## Nonclassical critical behavior of the square-well fluid

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In this paper we report the results of extensive numerical calculations on the equation of state of the square-well fluid in the immediate vicinity of its critical point, with the objective being the precise determination of the critical exponents  $\beta$  and  $\delta$ . These determinations were carried out using data generated by solving the Yvon-Born-Green equation for the pair distribution function (with superposition approximation) over an extended range of integration (~50 intermolecular diameters). When taken together with the value of the critical exponent  $\gamma$  reported previously by the authors ( $\gamma = 1.24 \pm 0.04$ ), the results obtained,  $\beta = 0.330 \pm 0.008$  and  $\delta = 4.4 \pm 0.2$ , suggest strongly that the essential physics of the gas-liquid transition in the neighborhood of the critical point is described correctly by an integral equation derived from the classical Bogoliubov-Born-Green-Kirkwood-Yvon theory of distribution functions.

### I. INTRODUCTION

The development of a comprehensive theory of the states of matter has been a long-standing goal in statistical mechanics. Ideally, such a theory should provide a single framework within which the equilibrium and transport properties of the gaseous, liquid and solid states can be calculated with reasonable quantitative accuracy, and which provides, as well, at least a qualitatively correct description of the possible transformations between (or among) these states. The success with which one realization of the BBGKY hierarchy, the Yvon-Born-Green (YBG) equation under the superposition approximation, is able to achieve these goals was reviewed recently by two of the authors.<sup>1</sup> Considering the particular case of the square-well fluid, perhaps the simplest model system for which both attractions and repulsions are taken into account in the governing intermolecular potential function, it was concluded on the basis of evidence available at that time that the YBG theory, although reasonably successful in accounting for the general features of pure phase phenomena, was, with respect to the description of coexistence phenomena in the neighborhood of the critical point, somewhat deficient. In particular, the numerical values of the critical exponents determined via analysis of equation-of-state data fell between the classical and accepted nonclassical values. Given the broad objectives cited earlier, this apparent deficiency in the theory demanded further investigation. Recognizing that phenomena in the neighborhood of the critical point are characterized by a correlation length  $\xi$  that greatly exceeds the range of pair interaction (and, in fact, diverges exactly at the critical

point), the authors decided to reopen the study of the YBG equation for the pair-correlation function  $g^{(2)}(x)$ , paying particular attention to the downrange behavior of this function. Accordingly, the range of the integral-equation calculation of  $g^{(2)}(x)$ was extended from ~15 intermolecular diameters (the range which characterized our earlier work) to ~50 diameters and, from these resulting, more accurate  $g^{(2)}(x)$  data, the behavior in the neighborhood of the critical point was reexamined. As reported earlier,<sup>2</sup> the value of the critical exponent  $\gamma$  deduced using these new data is consistent with the best available experimental and theoretical estimates. Although, as noted above, earlier studies on the YBG equation for the square-well fluid had uncovered some evidence for the emergence of nonclassical behavior in the vicinity of the critical point,<sup>3</sup> the quantitative accuracy realized in our recent study was so "unexpected" and the implications of the result so fundamental, that we immediately set about to examine the remaining critical exponents, again using  $g^{(2)}(x)$  data in which the down-range behavior of the function is very accurately determined. For we wish to rule out that the remarkable value of  $\gamma$  reported in Ref. 2 was the consequence of fortuitous cancellations of various (theoretical and/or numerical) approximations.

In this paper we present the results of further studies in our more refined analysis of the critical behavior of the square-well fluid; specifically, we present estimates of the critical exponents  $\beta$ and  $\delta$ . From these results, and considering our earlier determination of the critical exponent  $\gamma$ , we shall argue that the YBG theory of the squarewell fluid (with the underlying integral equation solved using the superposition approximation)

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seems to provide an essentially correct description of the critical region. We shall not attempt to address here the many deeper questions of interpretation, for example, why it is that the nonclassical behavior of a fluid is quantitatively portrayed by a nonlinear integral equation having the structure of the YBG equation or why the closure introduced to decouple the original hierarchy of nonlinear integral equations seems to be so harmless, although some discussion of these matters from the vantage point of modern nonlinear functional analysis has been presented in recent work by one of us.<sup>4,5</sup> Rather, our intention here is to focus on the numerical evidence relevant to the determination of  $\beta$  and  $\delta$  (Sec. II), paying particular attention to an assessment of the errors and confidence limits in the calculations. Then in Sec. III, we present a comparison of our results with known, theoretical and experimental estimates of the critical exponents  $\gamma$ ,  $\beta$ , and  $\delta$  and, where appropriate, comment on the compatibility of our data with certain rigorous relations (viz., inequalities) involving these exponents.

# II. DETERMINATION OF THE CRITICAL EXPONENTS $\beta$ AND $\delta$

In the spirit of Ref. 2, the YBG equation was solved for  $g^{(2)}(x)$  to the degree of convergence where, for all x, differences between the  $g^{(2)}(x)$ computed at successive iterations were  $10^{-6}$ . The range of  $g^{(2)}(x)$  was allowed to extend to a value at which  $g^{(2)}(x) = 1.000\ 000 \pm 10^{-6}$  is attained, i.e., the boundary condition of  $g^{(2)}(x) \equiv 1.0$  was applied at a value of  $x = x_{max}$ , where  $x_{max}$  exceeded the range. The resulting  $g^{(2)}(x)$  functions were then inserted into the isothermal compressibility equation for  $\kappa_T$ :

$$\kappa_T = 1 + \lambda_0 \int_0^\infty [g^{(2)}(x) - 1] x^2 \, dx \,, \tag{1}$$

where  $\lambda_0 = 4 \pi n \sigma_1^3$  is reduced density,  $\sigma_1$  is the molecular diameter (i.e., hard-core separation of two molecules), and *n* is the molecular number density (molecules/cm<sup>3</sup>). The  $\kappa_T$  function is central to the determination of both  $\beta$  and  $\delta$  and is most sensitive to long-range values of  $g^{(2)}(x)$  owing to the presence of the  $x^2$  factor in the integrand.

Initially it was assumed that the reduced reciprocal critical temperature  $\theta_c = \epsilon/kT_c$  was  $\theta_c = 0.3741$ , the value reported in Ref. 2 in our determination of  $\gamma$ . The determination of  $\beta$ , which describes the shape of the coexistence envelope in the vicinity of the critical point, offers an independent determination of what might be the appropriate value of  $\theta_c$ . Values of  $\kappa_T$  were found at

several subcritical isotherms outside the coexistence region, i.e., within stable fluid regions, and estimates of  $\lambda_{0G}$  and  $\lambda_{0L}$  were made by plotting  $\kappa_T^{-1}$  vs  $\lambda_0$  on each side of the coexistence region at constant  $\theta < \theta_c$  for  $\theta = 0.38$ , 0.377, 0.375, and 0.3741, the latter isotherm being studied to determine whether it might be subcritical. Table I presents the  $g^{(2)}(x)$  and  $\kappa_T$  data while Table II gives  $\lambda_{0G}$  and  $\lambda_{0L}$  as a function of  $\theta$ . The  $\beta$  exponent

TABLE I.  $x_{\max}$ , range of  $g^{(2)}(x)$ , and  $\kappa_T$  as a function of  $\theta$  and  $\lambda_0$ . This information was used to evaluate the  $\lambda_{0G}$  and  $\lambda_{0L}$  that appear in Table II. All calculations were performed to single precision.

θ	λ <sub>0</sub>	$x_{\max}$	Range	$\kappa_T^{a}$
•				********
0.3741 0	2.5	20	17.60	5.4195
	3.0	30	23.35	10.8256
	3.3	30	28.75	19.2496
	3.6	40	36.65	40.6670
	3.9	50	46.65	93.9000
	5.3	45	43.30	56.3405
	5.6	35	33.65	23.3682
	5.9	30	27.20	11.5321
	6.2	25	22.75	6.6016
	6.5	30	19.55	4.2091
	7.0	20	15.95	2.3557
0.375	3.25	40	36.60	19.9072
	3.50	40	36.70	38,4914
	3.65	45	40.80	59.6184
	5.45	45	41.35	47.4092
	5.70	40	36.65	23.3140
	6.00	40	34.70	11.1535
0.377	3.00	30	28.15	14.0207
	3.25	40	35.80	26.7511
	3.40	40	36.60	42.4388
	3.55	45	43.05	74.9975
	5.60	45	43.30	54.8363
	5.75	40	36.65	30.4867
	6.00	40	35.00	15.2194
	6.50	25	23.05	5.3284
0.380	2.50	20	19.15	6.7806
	3.00	30	28.15	19.0825
	3.25	40	37.45	47.5699
	3.35	45	42.55	76.0265
	5.85	45	43.10	52.6679
	6.00	40	35.40	26.7863
	6.50	25	23.05	6.8139
	7.00	20	17.65	3.1182

<sup>a</sup>Most of the  $\kappa_T$  values were refined to the point that a further-converged  $g^{(2)}(x)$  did not change the value of  $\kappa_T$  in the fourth decimal place. The author's experience is that  $\kappa_T$  should be reliable to at least two decimal places. See footnote *a* in Table III.

<sup>b</sup> Particularly at this value of  $\theta$ , an asymmetry in  $\kappa_T$  is noticeable with respect to using  $\lambda_{0c} = 4.60$ . However, the use of these data produced a coexistence envelope which appeared to be symmetrical about  $\lambda_0 = 4.60$ , to within the computational uncertainty.

TABLE II.  $\lambda_{0G}$  and  $\lambda_{0L}$  as a function of  $\theta$ , as determined by analysis of  $\kappa_T^{-1}$  vs  $\lambda_0$  plots. The values of  $\lambda_{0G}$  and  $\lambda_{0L}$  are estimated good to  $\pm 0.05$ .

θ	$\lambda_{0G}$	$\lambda_{0L}$
0.3471	4.40	4.80
0.375	4.07	5.12
0.377	3.83	5.38
0.380	3.55	5.67

can be found by using the relationship

$$\left|\lambda_{0}-\lambda_{0c}\right| \sim \left|\left(\theta-\theta_{c}\right)/\theta\theta_{c}\right|^{\beta}.$$
 (2)

Arguments introduced earlier by the authors<sup>1</sup> suggest that the lower bound on the limit of stability of pure phase should also signal those points on an isotherm where  $\kappa_T \rightarrow \infty$ . The function (see Ref. 1)

$$F(\lambda_0, \theta; u = 0) = 1 + \frac{1}{3}\lambda_0 [g^{(2)}(1_{\bullet}) - R^3(1 - e^{-\theta})g(R_{\bullet})] = 0$$
(3)

was examined for roots; in this equation, R is the ratio of  $\sigma_2/\sigma_1$  ( $\sigma_1$  and  $\sigma_2$  are the range parameters in the square-well intermolecular potential) and the x values of 1, and  $R_-$  are locations at the boundaries of, but within, the attractive well of the square-well potential. The results obtained using the criterion, Eq. (3), support those obtained using  $\kappa_T^{-1} \rightarrow 0$  as a criterion.

The results of the  $\beta$  analysis are that

 $\beta = 0.330 \pm 0.008$ 

and that  $\beta_{G}$  and  $\beta_{L}$  are identical to within the stated bounds of uncertainty. Furthermore, from these studies, it appeared that the isotherm  $\theta = 0.3741$ was slightly subcritical, and hence the value of  $\theta_{c} = 0.37405$  was adopted. However, use of  $\theta_{c}$ = 0.3471 rather than 0.37405 does not alter the value of  $\beta$  to any significant degree. Evaluation of  $\beta$  was done graphically. Included in the uncertainty of  $\beta$  is the uncertainty in  $\lambda_{0c}$ ; the uncertainty in  $\lambda_{0c}$  manifests itself more dramatically in the determination of  $\delta$  as will be described below.

It was pointed out in Ref. 2 that the exponent  $\gamma$  was sensitive to the value of  $\theta_c$  used. In fact, a large part of the uncertainty in the value of 1.24  $\pm 0.04$  reported was due to uncertainty in  $\theta_c$ . If one adopts the value of  $\theta_c = 0.37405 \pm 0.00005$ , a reevaluation of  $\gamma$  yields  $\gamma = 1.23 \pm 0.02$ . This confidence limit seems realistic in light of the additional input provided by the  $\beta$  determination to the evaluation of  $\theta_c$ .

To evaluate  $\delta,\,\,the\,\,shape\,\,of\,\,the\,\,critical\,\,isotherm,\,\,i.\,e.\,,$ 

$$\left|P^{*}-P_{c}^{*}\right| \sim \left|\lambda_{0}-\lambda_{0c}\right|^{6}$$
(4)

at  $\theta = \theta_c$ , the value of  $\theta_c = 0.37405$  was adopted and  $g^{(0)}(x)$  was evaluated along that isotherm at several densities on either side of the critical density  $\lambda_{0c}$ . In evaluating  $\gamma$  and  $\beta$ , a value of  $\lambda_{0c}$ = 4.60±0.05 was used. Examination of the critical isotherm indicates that  $\lambda_{0c}$  is probably less than 4.60. We find that  $\kappa_T \rightarrow \infty$  at  $\lambda_0 = \lambda_{0c}$  and, further,  $\kappa_T$  seems to be symmetrical at a value of  $\lambda_0$  between 4.55 and 4.60. The reduced pressure  $P^*$  (= $P\sigma_1^3/\epsilon$ ) can be evaluated from knowledge of  $\kappa_T$ ; specifically, one writes

$$P^* - P_c^* = (4\pi\theta_c)^{-1} \int_{\lambda_{0c}}^{\lambda_0} (\kappa_T^{-1}) d\lambda_0 , \qquad (5)$$

from which expression the exponent  $\delta$  may be determined. The symmetry in  $\kappa_T$  about  $\lambda_{0\sigma}$  implies that  $\delta_G = \delta_L$ .

Determination of  $\delta$  is much more difficult than either  $\gamma$  or  $\beta$  since long-range critical effects manifest themselves much further away from the critical point along the density coordinate than along the temperature coordinate (relative to the critical-point values  $\theta_c$  and  $\lambda_{0c}$ , respectively). This characteristic behavior is present in laboratory studies as well and leads to larger experimental uncertainties in  $\delta$  than in  $\gamma$  or  $\beta$ . Table III lists the values of  $\kappa_T$  and  $\lambda_0$  used in the determination of  $\delta$ . The correlation function  $g^{(2)}(x)$ was also evaluated at densities closer to  $\lambda_{0c}$  (up to  $|\lambda_0 - \lambda_{0c}| = 0.25$ ), but these calculations (not reported) were hampered by the range requirements,

TABLE III. Values of range of  $g^{(2)}(x)$  and  $\kappa_T$  as a function of  $\lambda_0$  at  $\theta = \theta_c = 0.37405$ . All computations of  $g^{(2)}(x)$  were performed at double precision.

λ <sub>0</sub>	Range <sup>a</sup>	κ <sub>T</sub> <sup>b</sup>
3.3 <sup>a</sup>	38,30	19.6708
3.6	52.30	42.5853
3.9	63.80	99.6183
5.3	63.75	64.2547
5.6	48.30	25.3615
5.9	37.20	12.0948

<sup>a</sup>Although "range" is symmetrical about  $\lambda_0 = 4.6$ , values of  $\kappa_T$  are not.  $\kappa_T^{-1}$  appears to be symmetrical at a value of  $\lambda_0$  closer to 4.55. In turn,  $\delta$  appears to be sensitive to the value of  $\lambda_{0c}$  adopted. (Symmetry implies  $\delta_G$  and  $\delta_L$  would be identical.)

<sup>b</sup> Due to use of double precision, the values of  $\kappa_T$  herein are higher than one would expect looking at  $\theta = 0.3741$ in Table I. However, use of single precision in gathering data for  $\beta$  in Table I appeared to be adequate, since values of  $\kappa_T$  are used *indivectly* in an extrapolative technique. Furthermore, the complementary use of F = 0, which depends on short-range values of  $g^{(2)}(x)$  and is insensitive to range used, supports the results of the extrapolative procedure. often exceeding 70 diameters. To ensure that the results obtained were reliable, double precision was used in the computer calculations. This made only a minor difference even though the function  $P^* - P_c^*$  calculated using the integral expression given above *is* very sensitive to values (shape) of the curve  $\kappa_T^{-1}$  vs  $\lambda_0$ . (In contrast, evaluation of  $\beta$  and  $\gamma$  were not sensitive to whether or not double precision was used). The value of  $\delta$  achieved was  $\delta = 4.4 \pm 0.2$  and is definitely the least reliable of the three exponents computed from the YBG equation.

In summary, the critical point for the squarewell intermolecular potential with R = 1.85, as determined from the YBG equation with superposition approximation, is

 $\theta_c = 0.47305 \pm 0.00005$ ,  $\lambda_{0c} = 4.57 \pm 0.05$ .

The critical exponents are

 $\gamma = 1.23 \pm 0.02$ ,  $\beta = 0.330 \pm 0.008$ ,  $\delta = 4.4 \pm 0.2$ ,

where  $\beta$  and  $\delta$  are symmetrical with respect to gas and liquid sides. These values and their uncertainties are based on the best values of the  $g^{(2)}(x)$  function (and the resulting function  $\kappa_T$ ) that we currently have available.

#### **III. DISCUSSION AND CONCLUSIONS**

A useful starting point for a discussion of the results presented in this paper (and their implications) is to review some remarks made by Widom<sup>6</sup> over a decade ago concerning similarities and differences between the Ising model and the square-well model. Since our concern here is not the solid-liquid transition, we comment only briefly on the role of repulsive forces in the two models. In the Ising model (or associated lattice gas), the metric imposed by the underlying lattice effectively brings in *intercellular* repulsive correlations among the particles in the system. In the square-well model, repulsive interactions are taken into account by means of a hard-core contribution to the potential-energy function, and the correlation propagated in the integral-equation theory via a continuous spatial variable. Given Widom's arguments on the importance of the "exclusion sphere," the latter model is expected to be more successful in describing the solidliquid transition, and it is. As we have shown, solutions of the YBG equation for the square-well model become periodic in the high-density  $regime^1$  and, in fact, we have shown recently<sup>7</sup> that solutions with apparently the correct qualitative behavior can even be found below the triple point. Considering now attractive forces, both models are characterized by Hamiltonians emphasizing nearest-neighbor interactions (only). In the Ising model, there are contributions to the Hamiltonian due to exchange interactions between nearest-neighbor spins aligned parallel or antiparallel. If one imagines the energy levels of the Ising Hamiltonian to be shifted. such that the value zero is assigned to the antiparallel configuration and the value  $-\epsilon$  assigned to the parallel one, then, again emphasizing the restriction to nearest-neighbor interactions (only), one simulates the interpretation given to the attractive part of the intermolecular potential function in the square-well model. Given this interpretation, one can argue that the square-well potential when incorporated within the framework of a distribution-function theory should play the same role in propagating (attractive) correlations as the Ising Hamiltonian plays when the latter is incorporated in a lattice theory, a premise of considerable relevance to the present study since it is generally believed that the gas-liquid transition is governed principally by the attractive forces between the particles in the system. In calculating the thermodynamic properties, one averages over all configurations of spins in the lattice theory and overall configurations of particles in the distribution-function theory. If these averages were performed with no approximation, Widom<sup>6</sup> argues that an essentially correct description of the thermodynamics (here, the gas-liquid transition) should result. Although, to be sure, approximations are introduced out of necessity when one attempts to investigate the behavior in three dimensions of the Ising model or the square-well model, one may still hope that the underlying conceptual similarity between the two models translates into a quantitative correspondence in the (numerical) characterization of the behavior of a fluid in the neighborhood of its critical point. We now examine the extent to which this hope is realized.

Consider first the critical exponent  $\gamma$ . This exponent scales the response function  $\rho^2 \kappa_T$  for a fluid or  $\chi_T$  for a magnet (where  $\chi_T$  is the isothermal susceptibility); in particular, one writes the power law

 $\rho^2 \kappa_T = \Gamma^{\pm} \left| \Delta T \right|^{-\gamma} . \tag{6}$ 

In Ref. 2 we reported the value  $\gamma = 1.24 \pm 0.04$ . Actually, the error estimate reported in Ref. 2 is a bit conservative; we can probably assign with confidence the value  $\gamma = 1.23 \pm 0.02$ . The experimental value deduced for this exponent ranges from 1.23 to 1.28, as updated for Xe, CO<sub>2</sub>, SF<sub>6</sub>, and impure SF<sub>6</sub> in the recent review of Sengers *et al.*<sup>8</sup> The precise value of the critical exponent  $\gamma$  for the three-dimensional, spin- $\frac{1}{2}$ Ising model (class n = 1, dimension d = 3) is still an open question. There is a small discrepancy between estimates obtained using high-temperature series expansions, and those obtained using renormalization-group theory. Recently, Gaunt and Sykes<sup>9</sup> reviewed and reexamined the hightemperature series estimates for  $\gamma$  (considering the simple cubic, face-centered-cubic, body-centered-cubic, and diamond lattices), and concluded that (for all four lattices), the value of  $\gamma$  was  $\frac{5}{4}$ . However, the various estimates obtained using the renormalization-group approach are different from this value by  $\sim \frac{4}{5}\%$  ( $\gamma = 1.241 \pm 0.002$  by Baker *et al.*,  $^{10} \gamma = 1.241 \pm 0.004$  by Brezin *et al.*,  $^{11}$ and  $\gamma = 1.2402 \pm 0.0009$  by Le Guillou and Zinn-Justin<sup>12</sup>), a discrepancy which, according to Gaunt and Sykes, is too large to be explained away, given the stated confidence limits in the calculations.<sup>13</sup> On the other hand, our determination of the exponent  $\gamma$  happens to be in "agreement" with both the series-expansion and renormalizationgroup estimates (by virtue of the wider confidence limits in our calculation of  $\gamma$ ). Given the great theoretical significance attached to the precise determination of  $\gamma$ , we intend in the near future to undertake a further refinement of our  $g^{(2)}(x)$ data with the objective of achieving a precision comparable to the series-expansion and renormalization-group calculations.

The exponent which governs the behavior of the order parameter  $[(\rho - \rho_c)$  for a fluid and the magnetization (M) for a magnet] is the critical exponent  $\beta$ . Specifically, the power law is written

$$(\rho - \rho_c) = B \left| \Delta T \right|^{\beta} . \tag{7}$$

In our study, we determined  $\beta = 0.330 \pm 0.008$ while the experimental estimates of  $\beta$ , again taken from Ref. 8 for the systems noted above, range from 0.321 to 0.328. In the series-expansion studies<sup>14</sup> on the Ising model,  $\beta \simeq \frac{5}{16} = 0.3125$ whereas the renormalization-group estimate<sup>8</sup> is 0.325.

Against the apparent agreement found between the values determined for the critical exponents  $\gamma$  and  $\beta$  in the Ising model (d=3, n=1) and the square-well model (and both of these models with experiment), more of a discrepancy is found when one examines data on the critical exponent  $\delta$ . This exponent monitors behavior along the critical isotherm; here one studies  $|P - P_c|$  versus the order parameter  $\rho - \rho_c$  for a fluid (or |H| versus the order parameter M for a magnet, where H is the magnetic field and M is the magnetization) and writes the power law

$$\left|P - P_{c}\right| = D \left|\rho - \rho_{c}\right|^{\delta}.$$
(8)

We have determined  $\delta=4.4\pm0.2$  whereas the series-expansion studies on the Ising model, yield

the estimate<sup>14</sup>  $\delta = 5.00 \pm 0.05$  while the renormalization-group studies<sup>8</sup> yield  $\delta = 4.82$ . Although these values are different, the computational difficulties involved in determining  $\delta$  modulate somewhat the seriousness of this difference. In any case, we can at least claim that the square-well result is well away from the classical value (3.0 exactly), and perhaps consistent with the value used by Green, Vicentini-Missoni, and Levelt Sengers<sup>15</sup> in their well-known scaling plot (based on the experimental data for helium-3, helium-4, Xe, CO<sub>2</sub>, and H<sub>2</sub>O), viz.,  $\delta = 4.5$ . Moreover, the value  $\delta = 4.4$ , when taken in conjunction with our estimates of  $\beta$  and  $\gamma$ , certainly satisfies the fundamental inequality  $\gamma \ge \beta$  ( $\delta = 1$ ), here 1.23 vs 1.12 for the left-hand and right-hand sides, respectively. Once again it should be noted that the value of  $\delta$  and its uncertainty are based on our currently existing  $g^{(2)}(r)$  data along  $\theta = \theta_c$ ; these data suggest that further refinements in this calculation may well increase the value of  $\delta$ , thereby leading to satisfaction of the equality,  $\gamma = \beta(\delta)$ - 1).

The emergence of the nearly exact quantitative agreement with the accepted nonclassical values of the exponents  $\gamma$ ,  $\beta$ , and (to a lesser extent)  $\delta$ suggests strongly that our earlier determination of the critical exponent  $\gamma$  was not the outcome of a fortuitous cancellation of (theoretical and/or numerical) approximations. Even so, the most cautious position to be taken at this point is to demand further evidence on the critical behavior of the square-well fluid before making any final iudgments on the YBG theory. Accordingly, in future work we intend to examine first the downrange behavior of the pair correlation function; as noted by Fisher,<sup>16</sup> the asymptotic behavior of this function expressed in terms of its spatial argument may be represented as a power law where the exponent depends on the dimension dand an index  $\eta$ , viz.,

$$g^{(2)}(r) \sim r^{-(d-2+\eta)}, \quad T = T_c.$$
 (9)

Although there are some computational difficulties here, it should be possible to determine the critical exponent  $\eta$ . Secondly, we intend to examine the behavior of the specific heat  $C_{\rm V}$  as a function of  $(T - T_c)/T_c$ , where the power-law dependence here is monitored by the critical exponent  $\alpha$ ; we remark that  $\alpha$  does not seem to be as range dependent as  $\gamma$ ,  $\beta$ , and  $\delta$ .<sup>17</sup> If, however, we may take as representative the (nearly quantitative) nonclassical behavior found thus far in our determination of  $\gamma$ ,  $\beta$ , and  $\delta$ , then we believe the evidence presented argues for the essential correctness of an approach to the study of critical phenomena based on the classical theory of distribution functions.

Given the paucity of formal theorems establishing (even) the *existence* of distribution functions outside the dilute-gas regime,<sup>18</sup> and given the spectacular success enjoyed by the recent renormalization-group theories of critical phenomena,<sup>19</sup> the (tentative) conclusion reached in the preceding paragraph seems almost presumptuous and certainly reactionary. But, supposing that there is at least an element of truth in the statement, a number of theoretical implications of this conclusion can be explored. For example, one can speculate that the very existence of critical exponents might be linked to the topological indices whose specification codes the existence and uniqueness properties of the Yvon-Born-Green or Kirkwood nonlinear integral equations. It was, in part, to unravel this idea that the research reported in Refs. 4 and 5 was undertaken. There, conditions on existence and uniqueness of solutions of integral equations derived from the BBGKY hierarchy were established for various potential functions using the methods of nonlinear functional analysis. Unfortunately, as regards critical phenomena, what is lacking in these formal studies is an integral equation derived from a distribution-function theory which is known to give an essentially correct description of the gasliquid transition, and against which the predictions of a given fixed-point theorem can be checked. Taking at face value the close agreement between the computed values of  $\gamma$ ,  $\beta$ , and  $\delta$  for the

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square-well model vis-à-vis the Ising model (and experiment), we may suggest that the YBG equation for the square-well fluid can be regarded as an acceptable model equation for such studies. In fact, with respect to the eventual goal of proving concrete theorems, perhaps even greater progress would be realized if one were to construct a representation of the YBG equation for the square-well model in *two* dimensions. For d=2, n=1 one has, of course, the exact solution of Onsager for the Ising model, and although it would be too much to expect that one could achieve an analytic solution of the corresponding YBG problem, at the very least one could calculate (numerically) the critical exponents for the d=2square-well model, and, if the apparent correspondence between the Ising model and the squarewell model is preserved in two dimensions, one could use the Onsager solution as a guide in examining the topological properties of the corresponding YBG equation. These studies are in progress and it may be hoped that the results obtained will cast light on the above problems and the underlying concept of universality.

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