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LETTER TO THE EDITOR

Critique of the cluster theory of critical point density fluctuations

For two-dimensional lattice gases which possess a critical point (but where interactions are not necessarily restricted to nearest neighbours), we have investigated the form of the pair correlation function computed by a partial cluster diagram summation at the critical point. Diagrams taken into account are the entire set that may be constructed from series and parallel connections of the fundamental Mayer cluster bond. Since the result fails ever to agree in its asymptotic large distance form with the known exact result for the special case of nearest neighbor interactions in the square lattice [1]), the inevitable conclusion must be drawn that the highly connected "basic" [2]) or "prototype" [3]) diagrams which were neglected, and which in any event are difficult to compute, are important in correctly determining fluctuation correlations in the critical region, at least in two dimensions.

The first attempts to predict the nature of critical pair correlations in classical fluids, by Ornstein and Zernike [4]), were based on assumption of independently variable Fourier components of microscopic density, and yielded a relation for

$$G(r) = g^{(2)}(r) - 1$$

($g^{(2)}$ is the ordinary pair correlation function) of the form:

$$\nabla^2 G = \kappa^2 G, \tag{1}$$

where κ is a constant which becomes zero at the critical point. In three dimensions, the appropriate spherically symmetric solution is well known to be an exponentially damped inverse distance function, which is perhaps qualitatively not unreasonable. Green [5]) however, has shown that the same partial cluster summation technique as we have used, when applied to the three-dimensional continuum gas, casts considerable doubt on the validity of the Ornstein-Zernike theory. The inadequacy of eq. (1) is especially apparent in two dimensions for which the critical point solution is proportional to log r, which diverges at large distances in contradiction to the known general properties of $g^{(2)}(r)$.

Kaufman and Onsager [1]) have computed the persistence of order for pairs of sites along a row at the critical point of the two-dimensional square Ising net. In the language of the corresponding lattice gas theory, the asymptotic form of the pair correlation function (now defined only for vector separations $\mathbf{r}$ between lattice sites) is apparently isotropic [6]), and is given by:

$$G(\mathbf{r}) \sim C(r/a)^{-\frac{1}{4}}$$
$$C = \exp\{\log(1 + 2^{-\frac{1}{2}}) - (1 + \gamma)/4 + \sum_{s=1}^{\infty} [s \log(1 - \tfrac{1}{4}s^{-2}) + \tfrac{1}{4}s]\} \tag{2}$$

(γ is Euler's constant, and a is the nearest-neighbor distance).

Van Leeuwen, Groeneveld and De Boer [2]) have shown that the Mayer cluster theory of the pair correlation function leads to a coupled set of functional equations for this quantity which, for the lattice gas with pair interaction $\varphi(\mathbf{r})$, may be exhibited in the form ($\beta = 1/kT$):

$$\begin{aligned} g^{(2)}(\mathbf{r}_{12}) &= \exp[-\beta\varphi(\mathbf{r}_{12}) + E(\mathbf{r}_{12}) + N(\mathbf{r}_{12})] \\ N(\mathbf{r}_{12}) &= \rho \sum_{\mathbf{r}_3} X(\mathbf{r}_{13}) [N(\mathbf{r}_{32}) + X(\mathbf{r}_{32})] \\ X(\mathbf{r}_{12}) &= g^{(2)}(\mathbf{r}_{12}) - N(\mathbf{r}_{12}) - 1 \end{aligned} \tag{3}$$

The density ρ is the fraction of lattice sites filled by particles. If φ is taken to be positively infinite for zero argument, the sum in the second of eqs. (3) may be extended over all lattice sites. E represents the sum of "basic" or "prototype" clusters connecting sites 1 and 2 which have bonds corresponding to factors $G(\boldsymbol{r}_{ij})$; the associated diagrams have no articulation points, nodes, or subdiagrams, and the field points (there must be two or more) are at least singly connected among themselves.

Green [5]) has pointed out how the continuum gas analogs of eqs. (3) may be analyzed to yield the asymptotic decay of $g^{(2)}$ at the critical point when the sum, E, of highly connected diagrams is disregarded. We have likewise found that the same approximation may be investigated as to the asymptotic nature of $g^{(2)}$ for the general two-dimensional lattice gas, with one site per unit cell, with result:

$$G(\boldsymbol{r}) \sim 4(3\pi^2)^{\frac{1}{3}}\rho_c^{-\frac{2}{3}}(r/a)^{-4/3} \tag{4}$$

where ρ_c is the value of ρ at the critical point, and a^2 is the area per site in the general lattice. This expression is independent of lattice chosen (hexagonal, square, triangular), and is valid whether or not interactions are restricted to nearest neighbors. We incidentally remark that although the value ρ_c should rigorously be $\frac{1}{2}$ in the model of Kaufman and Onsager, there is no assurance that the approximate versions of eqs. (3) will preserve this symmetry between filled and unfilled sites.

Thus the approximate cluster theory yields qualitatively reasonable results in two dimensions, unlike the Ornstein-Zernike approach; the rate of decay of G however, is predicted to be too great for the square lattice with nearest-neighbor interactions. On account of this apparant over-correction of the divergent Ornstein-Zernike theory, it is tempting to speculate that in the analogous three-dimensional case, the true critical particle pair density fluctuations drop off as $r^{-\alpha}$ with $1 < \alpha < 2$ (Green [5])).

In order to preserve the Kaufman-Onsager result (2) for the near-neighbor square lattice, it is easy to demonstrate that $E(\boldsymbol{r})$ necessarily is proportional to $r^{-\frac{1}{2}}$ for large r. Therefore, in spite of the fact that the set of clusters contributing to E is highly cross-linked, the resulting sum decays slowly to zero near the critical point. Furthermore, Eq. (2) suffices to demonstrate that many (though not all) of the clusters in E individually diverge at the critical point.

The conclusion to be drawn for the cluster theoretic approach to systems exhibiting cooperative behavior is that highly connected clusters must be considered in obtaining a proper description of at least the critical point, if not the condensed phase. It therefore appears fundamentally necessary, at least for two-dimensional systems, to seek a renormalization transformation of the terms in the E series to provide a convergent result under conditions of cooperative transition.

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REFERENCES

1) Kaufman, B. and Onsager, L., Phys. Rev. **76** (1949) 1244.
2) Van Leeuwen, J. M. J., Groeneveld, J. and De Boer, J., Physica **25** (1959) 792.
3) Meeron, E., J. math. Phys. **1** (1960) 192.
4) Ornstein, L. S. and Zernike, F., Proc. Acad. Sci. Amsterdam **17** (1914) 793.
5) Green, M. S., J. chem. Phys. **33** (1960) 1403.
6) Domb, C., Adv. Phys. **9** (1960) 199–201.