Broken particle–hole symmetry in critical fluids

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The quantitative validity of asymptotic particle–hole symmetry in a fluid at its liquid–vapor critical point is determined by means of the exact mapping of the fluid Hamiltonian onto that of an effective Landau–Ginzburg–Wilson model studied first by Hubbard and Schofield. A particular three-particle correlation of a reference fluid is identified as that which controls the breaking of liquid–vapor symmetry, as manifested in a linear mixing of the pure Ising-like scaling fields and a singularity in the coexistence curve diameter. The inherent smallness of the mixing coefficient in a pair-potential fluid is shown to reflect the weak density dependence of the second moment of the two-particle direct correlation function of the reference system. It is further demonstrated that three-body interactions of the Axilrod–Teller-type enhance the broken particle–hole symmetry found in a purely pairwise-additive Hamiltonian, and detailed calculations give diameter anomaly amplitudes which vary linearly with the fluid polarizability, in quantitative agreement with recent experiments.

I. INTRODUCTION AND SUMMARY OF RESULTS

Recent experimental and theoretical studies[1–3] of critical phenomena in fluids have revealed that the correspondence between liquid–vapor critical points and the Curie points of Ising ferromagnets depend sensitively on the existence of many-body interactions in fluids. Of central interest has been the validity of particle–hole symmetry in fluids, as expressed in the relationship of the true scaling variables to those implied by the lattice–gas model. The most notable manifestation of deviations from the rigorous symmetry obeyed by Ising ferromagnets is the celebrated *singularity in the coexistence curve diameter* which has been predicted from a variety of theories,[4] from a continuum model of fluids[5] to lattice models,[1,2,6] and by renormalization-group studies.[7,8]

This weak anomaly in the mean of the coexisting liquid and vapor densities, ρ_l and ρ_v, as they separately approach the critical density ρ_c along the coexistence curve takes the same form as the singular part of the internal energy, namely,

$$\rho_d \equiv \frac{\rho_l + \rho_v}{2\rho_c} \simeq 1 + A_{1-\alpha} t^{1-\alpha} + A_1 t + \cdots . \qquad (1)$$

Here, the reduced temperature $t \equiv (T_c - T)/T_c$, and $\alpha \simeq 0.11$ is the exponent of the divergence of the constant volume specific heat. The linear term represents the ever-present analytic background contribution. In systems with perfect particle–hole symmetry, such as the Ising model and the lattice gases to which it is equivalent, $A_{1-\alpha} = A_1 = 0$, as indeed are all higher terms, so that the classical analyticity of the diameter[9] holds trivially. In real fluids, for which the diameter has a measurable temperature dependence far from T_c, it is only very recently that there has appeared evidence for true broken particle–hole symmetry *in the form of the scaling variables*, namely $A_{1-\alpha} \neq 0$.

Analysis of those new high-precision experiments[1,3] on simple fluids has revealed that the amplitude of that anomaly and several other nonuniversal critical amplitudes are strongly and systematically dependent on the molecular polarizability α_p. This would not be the case if these fluids obeyed a law of corresponding states, for then all microscopic details would have been scaled out in defining the critical amplitudes. These systematic deviations from universal behavior have been ascribed[1–3] to the effects of weak three-body dispersion interactions of the Axilrod–Teller (AT) type which are argued to introduce a *new energy scale*. This can be seen from the fact that the amplitude of the AT potential scales like α_p^3, in contrast to the quadratic dependence on α_p of the amplitude of the pair interaction. Thus, the *relative* strength of triplet interactions is linear in the polarizability, and both a van der Waals model[3] and lattice models[2] of fluids with triplet interactions have successfully explained many of the experimental findings on this basis. In particular, the lattice models have indicated that repulsive triplet potentials (like the AT interaction) lead to a linear variation of the amplitude $A_{1-\alpha}$ with the dimensionless *critical polarizability product* $\alpha_p \rho_c$. Figure 1 shows that this is indeed the case for the estimated[1,3] amplitudes $A_{1-\alpha}$ of Ne, N_2, C_2H_4, C_2H_6, and SF_6.

The experimental determination of the anomaly amplitude is complicated by the numerical closeness of the leading singular and analytic exponents in ρ_d, so the estimated $A_{1-\alpha}$ is somewhat dependent on the range of data fit and the functional form assumed. In Fig. 1, we have indicated by circles the estimates obtained by single power-law fits to a subset of the data closest to the critical point. For the more extensive and precise data on Ne and N_2, estimates which include analytic background terms and corrections to scaling are also shown. Extrapolation to the limit of negligible triplet interactions, i.e., $\alpha_p \rho_c \to 0$, clearly reveals that there remains a small anomaly, and hence a residual breaking of particle–hole symmetry for systems with pairwise-additive forces.
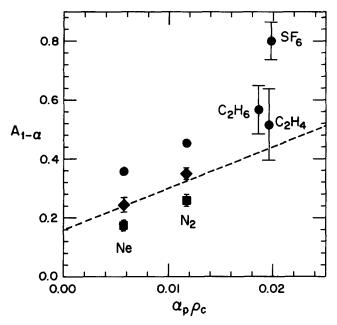
FIG. 1. Experimental values of the diameter anomaly amplitude $A_{1-\alpha}$ as a function of the critical polarizability product for Ne, N_2, C_2H_4, C_2H_6, and SF_6, from Ref. 3. Circles are results from single power-law fits of a subset of the data close to T_c, squares from a sum of linear and singular terms over entire data range, and diamonds are results from fits for Ne and N_2 including in addition a correction-to-scaling term.

Despite the theoretical progress mentioned above, especially that on the statistical mechanical lattice models, it has remained unclear the extent to which particle–hole symmetry should be valid *in fluids* governed either by pair potential Hamiltonians or in the presence of many-body interactions: There has been no theoretical discussion which explains quantitatively the data in Fig. 1. It is the purpose of this paper to examine the correspondence between fluids and magnets in the critical region and to derive the theoretical result shown as a dashed line in Fig. 1, which, without adjustable parameters, agrees quantitatively with the data. We first show in Sec. II A that the mapping from a fluid Hamiltonian to a continuous-spin effective Landau–Ginzburg–Wilson model first discussed on a purely formal basis by Hubbard and Schofield[10] may be carried out explicitly and exactly for a pair-potential fluid. The result is that the spin operators of the LGW model are completely expressible in terms of particular kinds of direct correlation functions of a reference system. Renormalization-group arguments are used to identify that operator which, to leading order in $\epsilon \equiv 4 - d$ (in d spatial dimensions), leads to so-called "revised" or linearly mixed scaling variables. When combined with a simple application of scaling-law arguments, this leads to a closed-form expression for the diameter anomaly amplitude in terms of measurable and calculable material properties. Important insight into the origin of the near particle–hole symmetry in fluids is obtained by the observation that this amplitude is governed by the *density dependence of the second moment of the direct correlation function* of the reference fluid, and in the case of a reasonable such system, a fluid of hard-spheres, this is shown to be an inherently small quantity. Within a simple approximation for the effects of the Axilrod–Teller triplet interactions on the structure of the

reference fluid, we show in Sec. II C that the observed variation in the anomaly amplitude with molecular polarizability may be quantitatively explained, as indicated by the calculated line in Fig. 1. The possibility of extending these results to metallic and semiconducting fluids is discussed in Sec. III.

II. THEORY
A. General results

In the context of an effective continuous-spin Landau–Ginzburg–Wilson Hamiltonian, the existence of revised scaling variables has been shown[7] by Nicoll to be related to the presence of a particular "asymmetric" operator. The precise connection between that operator and the microscopic Hamiltonian of a fluid, although implicitly contained in the work of Hubbard and Schofield,[10] has not until now been given. Consider then a system whose reduced Hamiltonian $\mathcal{H} \equiv H/k_B T$ can be written as a sum of an Ising-like operator $\mathcal{H}_I$ and an asymmetric operator $\omega \mathcal{H}_A$, with ω a small parameter. Let ϕ be the fluctuating field whose average is the order parameter of the fluid. These two Hamiltonians in d dimensions are

$$\mathcal{H}_I = \int d^d x \{ \tfrac{1}{2} \tilde{t}\phi^2(x) + \tfrac{1}{2} \tilde{b}(\nabla\phi)^2 + \tfrac{1}{4!} \tilde{u}\phi^4 - \tilde{h}\phi \} \quad (2)$$

and

$$\mathcal{H}_A = \int d^d x \{ \tfrac{1}{3!} \tilde{t}\phi^3 - \tfrac{1}{2} \tilde{b}\phi^2 \nabla^2 \phi + \tfrac{1}{12} \tilde{u}\varphi^5 \}, \quad (3)$$

where $\tilde{t}$ is the deviation from the mean field critical temperature, and $\tilde{u} > 0$. With $\Xi = \int \mathcal{D}\phi \exp(-\mathcal{H})$ the grand partition function of the system, it may be shown[7] through the use of correlation function identies arising from the "equation of motion" in field theory that to leading order in ω, the free energy $\Omega = -k_B T \ln \Xi$ of the system governed by $\mathcal{H}_I + \omega \mathcal{H}_A$ is equivalent to one governed solely by $\mathcal{H}_I$, but with an effective thermal scaling field

$$\tau = \tilde{t} + \omega \tilde{h}. \quad (4)$$

With this result, the measured amplitude of the diameter anomaly may be related to ω and more easily measured quantities by considering the scaling form[11] of the singular part of the reduced thermodynamic potential per unit volume $g_s(\tau,\mu) \equiv -\beta\Omega/V = \ln \Xi/V$,

$$g_s = D\tau^{2-\alpha} Y_{\pm} \left(E \frac{\zeta}{\tau^{\beta\delta}} \right), \quad (5)$$

where D and E are nonuniversal metric factors, $Y_{\pm}$ are universal scaling functions appropriate above and below the critical temperature, and for the present analysis we need only consider a linearly mixed thermal field τ and pure one-body field ζ of the form

$$\tau \approx \tilde{t} + \omega\zeta, \quad \zeta \approx (\mu - \mu_c)/k_B T \quad (6)$$

with $\tilde{t} \equiv (T_c - T)/T_c$. With these definitions, the thermodynamic density is $\partial g_s/\partial \zeta = \rho - \rho_c$. On the coexistence surface $\zeta = 0$ one finds from the symmetry properties of the scaling functions Y_- that

$$\rho_{\pm} - \rho_c = \pm DE Y'_-(0^+)\tilde{t}^{\beta}$$
$$+ (2-\alpha)DY_-(0)\omega\tilde{t}^{1-\alpha} + \cdots . \quad (7)$$

This allows the identification of the diameter anomaly amplitude as

$$A_{1-\alpha} = \frac{(2-\alpha)\omega D Y_-(0)}{\rho_c} . \tag{8}$$

To relate the quantities on the right-hand side of Eq. (8) to the measured specific heat anomaly we first define for convenience the reduced specific heat density[12] $\widetilde{C} \equiv (k_B T_c/P_c)c_v$, with c_v the specific heat per unit volume, and P_c the critical pressure. Further defining the specific heat amplitude A above T_c via $\widetilde{C} \simeq (A/\alpha)|t|^{-\alpha}$, and computing c_v from the asymptotic scaling equation,

$$c_v \simeq D(2-\alpha)(1-\alpha)Y_+(0)|t|^{-\alpha} \tag{9}$$

we obtain

$$A_{1-\alpha} = \omega \frac{A Z_c Y_-(0)}{\alpha(1-\alpha)Y_+(0)} , \tag{10}$$

where $Z_c \equiv P_c/\rho_c k_B T_c$ is the critical compressibility factor.

Note that the ratio $Y_-(0)/Y_+(0)$ is precisely the universal amplitude ratio conventionally denoted by A_-/A_+. Renormalization-group estimates[13,14] of this ratio give a value of $A_-/A_+ \simeq 1.9$ in $d=3$, close to the value of 2 in four dimensions. Experimental values cluster slightly below a value of $\simeq 2$. The compressibility factor for the simple fluids extrapolates[3] in the limit of negligible three-body forces to $Z_c \simeq 0.32$. Using the accepted value of $\alpha \simeq 0.11$, and typical values for the amplitude A as quoted by Sengers and Sengers,[12] namely $A \simeq 2$ for light noble gases, we find that $A_{1-\alpha} \simeq (13 \pm 1)\omega$.

Having established the relationship between the scaling variables at the critical point and the coefficients in the effective LGW Hamiltonian, it remains to make the connection between the latter and the Hamiltonian of a fluid in order to compute the field-mixing coefficient ω. The total Hamiltonian $\mathcal{H}$ of the fluid is partitioned as $\mathcal{H} = \mathcal{H}_0(\mathbf{r}^N) + \mathcal{H}_1$, where $\mathcal{H}_0$ is that of the reference system, typically consisting of purely repulsive potentials, and

$$\mathcal{H}_1 = \frac{1}{2} \sum_{i \neq j} \phi_1(r_{ij}) , \tag{11}$$

involves the attractive part ϕ_1 of the pair potential. The grand canonical partition function of the full interacting system is

$$\Xi(\mu, T) = \mathrm{Tr}\, e^{-\beta(\mathcal{H}_0 + \mathcal{H}_1) + \beta \mu N} \tag{12}$$

which may be rearranged to yield

$$\Xi(\mu, T) = \Xi_0(\mu_0, T)\langle e^{-\beta \mathcal{H}_1 + \beta(\mu - \mu_0)N} \rangle_0$$

$$= \Xi_0 \Xi_1, \tag{13}$$

the angular brackets denoting an ensemble average with respect to the reference system at chemical potential μ_0.

We introduce the density operator $\rho(\mathbf{r}) = \Sigma_i \delta(\mathbf{r} - \mathbf{r}_i)$ and its Fourier transform $\hat{\rho}(\mathbf{k}) = \Sigma_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i)$, and rewrite $-\beta\mathcal{H}_1$ as

$$\frac{1}{2} N\beta\phi_1(0) - \frac{1}{2V}\beta \sum_{\mathbf{k}} \hat{\rho}(\mathbf{k})\hat{\rho}(-\mathbf{k})\phi_1(\mathbf{k}) . \tag{14}$$

Defining the dimensionless chemical potential $\widetilde{\mu} \equiv \beta[\mu - \mu_0 + \phi_1(0)/2]$ and potential $\hat{v}_1(\mathbf{k}) \equiv -\beta\hat{\phi}(\mathbf{k})$, we obtain the *excess* free energy $\Omega_1 = -k_B T \ln \Xi_1$, where

$$\Xi_1(\mu, T) = \langle \exp\{\widetilde{\mu}\hat{\rho}(0) + \frac{1}{2V}\sum_{\mathbf{k}}\hat{\rho}(\mathbf{k})\hat{\rho}(-\mathbf{k})\hat{v}_1(\mathbf{k})\}\rangle_0 . \tag{15}$$

A Hubbard–Stratonovitch[10] transformation applied to Eq. (15) may be cast in the form

$$\Xi_1 \propto \int \prod d\varphi_{\mathbf{k}} \exp\left\{-\frac{1}{2V}\sum_{\mathbf{k}} \hat{v}_1(\mathbf{k})^{-1}\varphi_{\mathbf{k}}\varphi_{-\mathbf{k}}\right. $$
$$\left. + \frac{1}{V}\frac{\widetilde{\mu}\varphi_0}{\hat{v}_1(0)}\right\}\left\langle \exp\left(\frac{1}{V}\sum_{\mathbf{k}} \varphi_{\mathbf{k}}\hat{\rho}(-\mathbf{k})\right)\right\rangle_0 . \tag{16}$$

In writing this proportionality, we have suppressed all analytic factors coming from the Gaussian transformation since they do not contribute to the thermodynamic singularities at the critical point. It should be remarked that the ability to perform the transformation leading to Eq. (16) depends on the positive definiteness of the transform $\hat{v}(\mathbf{k})$.[15] The freedom to choose the partition of the full configurational energy into a reference potential and perturbing potential in principle allows a choice with $\hat{v}(\mathbf{k}) \geq 0$. Although simple prescriptions for defining $\phi_1(\mathbf{r})$ do not always accomplish this, the values of momentum for which $\hat{v} \leq 0$ are very high, of order the inverse hard core diameter, and are in any event irrelevant to the discussion of critical phenomena.

From the cumulant theorem, the expectation on the right-hand side of Eq. (16) may be written as the exponential of a sum of cumulant averages.,

$$\langle \cdots \rangle_0 = \exp \sum_{n=1}^{\infty} \frac{1}{n!}\frac{1}{V^{n-1}}\sum_{\mathbf{k}_1} \cdots \sum_{\mathbf{k}_n} \hat{G}_n(\mathbf{k}_1,...,\mathbf{k}_n)$$
$$\times \varphi_{-\mathbf{k}_1}\cdots\varphi_{-\mathbf{k}_n}\delta_{\mathbf{k}_1+\mathbf{k}_2+\cdots+\mathbf{k}_n,0} . \tag{17}$$

These reference system correlation functions are the Fourier transforms of thermodynamic derivatives of the form[16]

$$G_n(\mathbf{r}_1,...,\mathbf{r}_n) = \frac{\delta^n \ln \Xi}{\delta \ln z(r_1)\cdots \ln z(r_n)} , \tag{18}$$

where $z(\mathbf{r})$ is the (spatially varying) fugacity. These are the so-called "connected" correlation functions, and their Fourier transforms are nonzero only if the sum of their wave vectors vanishes.

Inserting Eq. (17) into Eq. (16), we conclude that the excess free energy is given by the functional integral Ξ_1,

$$\Xi_1 \propto \int \prod d\varphi \exp(-\mathcal{H}) , \tag{19}$$

where the reduced continuous-spin Hamiltonian $\mathcal{H}$ has the form

$$\mathcal{H} = \sum_{\mathbf{k}} \hat{K}_1(\mathbf{k})\varphi_{-\mathbf{k}}\delta_{\mathbf{k},0}$$
$$+ \frac{1}{2V}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\hat{K}_2(\mathbf{k},\mathbf{k}')\varphi_{-\mathbf{k}'}\varphi_{-\mathbf{k}}\delta_{\mathbf{k}+\mathbf{k}',0}$$
$$+ \frac{1}{3!V^2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\sum_{\mathbf{k}''}\hat{K}_3(\mathbf{k},\mathbf{k}',\mathbf{k}'')$$
$$\times \varphi_{-\mathbf{k}}\varphi_{-\mathbf{k}'}\varphi_{-\mathbf{k}''}\delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}'',0} + \cdots . \tag{20}$$

Using the diagrammatic expansion[16] of the $\hat{G}$s in terms of the direct correlation functions of the reference fluid, we obtain explicit expressions for the kernels $\hat{K}$:

$$\hat{K}_1(\mathbf{k}) = -\left(\frac{\tilde{\mu}}{\hat{v}_1(0)} + \rho_0\right), \tag{21}$$

$$\hat{K}_2(\mathbf{k},\mathbf{k}') = \left(\frac{1}{\hat{C}_2^t(\mathbf{k})} + \frac{1}{\hat{v}_1(\mathbf{k})}\right), \tag{22}$$

$$\hat{K}_3(\mathbf{k},\mathbf{k}',\mathbf{k}'') = -\hat{G}_3(h,h\,',h\,'')(\mathbf{k},\mathbf{k}',\mathbf{k}'')$$

$$= \frac{\hat{C}_3^t(\mathbf{k},\mathbf{k}',\mathbf{k}'')}{\hat{C}_2^t(\mathbf{k})\hat{C}_2^t(\mathbf{k}')\hat{C}_2^t(\mathbf{k}'')}, \tag{23}$$

etc., where in Eq. (23) we have used the Ornstein–Zernike relations to express the $\hat{G}_n$ in terms of the total direct correlation functions $\hat{C}_n^t$, which differ from the more usual excess functions $\hat{C}_n$ by the addition of the ideal gas contribution, i.e., $\hat{C}_n^t = \hat{C}_n - (n-2)!(-1)^n/\rho^{n-1}$.

To identify the relationship between the parameters in the LGW Hamiltonian and the reference system correlation functions, we expand the latter in momenta. Expressing the reference total two-body direct correlation function as $\hat{C}_2^t(\mathbf{k}) = \hat{C}_2^t(0) - b_R k^2 + \cdots$, and the Fourier transform of the attractive part of the potential as $\hat{v}_1(\mathbf{k}) = \hat{v}_1(0) - b_1 k^2 + \cdots$, we conclude that the parameters of the symmetric Hamiltonian are

$$\tilde{t} \equiv \frac{1}{\hat{C}_2^t(0)} - \frac{1}{\beta\hat{\phi}_1(0)} \simeq \frac{1}{\beta_c\hat{\phi}_1(0)}\frac{T_c - T}{T_c} \tag{24}$$

and

$$\tilde{h} = -\frac{\tilde{\mu}}{\beta_c\hat{\phi}_1(0)} + \rho_0 \tag{25}$$

to leading order in $T - T_c$, where T_c is the mean field critical temperature. To the same order, the effective range parameter $\tilde{b}$ is given by

$$\tilde{b} \equiv \frac{b_R}{[\hat{C}_2^t(0)]^2} + \frac{b_1}{[\beta_c\hat{\phi}_1(0)]^2}. \tag{26}$$

The effective Hamiltonian in Eq. (20) has odd (and momentum dependent) terms just like those in the simplified field-theoretic model Eq. (3), but they do not appear in the precise linear combination found in Nicoll's Hamiltonian $\mathcal{H}_A$. There thus arises the issue of identifying within the continuous-spin fluid Hamiltonian the particular terms which give rise to field-mixing, in other words, the *projection* of Eq. (20) onto the field-mixing operator. For this purpose, we note on general grounds and independent of the arguments which lead to Eq. (4) that in a scaling description of the behavior of the order parameter M near the critical point, we expect the amplitude of this mixing operator v_m to appear in the form

$$M = M_0 t^\beta W\left(E'\frac{h}{t^{\beta\delta}}, F'\frac{v_m}{t^{\lambda_m/\lambda_2}}\right). \tag{27}$$

the parameters M_0, E', and F' are nonuniversal metric factors, W is the universal scaling function, λ_m is the mixing eigenvalue, and λ_2 is the thermal eigenvalue. As long as the mixing perturbation is irrelevant, $\lambda_m < 0$, and we may expand the scaling function along the critical isochore as $t \to 0$, obtaining

$$M \simeq M_0 t^\beta [1 + M_1 t^{-\lambda_m/\lambda_2} + \cdots]. \tag{28}$$

Thus, an energy-like diameter anomaly, *viewed as a correc-*

tion to scaling, requires $\lambda_m = -\lambda_2(1 - \alpha - \beta)$. With the ϵ-expansion results $\lambda_2 \simeq 2 - \epsilon/3$, $\alpha \simeq \epsilon/6$, and $\beta \simeq 1/2 - \epsilon/6$, we find $\lambda_m \simeq -1 + \epsilon/6 + O(\epsilon^2)$.

Renormalization-group analyses[8,17] of momentum-independent operators show that no irrelevant eigenvalues of odd perturbations have this ϵ expansion. Thus, although the mixing term $\mathcal{H}_A$ has both momentum-independent and momentum-dependent components, *it has no projection on momentum-independent odd operators* to order ϵ. Therefore, under the assumption that the starting fluid Hamiltonian (20) is sufficiently close to the fixed-point Hamiltonian for a linear analysis to be valid, it is not possible to determine the field-mixing in fluids by examining the zero momentum values of the reference correlation functions $\hat{K}_n$. Indeed, Nicoll and Zia have shown that the operator $\varphi^2\nabla^2\varphi$ (which is actually mixed with φ^5), is precisely that responsible for the eigenvalue λ_m, at least to first order in an ϵ expansion. This implies that it is precisely this term of the three in $\mathcal{H}_A$ upon which we must focus attention to find field mixing. Considering the long-wavelength expansion of the three-body direct correlation function and invoking the thermodynamic identity

$$\frac{d\hat{C}_2^t(\mathbf{k})}{d\rho} = \hat{C}_3^t(\mathbf{k}, -\mathbf{k}, 0) \tag{29}$$

we find $\hat{K}_3(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = \hat{K}_3(0,0,0) - g_3\Sigma k_i^2$, where

$$g_3 = -\frac{(d\hat{C}_2^t(0)/d\rho)}{[\hat{C}_2^t(0)]^4} + \frac{1}{2}\frac{(db_R/d\rho)}{[\hat{C}_2^t(0)]^3}. \tag{30}$$

By comparison with the Fourier transform of the $\varphi^2\nabla^2\varphi$ term in the perturbing asymmetric Hamiltonian, $-\omega\tilde{b}/2$, we identify

$$\omega = g_3/\tilde{b}, \tag{31}$$

so that the field-mixing coefficient is expressible completely in terms of the reference system's correlation functions and the properties of the attractive potential. When combined with Eq. (10) we have an explicit numerical prediction for the diameter amplitude, $A_{1-\alpha} \simeq (13 \pm 1)(g_3/\tilde{b})$.

We shall see in Sec. II B that a sensible choice of the reference chemical potential is exactly that which sets the first term in Eq. (30) equal to zero, so that *a nonzero g_3 arises from the density dependence of the range of the direct correlation function* of the reference system. Within the conventional Ornstein–Zernike[18] view the second moment of $C_2(r)$ is governed by the range of the attractive part of the potential, and hence is independent of density. Here, for pair-potential fluids, we see that the residual density dependence arising from the hard-core exclusion governs the field mixing. Note that the terms in the full field-theoretic Hamiltonian $\mathcal{H}$ which scale like $(\text{momentum})^2$ may be combined together to give a coefficient $\tilde{b}(1 + 2\omega\phi)$, which can be viewed as a series expansion of an effective range parameter in the neighborhood of the critical density.

B. Application to a model fluid

The explicit application of the results of Sec. II to fluids requires a choice of reference system, and it is natural to take the potential $\mathcal{H}_0$ to be that of the hard-sphere fluid, namely,

$$\mathcal{H}_0(\mathbf{r}^N) = \frac{1}{2}\sum_{i\neq j}\phi_0(r_{ij}),\qquad (32)$$

where $\phi_0 = \infty$ for $r \leqslant \sigma$ and vanishes otherwise. The correlation functions of interest are known analytically within fairly accurate approximations, and to compute the field-mixing parameters, we shall evaluate those correlations at the mean field critical point, whose density and temperature are easily determined from the $\mathbf{k} = 0$ terms in the effective field theory (19).

From the mean field analysis of the LGW Hamiltonian the critical point is at a density ρ_c and inverse temperature β_c for which $\hat{K}_2(0,0) = \hat{K}_3(0,0,0) = 0$, that is to say, the vanishing of the leading-order relevant even and odd operators. These conditions are

$$\hat{C}_2'(0) = [\hat{C}_2(0)]_{\rho_c} - \frac{1}{\rho_c} = \beta_c\hat{\phi}_1(0) \qquad (33)$$

and

$$\frac{d\hat{C}_2'(0)}{d\rho} = \left(\frac{d\hat{C}_2(0)}{d\rho}\right)_{\rho_c} + \frac{1}{\rho_c^2} = 0. \qquad (34)$$

In the Percus–Yevick approximation, the direct correlation function $C_2(r)$ is known[19] to be

$$C_2(r) = \begin{cases} -\lambda_1 - 6\eta\lambda_2 r - \tfrac{1}{2}\eta\lambda_1 r^3, & r < \sigma, \\ 0, & r > \sigma, \end{cases} \qquad (35)$$

where $\lambda_1 = (1+2\eta)^2/(1-\eta)^4$, $\lambda_2 = -(1+\eta/2)^2/(1-\eta)^4$, and $\eta = \pi\rho\sigma^3/6$, σ being the hard-core diameter. This yields a critical density $\rho_c\sigma^3 \simeq 0.246$, and a critical temperature $-\beta_c\hat{\phi}(0) \simeq 11.2\sigma^3 = -\hat{C}_2'(0)$, at which the density derivative of the second moment of C_2 is $db_R/d\rho \simeq -1.36\sigma^8$, while b_R itself is $-0.665\sigma^5$. Note that the condition for criticality (34) renders the field-mixing quantity g_3 (30) equal to its second term alone. Although we have evaluated the reference correlation functions at the mean field critical density, their values are changed little (i.e., 5%–10%) by a shift of the reference system density to the critical density obtained in more refined calculations.[20]

The treatment of the short-distance behavior of the attractive part of the pair potential is somewhat arbitrary, but of little numerical significance for both the integrated strength of the potential and its range. We have adopted the simple Weeks–Chandler–Andersen[21] approach of extending the potential from its minimum to the origin with constant amplitude. In particular, we consider the Lennard-Jones potential

$$\phi_{LJ}(x) = 4\epsilon(x^{-12} - x^{-6}), \qquad (36)$$

with $x = r/\sigma$, which has a transform

$$\hat{\phi}_{LJ}(k) = -15.79\epsilon\sigma^3 - 7.68\epsilon\sigma^5 k^2 + \cdots. \qquad (37)$$

These results give the range $\tilde{b} \simeq 0.038\sigma^{-1}$. Combining all of the above results, we estimate the field-mixing coefficient to be $\omega \simeq 0.012$, so that intrinsic diameter anomaly amplitude in a pair-potential fluid is

$$A_{1-\alpha} \simeq 0.16 \pm 0.02. \qquad (38)$$

The uncertainty we have indicated is that associated with the known uncertainties in the exponents, critical amplitudes, and compressibility factor appearing in Eq. (10). As shown in Fig. 1, this prediction is in excellent agreement with the data in the limit $\alpha_p\rho_c \to 0$, and lends strong support to the identification of the field-mixing operator proposed here.

C. Fluids with many-body interactions

We have seen in Sec. II A that the field-mixing operator may be identified with the leading term in a small-momentum expansion of the transform of a reference three-particle direct correlation function, and hence with the long-range behavior of that function in real space. Clearly, the long-range components of three-body *interactions* will have an important contribution to this correlation function, and for insulating fluids it is well established that the relevant asymptotic behavior is that given by Axilrod and Teller,[22] namely

$$V_{AT}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = V_3 \frac{3\cos\theta_1\cos\theta_2\cos\theta_3 + 1}{r_{12}^3 r_{13}^3 r_{23}^3}. \qquad (39)$$

Here, the amplitude $V_3 = (9/16)\alpha_p^3\Delta$, Δ being a characteristic electronic excitation energy, the angle θ_i is that at the ith vertex of the triangle formed by the three particles, and the r_{ij} are the leg lengths.

Under the assumption that such interactions are weak, we have explored incorporating their effects *into the reference hard-sphere system* according to a low-order virial approximation. Let us recall the essential result obtained by Casanova et al.[23] for the lowest-order density expansion of the effective pair potential in a fluid with weak three-body interactions. If $\tilde{f}(12) = \exp[-\tilde{\phi}(12)/k_BT] - 1$ is the Mayer f function of the effective potential at density ρ, $f_0(12) = \exp[-\phi_0(12)/k_BT] - 1$ is that of the bare potential, and $f(123) = \exp[-\psi(123)/k_BT] - 1$ is that of the triplet potential ψ, then

$$\tilde{f}(12) \simeq f_0(12) + \rho e_0(12)$$

$$\times \int d\mathbf{r}_3\, e_0(13)e_0(23)f(123) + O(\rho^2), \qquad (40)$$

where $e(ij) = f(ij) + 1$. Linearization of Eq. (40) in the small shift $\delta\phi \equiv (\tilde{\phi} - \phi_0)/k_BT$ and small ψ/k_BT gives

$$-\beta\delta\phi(12) \simeq -\beta\rho\int d\mathbf{r}_3\, e_0(13)e_0(23)\psi(123). \qquad (41)$$

For the hard-sphere ϕ_0, the effect of the integration over $\mathbf{r}_3$ is simply to define a new triplet potential which vanishes for configurations corresponding to overlap of the spheres. If we incorporate the effects of that new potential on the reference system by means of a mean spherical *ansatz*, then in Fourier space we obtain for the case of the Axilrod–Teller potential

$$\hat{C}_2'(\mathbf{k}) = [\hat{C}_2'(\mathbf{k})]_{HS} - \rho\beta\hat{\mathscr{V}}_{AT}(\mathbf{k}, -\mathbf{k}, 0), \qquad (42)$$

where $\mathscr{V}$ is the AT function modified to satisfy the above overlap condition. The correlation function relationship (29) implies that the three-body direct correlation function then behaves as

$$\hat{C}_3'(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = [\hat{C}_3'(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)]_{HS} - \beta\hat{\mathscr{V}}_{AT}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3). \qquad (43)$$

To determine the small-k expansion of the Fourier transform of the Axilrod–Teller potential, we may use the known[23] analytical results for the integral

$$J(r_{12}) \equiv \int d^3r_3 \, e_0(13) e_0(23) \mathscr{V}_{AT} , \qquad (44)$$

For the case of a hard-sphere reference potential,

$$J(r) = \frac{2\pi V_3}{r^6} I(r) , \qquad (45)$$

where $I = (1/4)(r/\sigma)^4 - (1/24)(r/\sigma)^6$ for $r \leqslant 2\sigma$, and $I = 4/3$ for $r \geqslant 2\sigma$. To compute the Fourier transform, we note that

$$\int_\sigma^\infty d^3r \, e^{-i\mathbf{k} \cdot \mathbf{r}} J(r) = \hat{\mathscr{V}}_{AT}(\mathbf{k}, -\mathbf{k}, 0) . \qquad (46)$$

Defining the range parameter b_3 of this potential as

$$\hat{\mathscr{V}}_{AT}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \hat{\mathscr{V}}_{AT}(0,0,0) - b_3 \sum_i k_i^2 + \cdots , \qquad (47)$$

we may identify b_3 as one-half of the coefficient of $-k^2$ in the small-k expansion of Eq. (46). We find

$$b_3 = -\frac{119\pi^2}{90} \frac{V_3}{\sigma} . \qquad (48)$$

Note that within a Lennard-Jones model, the amplitude of the r^{-6} attraction between atoms is $4\epsilon\sigma^6 = (3/4)\alpha_p^2 \Delta$, so $V_3 = 3\epsilon\alpha_p\sigma^6$. The field-mixing quantity $db_R/d\rho$ has thus acquired an additional contribution from triplet interactions,

$$\frac{db_R}{d\rho} \simeq \left(\frac{db_R}{d\rho} \right)_{HS} - 112.6\alpha_p\rho_c , \qquad (49)$$

where we have used the mean field results for the critical temperature and density to recast the expression purely in terms of $\alpha_p\rho_c$. Combining all of these results, we arrive at the final prediction for the diameter anomaly amplitude,

$$A_{1-\alpha} = (0.16 \pm 0.02) + (14 \pm 1)\alpha_p\rho_c , \qquad (50)$$

which, as shown in Fig. 1, is in good agreement with the available experimental data. The amplitude of SF_6 appears to deviate significantly from the trend exhibited by the other fluids. We have no immediate explanation for this, although the possibility of artifacts due to the presence of wetting layers in the sample cell cannot be ruled out.[3,24]

It is significant to note that in the penetrable-sphere[5] model the sign of the anomaly is also like that found in real fluids, and this is consistent with the fact that this model is equivalent[25] to a fluid with attractive even-body interactions and repulsive odd-body interactions, like the Axilrod–Teller potential.

Finally, we have carried through the present calculation of the diameter anomaly within the context of certain two-dimensional lattice models for which exact results are known.[2] The results of the approximate calculation are within ~30% of the exact results, and we expect a closer correspondence in three dimensions, where fluctuations are less important.

III. CONCLUSIONS AND EXTENSIONS

From the early work on model systems to more recent studies with the renormalization group, it has become clear that a central concept in the fluid–magnet correspondence is that of *intermolecular potentials that are functions of thermo-*

dynamic variables. Most relevant to the nature of the scaling variables is the situation in which the effective potential, or the thermal scaling field, depends on the *chemical potential.* This was seen in the original work on penetrable-sphere models,[5] various decorated-lattice calculations,[6] and also in phenomenological studies.[11] The conjectures for the role of many-body interactions in such effective potentials which were advanced[2] on the basis the statistical mechanics of *lattice models* have been verified here for real continuum systems. The quantitative agreement achieved here with data on insulating fluids suggests that the ultimate origin of broken particle–hole symmetry in fluids has now been identified.

It remains an important problem to extend these results to the cases of semiconducting and metallic systems in light of recent studies of liquid–vapor equilibria in both Hg and in the alkali metals Cs and Rb.[26] All of these fluids exhibit extremely large amplitude diameter anomalies compared to the insulating fluids discussed here. An essential aspect of both kinds of conducting fluids is the strong dependence on thermodynamic state of their electronic properties in the neighborhood of the critical point, especially in the alkali metals for which the metal–nonmetal transition density is nearly ρ_c. This rapid variation in electronic structure implies[27] a corresponding variation in the nature of ion–ion interactions.

We suggest that the framework developed above for insulating fluids may provide a means of understanding those observations. In particular, note that while a metallic fluid is formally a two-component system, consisting of ions and electrons, the Born–Oppenheimer separation of ionic and electronic motions allows for the elimination of the electronic degrees of freedom in favor of state-dependent, many-ion interactions mediated by the electrons.[28] The linear response of the electron gas gives rise to screened pair potentials, while the nonlinear response controls the multi-ion interactions. The relationship between this nonlinear susceptibility and the properties of the three-particle direct correlation function may be the key to an understanding of the extreme liquid–vapor asymmetry exhibited by the metallic systems. Detailed calculations, which we have not undertaken, must account not only for the intrinsic state dependence of these effective potentials, but also for the proximity of the metal–nonmetal transition to the liquid–vapor critical point, and the semidegenerate nature of the electron gas.

[1] R. E. Goldstein, A. Parola, N. W. Ashcroft, M. W. Pestak, M. H. W. Chan, J. R. de Bruyn, and D. A. Balzarini, Phys. Rev. Lett. **58**, 41 (1987).
[2] R. E. Goldstein and A. Parola, Phys. Rev. A **35**, 4770 (1987).
[3] M. W. Pestak, R. E. Goldstein, M. H. W. Chan, J. R. de Bruyn, D. A.

Balzarini, and N. W. Ashcroft, Phys. Rev. B **36**, 599 (1987).

[4]For a review of these previous theoretical discussions, see R. E. Goldstein and A. Parola (preprint).

[5]B. Widom and J. S. Rowlinson, J. Chem. Phys. **52**, 1670 (1970); J. S. Rowlinson, Adv. Chem. Phys. **41**, 1 (1980).

[6]N. D. Mermin, Phys. Rev. Lett. **26**, 169, 957 (1971).

[7]J. F. Nicoll, Phys. Rev. A **24**, 2203 (1981).

[8]J. F. Nicoll and R. K. P. Zia, Phys. Rev. B **23**, 6157 (1981).

[9]L. Cailletet and E. Matthias, C. R. Acad. Sci. **102**, 1202 (1886); **104**, 1563 (1887).

[10]J. Hubbard and P. Schofield, Phys. Lett. A **40**, 245 (1972).

[11]J. J. Rehr and N. D. Mermin, Phys. Rev. A **8**, 472 (1973).

[12]J. V. Sengers and J. M. H. Levelt Sengers, Annu. Rev. Phys. Chem. **37**, 189 (1986).

[13]A. Aharony and P. C. Hohenberg, Phys. Rev. B **13**, 3081 (1976).

[14]C. Bervillier, Phys. Rev. B **34**, 8141 (1986).

[15]See the corresponding discussion for the case of Ising models; M. E. Fisher, in *Phase Transitions*, edited by F. H. W. Hahne (Springer, New York, 1983), p. 1.

[16]G. Stell, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5b, p. 205.

[17]C. Vause and J. Sak, Phys. Rev. A **21**, 2099 (1980).

[18]J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford, New York, 1982), p. 16.

[19]E. Thiele, J. Chem. Phys. **39**, 474 (1963); M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).

[20]Use of the more accurate Verlet–Weiss form of the direct correlation function for hard spheres [L. Verlet and J. J. Weis, Phys. Rev. A **5**, 939 (1972)] leads to results within 10% of those obtained with the Percus–Yevick approximation.

[21]J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[22]B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

[23]G. Casanova, R. J. Dullah, D. A. Jonah, J. S. Rowlinson, and G. Saville, Mol. Phys. **18**, 589 (1970).

[24]M. R. Moldover and R. W. Gammon, J. Chem. Phys. **80**, 528 (1984). See also R. F. Kayser, J. W. Schmidt, and M. R. Moldover, Phys. Rev. Lett. **54**, 707 (1985).

[25]B. Widom, J. Chem. Phys. **54**, 3950 (1971).

[26]S. Jüngst, B. Knuth, and F. Hensel, Phys. Rev. Lett. **55**, 2160 (1985); F. Hensel (private communciation).

[27]R. E. Goldstein and N. W. Ashcroft, Phys. Rev. Lett. **55**, 2164 (1985).

[28]See, for example, N. W. Ashcroft and D. Stroud, Solid State Phys. **33**, 1 (1978).