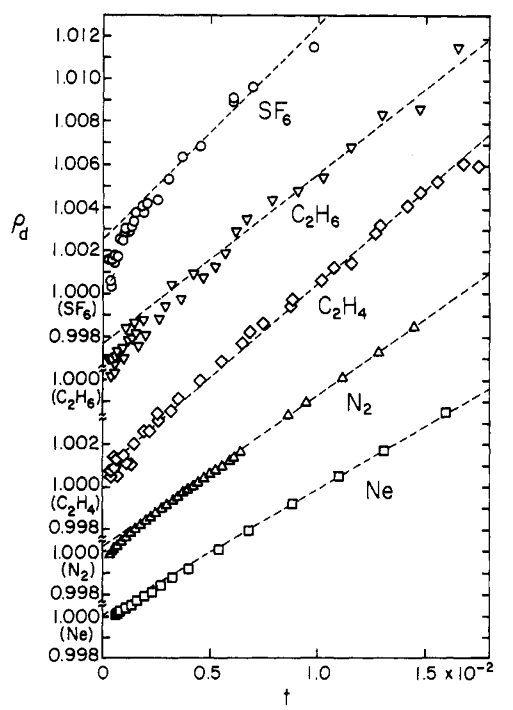

Figure 3. Coexistence curve diameters of Ne, N_2, C_2H_4, C_2H_6, and SF_6, illustrating the larger slope at large t and larger amplitude singular anomaly at small t with increasing critical temperature. Reprinted with permission from Pestak, M. W.; Goldstein, R. E.; Chan, M. H. W.; de Bruyn, J. R.; Balzarini, D. A.; Ashcroft, N. W. *Phys. Rev. B* **1987**, *36*, 599. Copyright 1987 The American Institute of Physics.

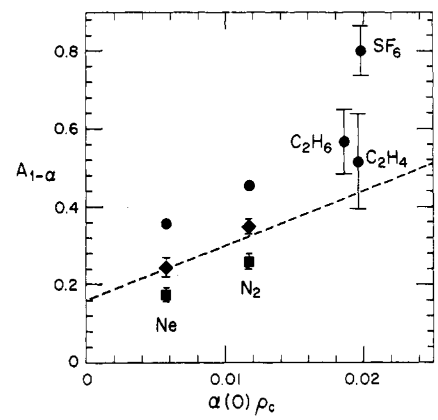

Figure 4. Experimental and theoretical diameter anomaly amplitudes versus the critical polarizability product. Dashed line is the theoretical prediction from ref 9. Circles denote amplitude estimates obtained from single power-law analysis of data closest to T_c, squares from fits over a larger temperature range with an analytic background included. Estimates shown by diamonds include in addition a correction to scaling term.

particular decorated-lattice models studied by Mermin[14] and others.[17] As shown by Fisher,[18] these models belong to a class whose thermodynamic properties may be mapped exactly onto those of simple Ising models. Their name derives from the existence of two classes of spins in the lattice: primary spins s_i, which reside at the vertices of the lattice and are coupled to each other with nearest-neighbor interactions, and secondary spins σ_i, which are located on the bonds between primary sites and interact only with their nearest-neighbor primary spins. In the penetrable-sphere model, these two classes of spins are replaced by two kinds of particles that form ideal gases with respect to others of their species but interact through some short-range potential with opposite types.

The mutual independence of the decorating spins σ_i implies that for any configuration of the s_i the trace over $\{\sigma_i\}$ in the "two-component" partition function may be performed separately and exactly, with the $\{s_i\}$ acting as a spatially varying external field. Thus, the full partition function is reducible to that of a one-component system involving only the primary sites, with some effective Hamiltonian coupling only nearest neighbors. The important point is that this effective nearest-neighbor interaction has an explicit dependence on the *one-body field* of the original model, the external magnetic field H, which corresponds to the chemical potential in a fluid. This dependence is embodied in the generic relationship between the free energy F of the original model and that of the simple Ising model F_I,

$$F(\{K\},H) = F_I[K_I(\{K\},H),H_I(\{K\},H)] + G(\{K\},H) \quad (3.1)$$

(17) Mulholland, G. W.; Zollweg, J. A.; Levelt-Sengers, J. M. H. *J. Chem. Phys.* **1975**, *62*, 2535.
(18) Fisher, M. E. *Phys. Rev.* **1959**, *113*, 969.

where $\{K\}$ is the set of original spin–spin coupling constants in the model, and where the effective nearest-neighbor Ising couplings K_I, magnetic field H_I, and additive term G are all *analytic* functions of their arguments. The thermodynamic density of interest is the magnetization conjugate to H, and one finds that the mean density on the coexistence surface has a term of the form $(\partial F_I/\partial K_I)(\partial K_I/\partial H)$. The first of these two factors is the dimensionless nearest-neighbor spin–spin correlation function of the Ising model, directly proportional to the internal energy; this is the quantity with a singularity of the form $t^{1-\alpha}$. The amplitude of the diameter anomaly is therefore nonzero only if *the effective spin–spin coupling depends on the bare external field*, that is, $\partial K_I/\partial H \neq 0$. In the language of a fluid, this is equivalent to an "intermolecular potential that is a function of thermodynamic variables"[19] (here, chemical potential). In general, this phenomenon is known as "field mixing".

Phenomenological Scaling. In 1973, Rehr and Mermin[20] generalized the scaling theory introduced by Widom[21] through a simple change of variables analogous to that seen in the decorated-lattice models. They proposed that the pressure P near the critical point varies as

$$P(\mu,T) = P_0(\zeta,\tau) + \tau^{2-\alpha}f(\zeta/\tau^{\beta\delta}) \quad (3.2)$$

where P_0 is an analytic background term analogous to that called G in eq 3.1 and f is the universal scaling function, with $\tau(t,h)$ and $\zeta(t,h)$ the two "scaling fields" which play the roles of the coupling K_I and magnetic field H_I in eq 3.1 near the critical point. It is assumed that τ and ζ are analytic in the bare variables t and $h \sim (\mu - \mu_{coex})/k_BT_c$, with μ the chemical potential and $\mu_{coex}(T)$ its value on the phase boundary. From eq 3.2, one finds that the density $\rho = (\partial P/\partial\mu)_T$ has a singular term proportional to $(\partial\tau/\partial h)\tau^{1-\alpha}$, a result completely equivalent to that found in the decorated-lattice models, with the crucial field-mixing derivative being $\partial\tau/\partial h$.

Field-Theoretic Analysis. Important progress in the study of liquid–vapor asymmetries in real fluids was made in 1981 by Nicoll,[22] who showed that certain symmetry-breaking terms in a Landau–Ginzburg–Wilson Hamiltonian $\mathcal{H}_{LGW}$ implied the existence of revised scaling variables. He considered a model in which $\mathcal{H}_{LGW} = \mathcal{H}_S + \omega\mathcal{H}_A$, a sum of "symmetric" and "asymmetric" parts, ω being a dimensionless small parameter. These two terms are the familiar fourth-order expansion in the local order parameter $\phi(x)$,

$$\mathcal{H}_S = \int d^dx \left(\frac{1}{2}t\phi^2 + \frac{1}{2}b(\nabla\phi)^2 + \frac{1}{4!}u\phi^2 - h\phi\right) \quad (3.3)$$

with t the deviation from the mean field critical temperature and h the external field, and a particular set of cubic and quintic operators,

$$\mathcal{H}_A = \int d^dx \left(\frac{1}{2}t\phi^3 - \frac{1}{2}b\phi^2\nabla^2\phi + \frac{1}{12}u\phi^5\right) \quad (3.4)$$

Application of certain fundamental identities obeyed by field-theoretic models shows that this model has a scaling law equation of state like that postulated by Mermin and Rehr, eq 3.2, with the revised thermal scaling field $\tau \simeq t + \omega h$, to leading order in ω. The relationship between the operators in $\mathcal{H}_A$ and revised scaling variables has also been demonstrated in a renormalization-group analysis by Nicoll and Zia.[23] While this relationship only holds for the particular linear combination of odd operators in eq 3.4, Reatto and Tau[24] remarked that the cubic terms in a coarse-grained Hamiltonian for systems with three-body interactions are strongly reminiscent of the odd operators in eq 3.4, and that such potentials may enhance field mixing.

IV. Many-Body Interactions at Criticality

General Approach. In analyzing the consequences of weak many-body dispersion interactions on critical behavior, we have relied on thermodynamic perturbation theory. Consider a system governed by a Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \omega\mathcal{H}_3$, with $\mathcal{H}_0$ a sum of reference potentials, ω a small parameter, and $\mathcal{H}_3$ a sum of triplet potentials ψ. $\mathcal{H}_0$ itself is further partitioned into a sum of repulsive and attractive potentials, ϕ_0 and ϕ_1, respectively. The first-order change in the free energy from its value in the reference system is[25]

$$\Delta F \simeq \frac{\omega}{3!}\int\int\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, \psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\rho_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + ... \quad (4.1)$$

where $\rho_0^{(3)}$ is the triplet distribution function of the reference system. Three applications of this simple result, a van der Waals theory, lattice–gas models, and a Landau–Ginzburg–Wilson Hamiltonian for fluids, illustrate the role of three-body interactions in liquid–vapor asymmetries.

Van der Waals Theory. The van der Waals (vdW) equation of state predicts that the diameter slope $A_1 = {}^2/_5$, which is reasonably accurate for fluids like neon with $T_c \leq 40$ K, suggesting it is a starting point for the application of eq 4.1. For N particles in a volume V at temperature T, the vdW Helmholtz free energy is modified to account for three-body interactions by including a mean field acting on each particle proportional to the square of the density,[6,8]

$$F = Nk_BT \ln\left[\frac{N\Lambda^3}{e(V - Nb)}\right] - aN\left(\frac{N}{V}\right) + qN\left(\frac{N}{V}\right)^2 \quad (4.2)$$

where Λ is the thermal de Broglie wavelength and b the excluded volume, a and q being related to the transforms of the potentials with suitable short-range cutoffs; $a = -({}^1/_2)\hat{\phi}_1(0)$ and $q = ({}^1/_6)\hat{\psi}(0,0)$.

One finds from a Maxwell construction applied to eq 4.2 near the critical point that three-body interactions do indeed introduce a new energy scale, with all critical amplitudes depending explicitly on the *nonuniversal* parameter $x \equiv q/ab \sim \alpha(0)\rho_c$. For weak repulsive three-body interactions ($0 < x \ll 1$), the diameter slope and order parameter amplitude both increase with x (and hence also with T_c), as in Figures 2 and 3. These

(19) Rowlinson, J. S. *Mol. Phys.* **1984**, *52*, 567.
(20) Rehr, J. J.; Mermin, N. D. *Phys. Rev. A* **1973**, *8*, 472.
(21) Widom, B. *J. Chem. Phys.* **1965**, *43*, 3898.
(22) Nicoll, J. F. *Phys. Rev. A* **1981**, *24*, 2203.
(23) Nicoll, J. F.; Zia, R. K. P. *Phys. Rev. B* **1981**, *23*, 6157.
(24) Reatto, L.; Tau, M. *Europhys. Lett.* **1987**, *3*, 527.
(25) See, e.g.: McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1973; Chapter 14.

and other semiquantitative correlations with experiment lend support to the conjectured role of triplet interactions.

The van der Waals model actually contains the notion of an effective, state-dependent potential in the sense that with the definitions of a and q we may consider the free energy in eq 4.2 to arise from a purely pair potential Hamiltonian with an effective interaction

$$\tilde{\phi}_1(r) = \phi_1(r) + \frac{1}{3}\rho \int_\sigma d\mathbf{r}' \, \psi(\mathbf{r},\mathbf{r}',\mathbf{r}-\mathbf{r}') \qquad (4.3)$$

a form analogous to that found by Casanova et al.[26] by more sophisticated techniques. If viewed as a virial expansion, ρ may be replaced by the fugacity z, giving a potential that depends on temperature and chemical potential, precisely what appears in decorated-lattice and penetrable-sphere models. This argument, while not immediately applicable to the critical region, is supported by more rigorous calculations for lattice models.

Lattice Models. We have studied[6,7] the effects of weak three-body interactions on lattice-gas Hamiltonians which in their absence display exact liquid-vapor symmetry and have found that the presence of revised scaling variables may be established rigorously. These model Hamiltonians are of the form

$$\mathcal{H} = \frac{1}{2!}\sum_{i\neq j} K_{ij}n_i n_j + \frac{1}{3!}\sum_{i\neq j\neq k} L_{ijk}n_i n_j n_k \qquad (4.4)$$

where $n_i = 0, 1$ is the occupation variable of site i, and the symmetry-breaking three-site interactions L_{ijk} are assumed small relative to the two-body interactions K_{ij} (≤ 0).

From first-order perturbation theory, we may write the thermodynamic potential Ω, viewed as a functional of the two- and three-body interactions, in terms of that of the reference system $\Omega_0[z,K] \equiv \Omega[z,K,L=0]$ as

$$\Omega[z,K,L] \simeq \Omega_0[z,K] + \frac{1}{3!}\sum_{i,j,k} L_{ijk}\rho_0^{(3)}(ijk) + ... \qquad (4.5)$$

where $\rho_0^{(3)}(ijk)$ is the reference three-body correlation function for the sites i, j, and k. To see how revised scaling variables arise from triplet interactions, we examine a functional expansion of the free energy of a perturbed reference system, with fugacity $z' \equiv z + \Delta z$ and potential $K' \equiv K + \Delta K$,

$$\Omega_0[z',K'] \simeq \Omega_0[z,K] - k_B T\sum_i \rho_0^{(1)}(i)\frac{\Delta z}{z} + \frac{1}{2}\sum_{i,j}\rho_0^{(2)}(ij)\Delta K(ij) + ... \qquad (4.6)$$

For a class of compact triplet and higher body interactions, an equivalence between eq 4.5 and 4.6 may be established by means of certain exact correlation function identities which relate the $\rho_0^{(3)}$ and the lower order pair and singlet distributions $\rho_0^{(2)}$ and $\rho_0^{(1)}$. These "Kirkwood-Salsburg" identities[27] reduce in the lattice models to a finite set of *linear algebraic* relations among the $\rho_0^{(n)}$, with the fugacity z and the temperature as parameters. The resultant free-energy map, precisely of the decorated-lattice form (3.1), relates the thermodynamic properties of a system with symmetry-breaking many-body interactions to that of a liquid-vapor symmetric system. It also shows the relevant field-mixing derivatives to be linear in the quantities $L_{ijk}/k_B T_c$, and therefore scaling as $T_c^{1/2}$ for dispersion interactions, and that the anomaly has a positive amplitude, as in experiment, for repulsive triplet interactions like the Axilrod-Teller potential. The variations of other critical amplitudes with the strength of the triplet potentials follow closely those found in the van der Waals theory.

Landau-Ginzburg-Wilson Model. While the field-theoretic connection between revised scaling variables and certain operators in a Landau-Ginzburg-Wilson Hamiltonian provides key insights into the origins of liquid-vapor asymmetry, the precise relationship between those operators and the Hamiltonian of a fluid was not clear. We have found[9] that the results of Hubbard and Schofield,[28] showing the formal relation between the operators in a Landau-Ginzburg-Wilson model and those of a microscopic Hamiltonian of a fluid, may be carried through in detail to arrive at a microscopic expression for the field-mixing operator. In addition, such a formal development allows for contact to be made with a variety of powerful field-theoretic techniques in critical phenomena, such as the renormalization group.

The derivation proceeds from the exact relation between the grand canonical partition function Ξ of a fluid at temperature T and chemical potential μ and that of a reference system Ξ_0 at T and μ_0,

$$\Xi(T,\mu,V) = \Xi_0(T,\mu_0,V)\langle \exp[-\beta\mathcal{H}_1 + \beta(\mu - \mu_0)N]\rangle_0 \qquad (4.7)$$

where the full Hamiltonian is $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$. The first application of this is to the case in which $\mathcal{H}_1$ contains the attractive part of the pair interactions, with $\mathcal{H}_0$ a sum of hard-sphere interactions. By rewriting the argument of the exponential in eq 4.7 in momentum space as a quadratic form in the Fourier components of the density, it is seen to be of a general Gaussian form. As such, a Hubbard-Stratonovich transformation[2] may be applied to obtain the free energy in terms of a functional integral over continuous fields, the Hamiltonian containing, among other terms, all of the operators in Nicoll's model, eq 3.3 and 3.4.

The crucial points in the above transformations are (i) that the operators t, b, u, etc., may be expressed *exactly* in terms of the pair potential $\hat{\phi}_1(k)$ and certain n-particle direct correlation functions of the *reference* system and (ii) that the properties of a hard-sphere fluid are known sufficiently well that a detailed calculation of the magnitude of the field-mixing operator is possible. Renormalization-group and scaling arguments can be used to show that in fact the dominant contribution to field mixing comes from the density derivative of $b_2 = (^1/_3)\int d^3r \, r^2 C_2(r)$, the second moment of the two-particle direct correlation function C_2. Note that Nicoll's two LGW operators combine to give a gradient-squared coefficient of $b(1 + 2\omega\phi)$, which is nothing but a Taylor expansion of the density dependence of b_2. Thus, the derivative $(\partial b_2/\partial\rho)$ is the intrinsically small quantity that breaks liquid-vapor symmetry in

(26) Casanova, G.; Dulla, R. J.; Jonah, D. A.; Rowlinson, J. S.; Saville, G. *Mol. Phys.* **1970**, *18*, 589.
(27) Kirkwood, J. G.; Salsburg, Z. W. *Discuss. Faraday Soc.* **1953**, *15*, 28.
(28) Hubbard, J.; Schofield, P. *Phys. Lett.* **1972**, *40A*, 245.

fluids. To put this in perspective, recall[29] that in the theory of fluids with a weakly inhomogeneous density $\rho(\mathbf{r})$ the free energy density $f(\mathbf{r})$ is of the form

$$f(\mathbf{r}) \simeq f_h(\rho(\mathbf{r})) + \frac{1}{2}m|\nabla\rho(\mathbf{r})|^2 + ... \qquad (4.8)$$

where f_h is that of a homogeneous fluid, and the coefficient of the gradient term (analogous to b in eq 3.3) is just $(k_BT/2)b_2$. Within the interpretation of van der Waals,[29] for instance, m is proportional instead to the second moment of the *pair potential*, rather than of C_2, and hence is *independent of density*, implying no field mixing. In reality, the weak density dependence of C_2 for pair-potential fluids gives rise to the small residual value of $A_{1-\alpha}$ seen in Figure 4 in the limit $\alpha(0)\rho_c \rightarrow 0$.

Three-body interactions like the Axilrod–Teller potential may be absorbed into the reference system properties by means of a low-order perturbation expansion analogous to that in eq 4.3, giving rise to a *linear density dependence to the range of* C_2, and hence a linear variation in the amplitude $A_{1-\alpha}$. The resulting parameter-free theoretical prediction of the variation of $A_{1-\alpha}$ with the critical polarizability product, based on a hard-sphere reference system, is shown in Figure 4 to be in semiquantitative agreement with the available experimental data.

(29) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Oxford: New York, 1982; p 16.

V. Discussion

Although the discussion in this review has been confined to critical phenomena in insulating fluids, it was in fact motivated primarily by the extraordinary experiments of the Marburg group[4] on metallic fluids, which exhibit extreme degrees of liquid–vapor asymmetry and strong diameter anomalies. These fluids are fundamentally distinct from insulators in that the interparticle potentials are not quantities related to intrinsically atomic properties, but rather depend strongly on the nature of the electron gas which screens the Coulombic interaction. In the neighborhood of the metal–nonmetal transition which, for the alkali metals, occurs at a density close to that of the critical point,[4] one might expect any "effective" potentials between ions to be strong functions of the thermodynamic state. In light of the results presented here, the large diameter anomalies might then be expected,[5] but it remains an important open problem to develop a microscopic theory of critical phenomena in systems with such rapidly changing electronic structure as metallic fluids.

We are grateful to our colleagues N. W. Ashcroft, D. A. Balzarini, J. R. de Bruyn, M. H. W. Chan, F. Hensel, and M. W. Pestak for a most enjoyable collaboration and to M. E. Fisher, J. J. Rehr, and B. Widom for their valuable insights and continued encouragement. This work was supported in part by the NSF, through Grant No. DMR84-15669 and 81-17011, and by a graduate fellowship (R.E.G.) from the Fannie and John Hertz Foundation.