Self-Consistent Ornstein-Zernike Approximation for Lattice Gases

Ronald Dickman[1,*] and George Stell[2,†]

[1]*Department of Physics and Astronomy, Lehman College, CUNY, Bronx, New York 10468-1589*

[2]*Department of Chemistry, State University of New York, Stony Brook, New York 11790-3400*

(Received 1 September 1995)

A self-consistent approximation for the structure factor of three-dimensional lattice gases yields remarkably accurate predictions (less than 3% error over most of the temperature range) for the correlation length, isothermal compressibility, specific heat, and the coexistence curve. Critical temperatures agree to within 0.2%, and other critical properties to within (1–2)%, of the best numerical estimates. Until temperature and density are within 1% of their critical values, the approximate *effective* critical exponents do not differ appreciably from their estimated exact form; they attain their limiting spherical-model values only much closer to critical. The method should prove useful for a variety of three-dimensional lattice-gas and fluid problems; it is inappropriate to two dimensions, where it predicts criticality at zero temperature. [S0031-9007(96)00786-7]

PACS numbers: 05.50.+q, 05.70.Ce, 64.60.Cn

Finding a quantitatively accurate method for phase transitions and criticality in three-dimensional fluids and lattice gases has been a central objective of statistical mechanics throughout the last half century. Following series analysis of criticality in lattice models [1], major steps toward understanding the mechanism underlying critical behavior were taken by Widom [2] and by Kadanoff [3], who proposed that the free energy is dominated by a term homogeneous in a densitylike and a temperaturelike variable. Wilson [4] then illuminated the microscopic basis of homogeneity using renormalization group methods, after which Wilson and Fisher [5] showed how expansions in $4 - d$ (d is the dimension) yield quantitative predictions of critical exponents. By the mid-1970s one might have supposed that a theory of the structure factor (or equivalently, the pair distribution function), providing thermodynamic and structural results for lattice gases and simple fluids over the whole temperature-density plane, including the critical region, was immanent.

Two decades later, however, the development of globally accurate treatments of such systems remains only partially realized, both on the purely thermodynamic level and on the deeper structural level embodied in the pair correlation function. For one of the nearest-neighbor lattice gases considered here (the bcc case), there is now in the literature a satisfactory set of approximants for thermodynamic functions [6], but there is nothing of comparable quality for lattice gases with extended cores or a longer range of interaction. For continuum-fluid models one has nothing approaching the precision afforded by series-based approximants, although some promising approaches are under development [7] and significant progress has been made toward expressions that fit experimental data over a reasonably wide range of thermodynamic states, including the critical point [8].

While lattice models and field theories have served as the key arenas in the theory of criticality, the complex interplay between short- and long-range structure typical of continuum fluids has been addressed primarily within the framework of integral equations, derived via closure of the Ornstein-Zernike relation. Because of the thermodynamic inconsistencies commonly attending such closures, this leads to the still more formidable challenge of treating the pair correlation function in a globally accurate way to yield self-consistent predictions, so that, for example, one obtains the same pressure whether one uses the pair correlation function to find the isothermal compressibility via fluctuation theory, or to weigh the pair potential in a direct assessment of the internal energy. The surprising result we report in this Letter is that by constructing an intrinsically self-consistent theory (rather than by imposing consistency with thermodynamic functions obtained in a separate calculation), we obtain thermodynamic and structural predictions of remarkable accuracy. Thus our approach promises to be a route by which a globally accurate theory for continuum fluids may be attained. We know of no competing approach with the same goals that has yielded comparable results. The only other theory of the pair correlation function capable of global accuracy, from which thermodynamic results have been obtained, is that of Parola and Reatto [9,10], but that is not a self-consistent approach in our sense.

Our results are obtained from a self-consistent Ornstein-Zernike approach (SCOZA) developed by Høye and Stell for application to three-dimensional lattice gases and continuum-fluid systems [11]. Here we apply the approach to the nearest-neighbor lattice gas, and give the solution of the partial differential equation which Høye and Stell derived (but did not solve) to describe the thermodynamic behavior of the parameters appearing in the structure factor. To avoid terminological confusion, we distinguish between the SCOZA considered here and related generalized mean-spherical approximations (GMSA's) also developed and studied by Høye, Stell,

 0031-9007/96/77(6)/996(4)$10.00

and their coauthors [12]. Although these GMSA's can also be described as self-consistent Ornstein-Zernike approximations, they differ in a crucial way from the one we consider in that their thermodynamic predictions are, by construction, precisely those of the mean-spherical approximation (MSA). The present method yields thermodynamic functions distinct from, and far superior to those of the MSA.

We consider three-dimensional lattices gases with nearest-neighbor interaction $w(r) = \infty$ for $r = 0$, $w(1) = -1$, and $w(r) = 0$ for $r > 1$ ($r \equiv |\mathbf{r}|$), where $\mathbf{r}$ is the separation of a pair of particles. In the MSA the direct correlation function is $c(r) = -\beta w(r)$ for $r > 0$ (β is inverse temperature), so that $c_1 \equiv c(1) = \beta$. Following Høye and Stell [11], by contrast, we let $c_1 = c_1(\beta, \rho)$, and determine this function by demanding consistency between the energy and compressibility routes for the pressure. $c_0 \equiv c(0)$ is fixed by the core condition on the total correlation function: $h_0 = -1$. Thermodynamic self-consistency is embodied in the relation $\rho \partial^2(\rho u)/\partial \rho^2 = \partial^2(\beta p)/\partial \beta \partial \rho$, where u is the internal energy per particle, p is the pressure, and ρ is the density or fraction of occupied sites. The internal energy per particle on a lattice with coordination number q is $u = -q\rho(1 + h_1)/2$, and the inverse compressibility is $\chi^{-1} = \partial(\beta p)/\partial \rho = 1 - \rho \tilde{c}(0) = 1 - \rho(c_0 + qc_1)$, where $\tilde{c}$ denotes the Fourier transform and the last equality reflects our truncation of c. We obtain further relations between the unknowns c_0, c_1, and h_1 from the Ornstein-Zernike equation (OZE), which in Fourier space is

$$1 + \rho \tilde{h} = (1 - \rho \tilde{c})^{-1}. \quad (1)$$

The core condition together with the OZE implies $-h_1 = [1 + (1 - \rho)c_0]/q\rho c_1$. A second expression for h_1 comes from inverting Eq. (1) at nearest-neighbor distance

$$\rho h_1 = \int_{-\pi}^{\pi} \frac{d^3k}{(2\pi)^3} \frac{\cos \mathbf{k} \cdot \mathbf{e}}{1 - \rho \tilde{c}(\mathbf{k})}. \quad (2)$$

Here $\mathbf{e}$ denotes a vector from the origin to one of its nearest neighbors, e.g., (1,0,0), (1,1,1), and (1,1,0), in the sc, bcc, and fcc lattices, respectively. The Fourier-transformed direct correlation function may be written $\tilde{c}(k) = c_0 + (q/g)c_1\Phi(k)$, where $g = 3$ for the sc and fcc lattices and $g = 1$ for bcc (g is the number of subgroups invariant under inversions). The nearest-neighbor sum $\Phi(\mathbf{k})$ is $\cos k_x + \cos k_y + \cos k_z$ (sc), $\cos k_x \cos k_y \cos k_z$ (bcc), and $\cos k_x \cos k_y + \cos k_x \cos k_z + \cos k_y \cos k_z$ (fcc).

Equating expressions for ρh_1, and introducing $\not{c} = (1-\rho)(1-\rho c_0)$, and $z = [q\rho(1-\rho)c_1]/\not{c}$, we have $\not{c} = P(z) = \pi^{-3}\int_0^{\pi} d^3k[1 - (z/g)\Phi]^{-1}$. This is the lattice Green's function for the Helmholtz equation, which may be evaluated in terms of elliptic integrals [13,14]. The internal energy and inverse compressibility are given by $\rho u = -(q\rho^2)/2 - (\not{c} - 1)/2c_1$ and $\chi^{-1} = \not{c}/(1 - \rho) - q\rho c_1$, which are faithful to the hole-particle symmetry of the lattice gas. Differentiating with respect to β, rearranging, and using the self-consistent relation, we obtain

$$\frac{\partial c_1}{\partial \beta} = \frac{1}{q} \frac{\partial^2(-\rho u)}{\partial \rho^2} \left[1 - \frac{\not{c} P'}{\not{c}^2 + q\rho(1 - \rho)c_1 P'} \right]^{-1}, \quad (3)$$

where $P' = dP/dz$. Given the boundary values $c_1(\rho, \beta = 0) = 0$ and $\not{c}(\rho, \beta = 0) = 1$, we evaluate $\partial c_1/\partial \beta$ via Eq. (3), and integrate to find $c_1(\rho, \Delta\beta)$. Then we compute $\not{c}(\rho, \Delta\beta)$, construct $\partial c_1/\partial \beta$, and so on. In the course of this procedure, we also require c_1 and $\not{c}$ at the boundaries $\rho = 0$ and $\rho = 1$. Using $P(z) \simeq 1 + z^2/q + O(z^4)$, one finds that $\partial c_1/\partial \beta = c_1 + 1$ for $\rho = 0$ or 1. For the bcc lattice, $P(z) = \overline{K}(k)^2$, where $\overline{K}(k)$ is $2/\pi$ times the complete elliptic integral of the first kind, and $k^2 = [1 - \sqrt{1 - z^2}]/2$ [13]. Similar, but more complex expressions are known for the other lattices [14].

The inverse compressibility vanishes when $z = 1$. This condition defines the spinodal line, and for $\rho = 1/2$, the critical point. Thus $\not{c} = qc_1/4 = P(1)$ at the critical point, which permits us to write the internal energy: $u_c = -q[P(1) - 1]/4P(1)$. [While the MSA yields the same expression for u_c, one has $\beta_{c,\mathrm{MSA}} = 4P(1)/q$, which is rather inaccurate; for the sc lattice, $\beta_{c,\mathrm{MSA}} = 1.0109$, about 14% too large. It is worth noting that away from the critical point, the SCOZA spinodal lies well inside the coexistence curve.] Another simple consequence of $z_c = 1$ is that our theory predicts $T_c = 0$ in one and two dimensions, because the lattice Green's function diverges at $z = 1$ for $d \le 2$. Although SCOZA is exact for the one-dimensional lattice gas, it is unsuited to the two-dimensional model, which presents the unusual combination of a divergent Green's function and a nonzero T_c.

Details on the numerical procedure are given in Ref. [15]; we now summarize our results. We plot the isothermal compressibility as a function of β, for $\rho = 1/2$, in Fig. 1. Extrapolating from the last few data points for $\beta < \beta_c$ [for which χ^{-1} is already $\mathcal{O}(10^{-6})$], we determine β_c via $\chi^{-1}(\beta_c, 1/2) = 0$. The resulting values, listed in Table I, are within 0.2% of the best series estimates. For comparison we note that for the sc lattice, simple mean-field theory yields $\beta_c = 2/3$, the quasichemical approximation gives $\beta_c = 0.8109$, and Kikuchi's cluster variation method (using a cubic cluster), predicts $\beta_c = 0.8739$ [16,17]. Figure 1 shows that the SCOZA prediction is in good agreement with the compressibility derived from Liu and Fisher's whole-range approximants for the Ising model [6]. For $\beta \le 0.9\beta_c$, the discrepancy between SCOZA and the approximant

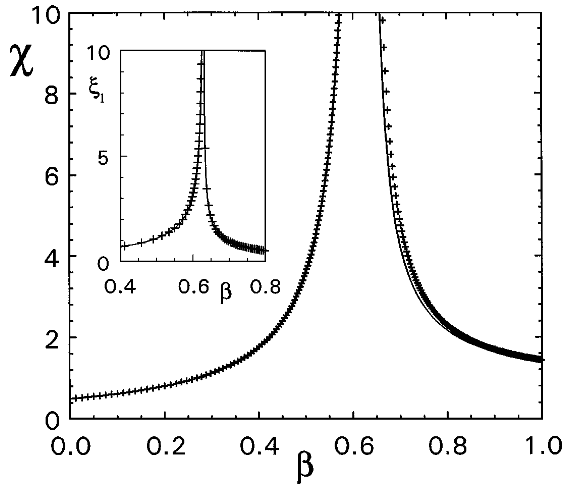

FIG. 1. Compressibility versus inverse temperature β for the bcc lattice. +: SCOZA; solid lines: Liu-Fisher approximants [6]. The inset is a similar plot of the correlation length, ξ_1.

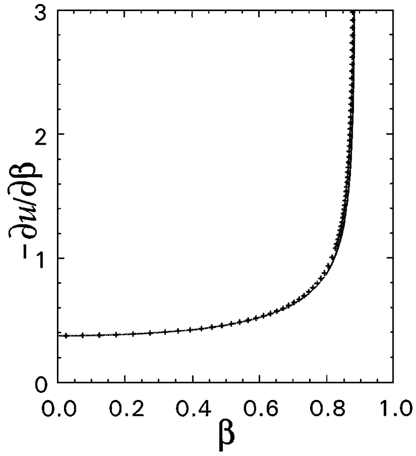

FIG. 2. Derivative of internal energy with respect to β versus β (sc lattice). +: SCOZA; dotted line: Padé approximant to high-T series; solid line: scaling form (see text).

(which represents the best available numerical estimate) is $\lesssim 2\%$; for $\beta = 0.95\beta_c$ this grows to about 6%. Above β_c the error is larger (about 14% for $\beta = 1.1\beta_c$).

Table I includes critical values of the internal energy per particle, u_c [evaluated using exact results for $P(1)$ [18,19]], the entropy per particle s_c and the pressure. Remarkably, the difference between SCOZA predictions and the best series estimates is at most 0.7% for the critical internal energy, 1.1% or less for the critical entropy, and at most about 1.4% for the pressure. In Fig. 2 we plot $-\partial u/\partial \beta$ at $\rho = 1/2$. In our theory, this derivative does not diverge at the critical point, but rather attains the limiting values 9.34 (sc), 15.98 (bcc), and 42.96 (fcc). Notwithstanding the finiteness of the specific heat at the critical point, Fig. 2 shows that the SCOZA is otherwise in close agreement with the series prediction. The latter is derived, for $\beta \leq 0.8$, from a Padé approximant to a 9-term series [20]; for $\beta > 0.8$ we use the asymptotic form $c \simeq 1.135(1 - \beta/\beta_c)^{-1/8} - 1.242$. Figure 3 compares the SCOZA prediction for the coexistence curve in the bcc lattice against that of the whole-range approximant of Liu and Fisher [6]. Outside the immediate vicinity of the critical point, the SCOZA coexistence density differs from that of the approximant by less than 3%.

As a further test of the SCOZA, we compare its prediction for the second-moment correlation length ξ_1, against Liu and Fisher's approximant [6]. Writing $\tilde{h}(k) = \tilde{h}(0) + h_2 k^2 + \cdots$, our theory yields $\xi_1^2 = -h_2/3[\tilde{h}(0) + 1/\rho]$, which becomes $4\rho\chi c_1/3$ for the bcc lattice. We obtain ξ_1 to within 3% for $\beta \leq 0.95\beta_c$, and to within 5% for $\beta \geq 1.05\beta_c$ (see inset of Fig. 1).

As we shall show elsewhere, the true critical exponents correspond to those of the spherical model [15], but the spherical-model values ($\gamma = 2$, $\delta = 5$, $\beta = 1/2$, $\alpha = 0$) are discernable only for $|t| < 10^{-3}$ and/or $|\rho - \rho_c| < 10^{-3}$. [Here $t \equiv (\beta_c - \beta)/\beta_c$ is the reduced temperature.] The effective critical exponents, i.e., the slopes of log-log plots of various properties versus t or $|\rho - \rho_c|$, agree surprisingly well with the exact behavior of the 3D Ising effective exponents over a considerable range [11]. The inverse-compressibility plot of Fig. 4, for example, yields $\gamma_{\text{eff}} \simeq 1.26$ for $-4 \leq \ln t \leq 0$. Similar plots yield $\beta \simeq 1/3$, $\alpha \approx 0$, and $\delta \simeq 4.5$–4.7 over a considerable range of the data. (The true 3D Ising model exponents are estimated to be $\gamma = 1.239$, $\beta = 0.326$, $\alpha = 0.119$, and $\delta = 4.80$ [23]. The effective exponents of the SCOZA are quite different from those of the MSA. In the latter theory, for example, γ_{eff} varies from about 1.6, far from the critical point, to the spherical model value of 2. There is no range of β for which the MSA gives γ_{eff} near the 3D Ising value.) The recent application of the theory of Parola and Reatto [9] by

TABLE I. Comparison of SCOZA (sc) and best-estimate (BE) critical parameters.

Lattice	$\beta_{c,\text{sc}}$	$\beta_{c,\text{BE}}$	$u_{c,\text{sc}}$	$u_{c,\text{BE}}$	$s_{c,\text{sc}}$	$s_{c,\text{BE}}$	$(\beta p)_{c,\text{sc}}$	$(\beta p)_{c,\text{BE}}$
sc	0.88497	0.88662[a]	−2.010806	−1.9961[b]	1.1037	1.1158[b]	0.1140	0.1124
bcc	0.62848	0.62947[c]	−2.564460	−2.5464[b]	1.1542	1.1641[b]	0.1256	0.1244
fcc	0.40772	0.40825[c]	−3.768955	−3.7423[b]	1.1703	1.1804[b]	0.1302	0.1292

[a]Reference [21]. [b]Reference [22]. [c]Reference [6].

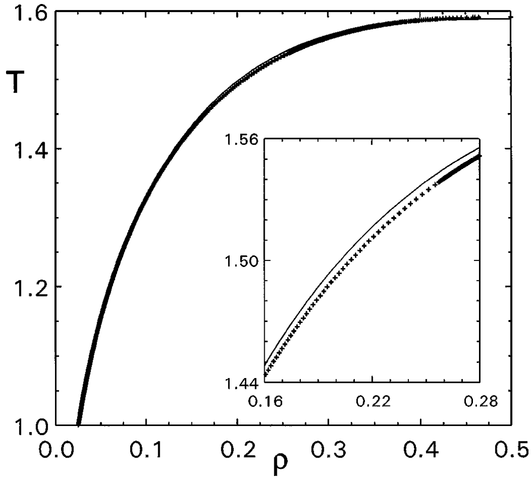

FIG. 3. The bcc lattice coexistence curve according to SCOZA (+), and Liu and Fisher's whole-range approximant [6].

Pini *et al.* [10] to the simple cubic lattice gas facilitates a direct comparison with our results. Our error in critical temperature is 0.18% while theirs is 0.4%; a comparison of our Fig. 3 with their Fig. 1 shows that our coexistence curve also has considerably higher overall accuracy. A further comparison of the two approaches will be given as part of a more detailed report [15].

For $d \geq 3$, the sole approximation in SCOZA theory—the identification of the range of $c(\mathbf{r})$ with that of $w(r)$—distorts $h(\mathbf{r})$ $[\approx f(r/\xi)/r^{d-2+\eta}$ for $r \gg 1]$, only very slightly ($\eta = 0$ instead of $\eta \approx 0.06$ for $d = 3$), and this distortion is apparent only in the vicinity of the critical point, where $f(r/\xi)$ is constant, rather than exponentially damped. The basis of the SCOZA is to make this the *only* approximation in the theory, so that for $d \geq 3$ the attendant error in the thermodynamics is very small except at or close to critical.

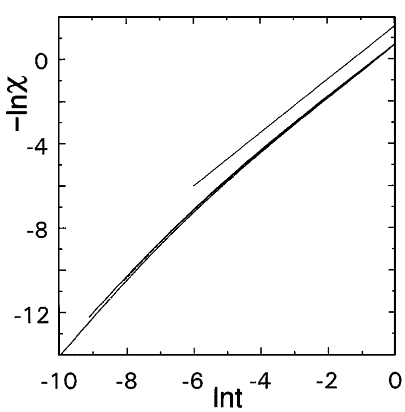

FIG. 4. Inverse compressibility versus reduced temperature. The curves (indistinguishable over most of this scale) represent predictions of SCOZA for the sc, bcc, and fcc lattices. The slope of the straight line is 1.26.

We are grateful to Johan Høye and Michael Fisher for helpful correspondence and to Davide Pini for illuminating conversations. The work of R. D. was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. The work of G. S. was supported by the National Science Foundation.

*Electronic address: dickman@lcvax.lehman.cuny.edu
†Electronic address: gstell@sbchm1.chem.sunysb.edu

[1] See, e.g., *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, London, 1974), Vol. 3.
[2] B. Widom, J. Chem. Phys. **43**, 3898 (1965).
[3] L. Kadanoff, Physics **2**, 263 (1966).
[4] K. G. Wilson, Phys. Rev. B **4**, 3174 (1971); K. G. Wilson and J. B. Kogut, Phys. Rev. C **12**, 2 (1974).
[5] K. G. Wilson and M. E. Fisher, Phys. Rev. Lett. **28**, 240 (1972).
[6] A. J. Liu and M. E. Fisher, Physica A **156**, 35 (1989).
[7] See, for example, M. A. Anisimov, S. B. Kiselev, J. V. Sengers, and S. Tang, Physica A **188**, 487 (1992); J. A. White and S. Zhang, J. Chem. Phys. **99**, 2012 (1993).
[8] See, for example, J. V. Sengers, in *Supercritical Fluids*, edited by E. Kiran and J. M. A. Levelt-Sengers (Kluwer-Academic Pub., Dordrecht, 1994), and references therein.
[9] A. Parola and L. Reatto, Phys. Rev. Lett. **53**, 2417 (1984); Phys. Rev. A **31**, 3309 (1985); A. Parola, A. Meroni, and L. Reatto, Phys. Rev. Lett. **62**, 2981 (1989); A. Parola and L. Reatto, Phys. Rev. A **44**, 6600 (1991).
[10] D. Pini, A. Parola, and L. Reatto, J. Stat. Phys. **72**, 1179 (1993).
[11] J. S. Høye and G. Stell, Mol. Phys. **52**, 1071 (1984); Int. J. Thermophys. **6**, 561 (1985); see also Sec. IV of J. S. Høye and G. Stell, J. Chem. Phys. **67**, 439 (1977).
[12] J. S. Høye, J. L. Lebowitz, and G. Stell, J. Chem. Phys. **61**, 3253 (1974); G. Stell and S. F. Sun, J. Chem. Phys. **63**, 5333 (1975); J. S. Høye and G. Stell, Mol. Phys. **32**, 195 (1976); J. Chem. Phys. **67**, 524 (1977).
[13] G. S. Joyce, J. Math. Phys. **12**, 1390 (1971).
[14] G. S. Joyce, J. Phys. C **4**, L53 (1971); J. Phys. A **5**, L65 (1972).
[15] G. Stell, R. Dickman, and J. S. Høye (to be published).
[16] R. Kikuchi and S. G. Brush, J. Chem. Phys. **47**, 195 (1967).
[17] D. M. Burley, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, New York, 1972), Vol. 2.
[18] W. F. Van Peijpe, Physica (Utrecht) **5**, 465 (1938).
[19] G. N. Watson, Q. J. Math. (Oxford) **10**, 266 (1939).
[20] M. F. Sykes *et al.*, J. Phys. A: Math. Gen. **5**, 667 (1972).
[21] C. F. Baillie *et al.*, Phys. Rev. B **45**, 10 438 (1992).
[22] M. F. Sykes *et al.*, J. Phys. A: Math. Gen. **5**, 640 (1972).
[23] A. M. Ferrenberg and D. P. Landau, Phys. Rev. B **44**, 5081 (1991).