tions and Critical Phenomena (Clarendon, Oxford, England, 1971).

[9]The authors thank G. Stell for suggesting that the rectilinear diameter of a binary liquid system should be analyzed in terms of volume fractions instead of mole fractions.

[10]If the rectilinear diameter in terms of volume fractions is as given in the text, then its slope in terms of mole fractions is of the form $(\partial/\partial t)\frac{1}{2}(X' + X'') = 3.05t^{-\alpha} + 0.0012t^{2\beta-1}$ for the present case, where $1-\alpha = 0.86 = f$. Even though $t^{2\beta-1}$ diverges faster as $t \to 0$, the coefficients make this term negligible even in the limit

of the present resolution. In fact, an analysis of the diameter in terms of mole fractions apparently gives the same fit as for volume fractions with $b = -0.000\,85$, $F = 5.0$, $f = 0.87$, $G = 5.8$, $h = 0.19$.

[11]Chandra Sekhar, Subramanyam, and Gopal, Ref. 2. Additional discussion of earlier data is presented in the detailed paper to be published elsewhere.

[12]J. M. H. Levelt Sengers, J. Straub, and M. Vicentini-Missoni, J. Chem. Phys. **54**, 5034 (1971); J. A. Zollweg and G. W. Mulholland, J. Chem. Phys. **57**, 1021 (1972); A. B. Cornfeld and H. Y. Carr, Phys. Rev. Lett. **29**, 28 (1972).

Critical Behavior of Polar Fluids

G. Stell*
Mathematics Department, The Rockefeller University, New York, New York 10021
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A simple argument demonstrates that one should expect polar and nonpolar fluids to have the same critical exponents.

There has been no adequate theory as yet to cope with the critical behavior of a polar fluid, and existing clues have been ambiguous. On the one hand, it has been known for some time[1] that if the pair potential $w(12)$ of a system is of sufficiently long range, one must expect the range to be an active parameter in determining the critical behavior of the system. More precisely, if $w(12) \sim \text{const} \times r^{-\sigma-d}$ for large r (d = dimension and $\sigma > 0$), then we expect the critical exponents to depend upon σ whenever σ is less than a certain value $\sigma_m(d)$, which is a bit less than 2 for $d = 3$.[1,2] For $\sigma \to 0$, we further expect to recover mean-field behavior.[1-3] For polar fluids, $w(12) \sim f(\varphi, \theta_1, \theta_2)r^{-3}$, where $\varphi, \theta_1, \theta_2$ are angles that describe the relative orientation of two dipolar molecules; thus, one might naively predict mean-field behavior, or at least a considerable departure from the large-σ behavior characteristic of nonpolar molecules. On the other hand, there appears to be no compelling experimental evidence that the critical exponents of polar fluids differ in any substantial way from those of nonpolar fluids.[4] One would guess that the angular-dependent $f(\varphi, \theta_1, \theta_2)$ must be crucial in tempering the effect of the r^{-3} in this connection, and the results of recent theoretical studies[5] of dipolar spin systems indeed show that the angular dependence reduces (but does not completely eliminate)

the effect of the long range of the potential. However, fundamental symmetry differences between such spin systems and a fluid of freely rotating dipolar molecules rule out the direct use of those results in treating polar fluids.

Our treatment here begins with the observation that the thermodynamics of a polar system can be identified with the thermodynamics of an exactly equivalent hypothetical nonpolar system with many-body temperature-dependent forces among molecules.[6] Let the configuration integral of the polar system of N particles be

$$Q_N = (N!\Omega^N)^{-1}\int d(1)\circ\circ\circ d(N)\exp[-\beta W(1,\dots,N)],$$

where $\beta = 1/kT$, $i = (\vec{r}_i, \vec{\omega}_i)$ describes both the orientation $\vec{\omega}_i$ and location $\vec{r}_i$ of the ith particle, and $\Omega = \int d^3\omega_i$. In general we have

$$W(1,\dots,N) = \sum_{i<j} w_2(ij) + \sum_{i<j<k} w_3(ijk) + \dots . \quad (1)$$

It is often convenient to further decompose each w_n into the sum of an orientation-independent term, call it $q_n(\vec{r}_1,\dots,\vec{r}_N)$, and a term that includes all the $\vec{\omega}_i$ dependence. For example, in the simplest case of interest, $w_n = 0$ for $n > 2$ and

$$w_2(12) = q(r) + w^{\text{ID}}(12), \quad (2)$$

where $r = |\vec{r}_1 - \vec{r}_2|$ and $w^{\text{ID}}(12)$ is the ideal dipole term $w^{\text{ID}}(12) = \vec{\mu}_1 \cdot \overleftrightarrow{T}(12) \cdot \vec{\mu}_2$ for a dipole strength μ. Here $\overleftrightarrow{T}(12) = 3(\vec{r}_{12}\vec{r}_{12})r^{-5} - \overleftrightarrow{I}r^{-3}$. We introduce $\Psi_N(\vec{r}_1, ..., \vec{r}_N)$ by writing

$$\exp[-\beta\Psi_N(\vec{r}_1,...,\vec{r}_N)] = \Omega^{-N} \int d^3\omega_1 \cdots d^3\omega_N \exp[-\beta W(1,...,N)],$$

so that

$$Q_N = (N!)^{-1} \int d^3r_1 \cdots d^3r_N \exp[-\beta\Psi_N(\vec{r}_1,...,\vec{r}_N)]. \tag{3}$$

We can uniquely decompose Ψ_N into a sum of n-body terms by writing

$$\Psi_N = \sum_{i<j}\varphi_2(\vec{r}_1\vec{r}_j) + \sum_{i<j<k}\varphi_3(\vec{r}_1\vec{r}_j\vec{r}_k) + ...,$$

where $\varphi_2 = \Psi_2$, $\varphi_3 = \Psi_3 - \sum_{i<j}\varphi_2(\vec{r}_1\vec{r}_j)$, etc. We note that (3) is just the configuration integral of a system with orientation-independent potential Ψ_N.

With W given by (1) and (2), direct computation gives an explicit expression for the longest-range term of φ_n that is added to the $q(r)$ of (2). Denoting this term as φ_n^{LR} we have

$$-\beta\varphi_n^{\text{LR}} = (-1)^n(n-1)!(\beta\mu^2/3)^n \text{Tr}\overleftrightarrow{T}^n/2, \tag{4}$$

where the tensor $\overleftrightarrow{T}^n$ is the product of a chain of n tensors $\overleftrightarrow{T}$.[7] The terms in φ_n not given by φ_n^{LR} are both of shorter range and of higher order in $\beta\mu^2$ than the term shown; for example, the full φ_2 is given by

$$-\beta\varphi_2 = -\beta q(r) + (\beta\mu^2)^2 r^{-6}/3 - 7(\beta\mu^2)^4 r^{-12}/450 + ... \tag{5}$$

The r^{-6} term is the right-hand side of (4) explicitly evaluated for $n = 2$.

A striking aspect of the φ_n given by (4) is that it has precisely the same $\vec{r}_i$ dependence, and hence range, as the longest-ranged dispersion term that one already finds in the potentials of real nonpolar molecules, which is also proportional to $\text{Tr}\overleftrightarrow{T}^n$ and differs from (4) only in the form of the coefficients, with polarizability α appearing instead of $\beta\mu^2/3$.[8] Thus, for example, the r^{-6} term in (5) has the same r dependence as the two-body London dispersion term. Similarly the long-range contribution to $-\beta\varphi_3$ given by (4) has precisely the $\vec{r}_i$ dependence of the three-body Axilrod-Teller dispersion term, etc.

In a real polar fluid, rather than one with W given by (1) and (2), the situation remains essentially the same with regard to the correspondence between terms in φ_n and terms already found in monatomic fluids. One finds a full set of dispersion terms independent of μ in the φ_n as well as a set of mixed (i.e., "induction") terms in φ_n arising from dipole–induced-dipole effects. For example one finds in $-\beta\varphi_2$ the "Falkenhagen term" $2\alpha\beta\mu^2/r^{-6}$ as well as the "Keesom term" $(\beta\mu^2)^2 r^{-6}/3$ already in (5). One also expects dipole-quadrupole and other higher-multipole terms; these too can be analyzed in detail but they are clearly of shorter range than the terms arising from purely dipolar effects. The key conclusion is that from no contribution to the φ_n can one find terms of longer range than those already given by the $\text{Tr}\overleftrightarrow{T}^n$ of (4).

From these observations one sees that the structure of the hypothetical fluid associated with the potentials φ_n is the same as that of a monatomic fluid in all respects that are currently believed to bear upon critical behavior; in particular the range and symmetry of the interaction potential is the same. To be sure, the φ_n are temperature dependent, through the appearance of a β associated with each μ^2. However, the temperature dependence thus introduced in each term is analytic in β and hence can be neglected in assessing exponents on the same grounds that the ubiquitous analytic "background" terms in the free energy of any system can be neglected in assessing its critical singularities. Our conclusion is that one should expect no more difference between polar and nonpolar values of critical exponents that describe thermodynamic behavior than among their values for simple nonpolar fluids, which we would expect to be universal for a given d.

There still remains the question of how much difference one should expect between the real fluid values, the Lennard-Jones fluid values, and the Ising-model values of the exponents. We do not attempt to answer that here, but from our above remarks one sees that the presence of the n-body dispersion terms for $n \geq 3$ represents the major difference between argon, say, and the Lennard-Jones fluid. This suggests that an in-

vestigation should be made to determine whether these terms can affect critical exponents; to our knowledge no such investigation has so far been made.[9]

In conjunction with our arguments, the work of Fisher and Aharony,[5] using field-theoretic techniques of Wilson, reveals an interesting difference in the role of dipolar forces in fluid and spin-system critical behavior. In the Wilson approach one customarily begins by replacing the statistical-mechanical system of interest by a field theory with a Lagrangian into which one has built what appears to be all the active variables[10]; one then invokes a universality hypothesis to argue that nothing important has been left out. On this somewhat coarse-grained level of scrutiny one acknowledges no difference between a simple fluid and the Ising model. Hence, from our argument, one will find no difference at all between the polar fluid and the Ising-model exponents on this level of description, whereas one *does* find[5] a small but unambiguous difference on this level between the exponents of the polar spin system and the Ising model with short-range interactions. To go further with such an approach and probe the subtle differences between a fluid and the Ising model will require considerable further effort.[11] Thus it seems, paradoxically, that it is easier to argue that the exponents of real polar fluids and real nonpolar fluids will be the same—despite the enormous differences in the range and symmetry of their Hamiltonians —than it is to assert with assurance that the exponents of argon and the Ising model (or a Lennard-Jones fluid, for that matter) should be the same.

In closing, we note that the hypothetical fluid with potentials φ_n affords a convenient means of defining a set of exponents, such as η and ν, that describe the correlation in such a fluid. These exponents automatically incorporate the correlations arising from ensemble averaging over the complicated orientational dependence in the corresponding polar fluid.

*Permanent address: Department of Mechanics, State University of New York, Stony Brook, N.Y. 11790.

[1]See Sect. 4 of G. Stell, Phys. Rev. B 1, 2265 (1970), which is based upon the simplest tenable homogeneity assumptions.

[2]Further general results for long-range potentials are given in G. Stell, Phys. Rev. B 5, 981 (1972), and 8, 1270 (1973). The results of Ref. 1 have been recovered through the first few orders of $\epsilon = 4-d$ by J. Sak, Phys. Rev. B 8, 281 (1973), under the usual assumptions of a field-theoretic approach (which are somewhat different from those of Ref. 1, but again not rigorous) for a field theory designed to reproduce the behavior of an n-component Heisenberg model of a magnet. For numerical work on the Ising chain, see J. S. Nagle and J. C. Bonner, J. Phys. C: Proc. Phys. Soc., London 3, 352 (1970).

[3]In fact for all $\sigma/d < \frac{1}{2}$, we expect mean-field thermodynamic exponents.

[4]See, e.g., J. M. H. Levelt Sengers and S. C. Greer, Int. J. Heat Mass Transfer 15, 1865 (1972), and references therein for H_2O.

[5]M. E. Fisher and A. Aharony, Phys. Rev. Lett. 30, 559 (1973); A. Aharony and M. E. Fisher, Phys. Rev. B 8, 3323 (1973); A. Aharony, Phys. Rev. B 8, 3342 3349, 3358, 3363 (1973).

[6]The development here has already been used in studying the noncritical behavior or polar systems by G. Stell, J. C. Rasaiah, and H. Narang, to be published. On the level of $n = 2$ it goes back to D. Cook and J. S. Rowlinson, Proc. Roy. Soc., Ser. A 219, 405 (1953). See also G. Stell, J. C. Rasaiah, and H. Narang, Mol. Phys. 23, 393 (1972).

[7]For details concerning the $\overline{T^n}$ and the way their traces enter into the dispersion, induction, and orientation terms of the free energy, see B. Linder, Advan. Chem. Phys. 12, 225 (1967).

[8]There is a further difference in β dependence associated with the appearance of a characteristic dispersion energy. See, e.g., Ref. 7, pp. 258–260, for a detailed discussion of the potential terms mentioned here, including their physical origin and the full analytic forms of the London and Axilrod-Teller terms, which arise from induced-dipole–induced-dipole and induced-dipole–induced-dipole–induced-dipole effects, respectively. The Falkenhagen term arises as a permanent-dipole–induced-dipole interaction, while the Keesom term is a permanent-dipole–permanent-dipole effect.

[9]As yet we have found no evidence that these terms are active. Our preliminary investigation of the three-body dispersion term indicates that it is thermodynamically equivalent to a two-body term that falls off like r^{-6} as $r \to \infty$, and hence is not of sufficient range to change exponents; we would expect similar results for each $n > 3$. Our tentative conclusion is that n-body terms could only be critically active through a subtle cooperative effect involving all n.

[10]See, e.g., Ref. 5 and the work of Sak, Ref. 2.

[11]This is discussed more fully by G. Stell, Phys. Rev. B 8, 1270 (1973). See also J. Hubbard and P. Schofield, Phys. Lett. 40A, 245 (1972).