be described by (4) and (4′) with $\nu = 0.64 \pm 0.02$ and $\xi_0 = 1.6 \pm 0.2$ Å for $T > T_c$ and with $\nu' = 0.65 \pm 0.02$ and $\xi_0' = 0.78 \pm 0.09$ Å for $T < T_c$. The agreement of ν and ν' and also the fact that the new results for ν, ν', ξ_0, and ξ_0' agree well with our earlier work[5] are evidence for the reliability of the matching process used to construct the curves in Fig. 1.

The ratio $\xi_0/\xi_0' = 2.05 \pm 0.22$ is in good agreement with the values 1.96 and 1.91 calculated by Tarko and Fisher[16] and Brézin, Le Guillou, and Zinn-Justin,[18] respectively.

We used (1) and (2) with the values of $D(q^2\xi^2, \theta)$ to find $I(0)$ for each scattering curve. Since we had determined $I_e Ad$ previously,[5] we then could compute $(\rho/\rho_c)^2 P_c K_T$. From our values of $(\rho/\rho_c)^2 P_c K_T$, we found that $\Gamma = 0.066 \pm 0.01$, $\Gamma' = 0.0130 \pm 0.002$, $\gamma = 1.22 \pm 0.03$, and $\gamma' = 1.23 \pm 0.03$. These results are in good agreement with those we presented in Ref. 5.

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[1] J. E. Thomas and P. W. Schmidt, J. Chem. Phys. 39, 2506 (1963).

[2] J. E. Thomas and P. W. Schmidt, J. Amer. Chem. Soc. 86, 3554 (1964).

[3] H. D. Bale, B. C. Dobbs, J. S. Lin, and P. W. Schmidt, Phys. Rev. Lett. 25, 1556 (1970).

[4] J. S. Lin and P. W. Schmidt, Phys. Lett. 48A, 75 (1974).

[5] J. S. Lin and P. W. Schmidt, Phys. Rev. A (to be published). (Preprints available from P. W. Schmidt.)

[6] H. B. Tarko and M. E. Fisher, Phys. Rev. B (to be published), Eqs. (15) and (16).

[7] Tarko and Fisher, Ref. 6, Sect. 4.2.

[8] M. E. Fisher, in *Critical Phenomena, Proceedings of the International School of Physics "Enrico Fermi," Course LI,* edited by M. S. Green (Academic, New York, 1971), p. 36.

[9] B. Widom and F. H. Stillinger, J. Chem. Phys. 58, 621 (1973), Table I; H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, London, 1971), p. 46, Eq. (3.15).

[10] Stanley, Ref. 9, p. 196, Eq. (12.29).

[11] M. E. Fisher, J. Math. Phys. (N. Y.) 5, 959 (1964), Eq. (5.3a).

[12] C. A. Tracy and B. M. McCoy, Phys. Rev. Lett. 31, 1500 (1973).

[13] V. P. Warkulwiz, B. Mozer, and M. S. Green, Phys. Rev. Lett. 32, 1410 (1974).

[14] Tarko and Fischer, Ref. 6, Eq. (7.5).

[15] Tarko and Fischer, Ref. 6, Eq. (5.26).

[16] H. B. Tarko and M. E. Fisher, Phys. Rev. Lett. 31, 929 (1973).

[17] G. W. Mulholland, J. A. Zollweg, and J. M. H. Levelt-Sengers, to be published.

[18] E. Brézin, J.-C. Le Guillou, and J. Zinn-Justin, Phys. Lett. 47A, 285 (1974).

Dielectric Constant and Mean Polarizability in the Critical Region

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It is found that the static dielectric constant and mean polarizability of a simple nonpolar fluid share the singularity of the internal energy at the critical point. This singularity can also be expected in the index of refraction at nonzero frequencies along with a more singular term that vanishes as the frequency goes to zero.

In studying the properties of fluids near the critical point, it is extremely difficult to make direct thermodynamic measurements of number density ρ with high precision. To gain information about ρ, many experimentalists therefore resort to measurements of the index of refraction $n(\omega)$ or dielectric constant $\epsilon = n^2(0)$, assuming a nonsingular relation between changes in $n(\omega)$ and changes in ρ based upon the Lorentz-Lorenz equation or some simple variant of it. (Here ω is frequency.)

Such a stratagem has permitted changes in ρ to be assessed with much higher precision over most of the critical region[1] than could be achieved through direct measurement, but it also has raised the question of whether there is any singularity at the critical point in n itself. If there is, and if it were not properly taken into account, then the use of n to determine ρ could give rise to errors in the apparent critical-point relations between ρ and other quantities. The resulting uncertainty has become an important concern of experimentalists probing increasingly subtle aspects of critical phenomena.[2]

In this note we give a theoretical analysis of the static dielectric constant ϵ for a simple polarizable but nonpolar fluid. Our conclusions are based primarily on models[3,4] in which the polarizability of an isolated molecule can be used as a parameter of smallness; to third order in polarizability we find that the most singular contribution to ϵ in the critical region shares the critical behavior of the internal energy per particle, u. In such models there is no way that the singularities of the higher-order terms can cancel those of the lower-order terms for arbitrary fixed polarizability since we expand in that quantity. Moreover, for particles with sufficiently low polarizability the singularity we investigate would be the only one detectable in the critical region. We are further able to include the effect upon polarizability of pair overlap and exchange terms that are absent in the low-order terms of the polarizability expansion developed by early workers[3,4] but included in more recent treatments[5] of polarizable fluids. We find that these terms do not alter the singularity. We therefore conclude that *ϵ itself can be expected to remain finite at the critical point but that $\partial\epsilon/\partial T$ can be expected to become infinite*, where T is temperature. This is our main result. In addition we find that the mean polarizability per particle also includes a term that behaves like u in the critical region, and we note that such a term can also be expected in $n(\omega)$ for any ω.

Our work extends an earlier analysis of $n(\omega)$ by Hocken and Stell[6] that was restricted to the term of second order in the polarizability expansion of the Lorentz-Lorenz function. That term, which was found to have a sharper singularity than that of u for small $k\xi$ (ξ is correlation length and k is magnitude of the wave vector of incident radiation) vanishes as $k \to 0$. Thus that analysis did not extend to high enough order in polarizability to probe the singular behavior of the static ϵ.

We shall first set forth some details of our conclusions and then sketch their demonstration. Throughout we let θ rather than the usual α refer to polarizability simply to avoid confusion with the critical exponent α; θ_0 will denote the polarizability of an isolated molecule while ΔF_{CM} will denote the deviation of the Clausius-Mosotti function from $4\pi\theta_0/3$. Thus $\Delta F_{\mathrm{CM}} = (\epsilon - 1)/[(\epsilon + 2)\rho] - 4\pi\theta_0/3$. It is convenient to think of ΔF_{CM} as a background term $\Delta F_{\mathrm{CM},B}$ that is analytic in the two variables ρ and T about the critical point (ρ_c, T_c) plus a term $\Delta F_{\mathrm{CM},S}$ that is singular at (ρ_c, T_c). Letting $t = T - T_c$ we find that for $\rho = \rho_c$, $t > 0$, one should expect $\Delta F_{\mathrm{CM},S}$ to remain finite[7] but have infinite derivatives with respect to t, to give, when added to $\Delta F_{\mathrm{CM},B}$,

$$\Delta F_{\mathrm{CM}} \approx A_1 t^{1-\alpha} + A_2 t + \dots . \tag{1}$$

Here the A_i are constants and α is the specific-heat exponent. (In many fluids α seems to be about $\frac{1}{8}$.) The behavior along the critical isotherm ($t = 0$, $\rho \neq \rho_c$) or coexistence curve ($-t^{\beta} \sim \rho - \rho_c$) is not as readily analyzed, but under the simplest tenable scaling assumptions we find a very weak singularity. Along with an expected M^2 contribution from $\Delta F_{\mathrm{CM},B}$ it gives

$$\Delta F_{\mathrm{CM}} \approx B_1 M^2 + B_2 M^{(1-\alpha)/\beta}, \tag{2a}$$

where $M = |\rho - \rho_c|/\rho_c$. Correspondingly, along the coexistence curve we find[8]

$$\Delta F_{\mathrm{CM}} \approx A_1' t^{2\beta} + A_2' t^{1-\alpha} + \dots . \tag{2b}$$

For $n(\omega)$, the situation cannot be so easily summarized because of the difference in behavior between the small-(k/κ) and the large-(k/κ) cases, where κ is the inverse correlation length in the problem. In the regime of k/κ small, $\kappa \to 0$, Hocken and Stell found the dominant singularity in the deviations from the Lorentz-Lorenz function $\Delta F_{\mathrm{LL}} \equiv (n^2 - 1)[(n^2 + 2)\rho] - 4\pi\theta_0/3$ to be given by

$$\Delta F_{\mathrm{LL},S} = Bk^2 t^{(-1+\eta)\nu} + \dots \tag{3}$$

for $t > 0$, $\rho = \rho_c$, where $\kappa \sim t^{\nu}$, and η is the exponent that measures the decay of the pair-correlation function at the critical point. The arguments of this note suggest in addition that the weaker singularity that remains when $\omega \to 0$ is present for all ω. Summing these two contributions to $\Delta F_{\mathrm{LL},S}$ gives, for k/κ small, $t > 0$, $\rho = \rho_c$,

$$\Delta F_{\mathrm{LL},S} = Bk^2[t^{(-1+\eta)\nu} + \dots] + At^{1-\alpha} + \dots, \tag{4}$$

where B is $O(\theta_0^2)$ and A is $O(\theta_0^3)$. If (4) held for all k as $\kappa \to 0$, $\Delta F_{\mathrm{LL},S}$ would thus diverge at the critical point, and for any $k \neq 0$, the $t^{1-\alpha}$ term would be negligible for sufficiently small t. However, the $O(k^2)$ term in fact remains finite at the critical point, as discussed in Ref. 6.

For clarity of presentation we shall begin our analysis for a classical system of particles such that each particle carries a fixed scalar polarizability θ_0 and no permanent dipole or multipole moments. When the pair potential between particles depends only upon the distance r between particles, ΔF_{CM} then has the form[3,4]

$$\Delta F_{\text{CM}} = (4\pi\theta_0{}^3/3)(I_2 + J_3) + O(\theta_0{}^4), \qquad (5a)$$

where I_2 and J_3 are the volume integrals [$d(i)$ is our notation for $d^d r_i$]

$$I_2 = \rho \int d(2) g_2(12) \vec{e} \cdot \overleftrightarrow{\mathrm{T}}(12) \cdot \overleftrightarrow{\mathrm{T}}(21) \cdot \vec{e}, \qquad (5b)$$

$$J_3 = \rho^2 \int d(2) d(3) g_3(123) \vec{e} \circ \overleftrightarrow{\mathrm{T}}(12) \cdot \overleftrightarrow{\mathrm{T}}(23) \cdot \vec{e}. \qquad (5c)$$

Here $\overleftrightarrow{\mathrm{T}}(12)$ is the dipole tensor $3(\vec{r}_{12}\vec{r}_{12})r_{12}{}^{-5} - \overleftrightarrow{\mathrm{I}} r_{12}{}^{-3}$, $\vec{e}$ is a unit vector, $g_2(12)$ is the radial distribution function, and $g_3(123)$ is the triplet distribution function. The $g_2(12)$ can be written more simply as $g(r)$ and the I_2 as the scalar integral $8\pi\rho\int_0^\infty g(r) r^{-4} dr$. For molecules with hard cores of diameter R, $g_2(ij) = 0$ and $g_3(ijk) = 0$ for $r_{ij} < R$, so that $\overleftrightarrow{\mathrm{T}}(ij)$ can be replaced by $\overleftrightarrow{\mathrm{T}}_R(ij)$ in (5), where $\overleftrightarrow{\mathrm{T}}_R = \overleftrightarrow{\mathrm{T}}$ for $r_{ij} > R$ and $T_R = 0$ for $r_{ij} < R$. Our analysis is at its simplest for hard-core particles. In particular, for the pair potential $\varphi(r) = \infty$ for $r < R$, $\varphi(r) = -\epsilon(R/r)^6$ for $r > R$, $-\frac{1}{4}\epsilon R^6 I_2$ is exactly the configurational internal energy per particle, u. For other reasonable potentials it is likewise to be expected that I_2 will share its dominant singularity with u, since for fixed small r, $g(r)$ itself can be expected[6,9] to vary as u with ρ and T in the critical region. Hence any integral with an integrand of $g(r)$ times a function that falls off rapidly with increasing r can be expected to have this same singularity unless some special cancelation occurs to repress it. We can verify this explicitly for the Lennard-Jones potential $4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, for which I_2 can be exactly expressed in terms of the u, pressure p, and kT, where k is Boltzmann's constant:

$$-2\epsilon\sigma^6 I_2 = 4u - (p/\rho) + kT. \qquad (6)$$

In the critical region, we decompose u into an analytic background part u_B and a singular part u_S and write for $\rho = \rho_c$, $t \geqslant 0$, $u_S \approx \text{const}\, t^{1-\alpha}$. Along the coexistence curve we write $u_S \approx \text{const} \times |-t|^{1-\alpha'}$, while along the critical isotherm we write $u_S \approx \text{const} M^{(1-\alpha^0)/\beta}$, where we assume that $(-t)^\beta \sim M$ describes the coexistence curve in the critical region.[8] Simple scaling considerations then lead one to expect $\alpha = \alpha' = \alpha^0$. The critical behavior of p/ρ is much less singular than that of u (for example, one expects $p_S \sim t^{2-\alpha}$ for $\rho = \rho_c$, $t > 0$, where p_S is the singular part of p) and hence can be neglected in (6).

In the hard-core case we can rewrite J_3 in the form

$$J_3 = I_3{}^{(2)}[h] + I_3{}^{(3)}[h_3] - I_2, \qquad (7)$$

where $I_3{}^{(2)}[h]$ is the integral

$$I_3{}^{(2)}[h] = \rho \int d(2) d(3) \vec{e} \cdot \overleftrightarrow{\mathrm{T}}_R(13) \cdot \overleftrightarrow{\mathrm{T}}_R(32) \cdot \vec{e}[h(12) + \delta(12)/\rho]$$

involving the two-particle cluster function $h(r) = g(r) - 1$, and $I_3{}^{(3)}$ is a similar integral that involves h_3, the three-particle cluster function. We treat $I_3{}^{(3)}$ by observing that in a lattice gas[10] or any system with lattice-gas (hole-particle) symmetry about ρ_c, $I_3{}^{(3)}$ is identically zero when $\rho = \rho_c$ for all $T \geqslant T_c$. The dominant critical singularities of real fluids appear to have this lattice-gas symmetry about ρ_c, with deviations from it appearing only in higher-order terms. Thus we shall neglect any such deviations in considering the leading singularity of ϵ, assuming that $I_3{}^{(3)} \approx 0$ when $\rho = \rho_c$ for all $T > T_c$. The I_2 we have already analyzed. Similar analysis of $I_3{}^{(2)}$ shows that it can be rewritten as a volume integral over $h(12) + \delta(12)/\rho$ times a short-ranged function of r. Thus it too behaves like I_2, sharing the singularities of u. As with I_2, one clearly must also expect these singularities for potentials that do not have perfectly hard cores.

The above considerations immediately yield Eq. (1). When $\rho \neq \rho_c$, $I_3{}^{(3)}$ is no longer zero even for a system with lattice-gas symmetry. However we can invoke the usual scaling assumption that if a singular function (in this case $\Delta F_{\text{CM},\,S}$) goes as t^x for $M = 0$, $t \to 0$, it will go as $M^{x/\beta}$ along both the coexistence curve and critical isotherm. This assumption yields Eq. (2).[8] (Simply neglecting $I_3{}^{(3)}$ altogether yields the same result.)

The major difference between the model considered above and a system of real monatomic molecules lies in the fact that the polarizability carried by a real molecule is only a fixed scalar θ_0 when the molecule is far from neighboring molecules. More generally it is a tensor $\overleftrightarrow{\theta}$ that depends upon the coordinates of neighboring molecules and hence changes from moment to moment. A generalization of the model that involves such a nonconstant polarizability has been studied,[4] and for it ΔF_{CM} is still given by (5a) with I_2 replaced by $A_0 I_2$, where A_0 is a constant of order unity characteristic of the molecule. In this model[4] the thermal average $\langle\overleftrightarrow{\theta}\rangle$ has the form[4,11]

$$\langle\overleftrightarrow{\theta}\rangle = \theta_0 \overleftrightarrow{\mathrm{I}} + \theta_0{}^3(A_0 - 1) I_2 \overleftrightarrow{\mathrm{I}} + O(\theta_0{}^4), \qquad (8)$$

with $\overleftrightarrow{\mathrm{I}}$ a second-rank unit tensor. Thus the components of $\langle\overleftrightarrow{\theta}\rangle - \theta_0\overleftrightarrow{\mathrm{I}}$, with ΔF_{CM}, behave like u in the critical region. The most recent and accurate assessments[5] of $\overleftrightarrow{\theta}$ for real molecules do not lend themselves to expansion in θ_0, but nevertheless suggest that (5) and (8) taken through $O(\theta_0^3)$ represent adequate approximations if $A_0 I_2$ is replaced by the integral $I_\alpha = \rho\int g(r)\alpha(r)d^3\vec{r}/2\theta_0^3$, where $\alpha(r)$ is the variation in the trace of the pair polarizability tensor.[5,12]. Although the resulting $\alpha(r)$ is not proportional to r^{-6} for small r, it is for large r, so that I_α, like I_2, can still be expected to share the internal-energy singularity. Thus ΔF_{CM} and $\langle\overleftrightarrow{\theta}\rangle$ can also.

Corresponding treatments of $\langle\overleftrightarrow{\theta}(\omega)\rangle$ based upon the work of Mazur and Mandel[13] include this same singularity for all nonzero frequencies ω as well as for $\omega = 0$. From the way ΔF_{LL} depends upon $\langle\overleftrightarrow{\theta}(\omega)\rangle$, as given in that reference, one further concludes that ΔF_{LL} for $\omega \neq 0$ would pick up the internal-energy singularity from $\langle\overleftrightarrow{\theta}(\omega)\rangle$ even if it were free of this singularity in the constant-polarizability case for $\omega \neq 0$. (More likely ΔF_{LL}, like ΔF_{CM}, already shares the u singularity even in this case, but the analysis of Ref. 6 would have to be extended to order θ_0^3 to settle this issue.) These remarks, together with Eq. (3), give (4) and complete our analysis. A more detailed account is in preparation.[14]

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[1] D. Balzarini and K. Ohru, Phys. Rev. Lett. 29, 840 (1972).

[2] See, e.g., J. Weiner, K. H. Langley, and N. C. Ford, Jr., Phys. Rev. Lett. 22, 879 (1974).

[3] J. de Boer, F. van der Maesen, and C. A. ten Seldam, Physica (Utrecht) 19, 265 (1953).

[4] L. Jansen and P. Mazur, Physica (Utrecht) 21, 193, 208 (1955); L. Jansen, Phys. Rev. 112, 434 (1958).

[5] E. F. O'Brien *et al.*, Phys. Rev. A 8, 690 (1973), and references therein; W. Gelbart, to be published.

[6] R. Hocken and G. Stell, Phys. Rev. A 8, 887 (1973).

[7] To define uniquely the decomposition of ΔF_{CM} into an analytic and singular part, one can set $\Delta F_{\mathrm{CM},S} = 0$ at (ρ_c, T_c). It turns out that the uniqueness of the decomposition is not an issue in any of our results here, however.

[8] The functions $w(t) = u_B(M,t)$ and $\Delta(t) = \Delta F_{\mathrm{CM},B}$ defined along the coexistence curve are in general also singular functions of t, despite the fact that u_B and $\Delta F_{\mathrm{CM},B}$ are by definition regular functions of M and t, simply because $M \sim t^\beta$. This is the genesis of the $t^{2\beta}$ term in Eq. (2b).

[9] For e.g., the nearest-neighbor lattice gas, this can be immediately verified; for more general fluids it involves a scaling assumption as discussed in detail in Section II of Ref. 6.

[10] In the lattice-gas case, $\overleftrightarrow{\mathrm{T}}_R(12) = 0$ for particles in the same cell, instead of for $r_{12} < R$, and all integrals are actually sums over cells.

[11] We neglect here induced dipole-quadrupole coupling, the inclusion of which simply adds another term that goes like u.

[12] Similar replacement of the $\overleftrightarrow{\mathrm{T}}(12)\cdot\overleftrightarrow{\mathrm{T}}(23)$ in J_3 might well be necessary for quantitative accuracy at higher densities, but this would not alter our conclusion.

[13] P. Mazur and M. Mandel, Physica (Utrecht) 22, 299 (1956). For the constant-polarizability model, D. Bedaux and P. Mazur [Physica (Utrecht) 67, 23 (1973)], have extended the Mazur and Mandel work to include an analysis of the critical region but use an approximate $g(r)$ which the relation between the true u and the small-r behavior of $g(r)$ is lost. As a result, their analysis did not reveal the relation between u and ϵ that we find here.

[14] Numerical evaluation of Eq. (5) for a hard-sphere system has already been given by G. Stell and G. S. Rushbrooke, Chem. Phys. Lett. 24, 531 (1974).