

Precise Determination of the Critical Exponent γ for the Yvon-Born-Green Square-Well-Potential Fluid

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Using the Yvon-Born-Green equation of state for a square-well-potential fluid, we have determined the critical exponent γ , where $K_T \propto |T - T_c|^{-\gamma}$ along the critical isochore, to be 1.24 ± 0.04 . This nonclassical value is consistent with the best experimental and theoretical estimates of γ and suggests strongly that a distribution-function theory with superposition approximation can correctly describe the equation-of-state behavior of a classical fluid in the vicinity of the single-component critical point.

It has never been demonstrated convincingly that a description starting from an integral equation for the pair correlation function $g^{(2)}(r)$ describes interparticle spatial correlations with sufficient accuracy that the critical region of a classical fluid is characterized correctly. In this note, we report a calculation of the critical exponent γ for a single-component, square-well-potential fluid as predicted by one realization of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) formulation, namely the Yvon-Born-Green (YBG) equation for the pair correlation function $g^{(2)}(r)$ with the Kirkwood superposition approximation.

Although it is unrealistic to expect that a three-parameter potential function as simple as the square-well potential can describe the subtleties of intermolecular interactions, it is nonetheless believed, as Widom stated¹ that, "what matters is not the quantitative accuracy of (the intermolecular potential) $\varphi(r)$ but rather the qualitative accuracy of the resulting spatial correlations of molecular positions." Widom predicted that use of an intermolecular potential such as the square well *within a proper statistical-mechanical framework* "would undoubtedly result [in] an essentially correct description of all the macroscopic properties of matter throughout a vast region of the P - T plane, including the neighborhoods of the triple and critical points." Luks and Kozak² and the study presented by Co, Luks, and Kozak³ appear to support these contentions.

In a more recent article, Levelt Sengers, Hocken, and Sengers⁴ discuss the large-scale fluctuations of the order parameter $\rho - \rho_c$ near the critical point and state that "because the fluctuations extend over regions containing many particles, the details of the particle interaction are irrelevant." A striking demonstration in support of

this view is offered by the results of the three-dimensional (3D) Ising and other related models representing lattice systems.

Consider now the critical behavior of the square-well-potential fluid. Alder, Young, and Mark⁵ exhaustively studied the molecular dynamics of a system of 512 square-well-potential particles in the vicinity of the critical point and found the critical exponents to be distinctly classical. However, the unit cell in this system is "small" in that from its center it measures roughly four molecules (or about four molecular diameters) to its boundary, and most likely the resulting classical exponents can be attributed to the restricted range in the unit cell over which correlations can propagate. On the other hand, the study of Co, Kozak, and Luks⁶ examined the behavior of $g^{(2)}(x)$ (where $x = r/\sigma_1$ and σ_1 is a molecular diameter) out to $x = 15$, at which point interparticle correlations were assumed to be randomized, i.e., $g^{(2)}(x) = 1$ at $x > x_{\max} = 15$. Some nonclassical behavior was observed.

More specifically, the values of γ , β , and δ were found to fall between the classical values and the generally accepted experimental values. The latter result is interesting in light of an argument presented by Levelt Sengers, Hocken, and Sengers,⁴ in which it is pointed out that because of gravitational forces, the correlation length in a classical fluid would not become much larger than 10^{-3} mm; in the above notation, this correlation length corresponds to a value of about $x_{\max} = 3000$. It follows that there are enough molecules present in a spatial sample measuring $4\pi x_{\max}^3/3$, where $x_{\max} = 15$, for nonclassical behavior to begin to manifest itself, and further it suggests that if the down-range behavior of the pair correlation function were precisely charac-

terized, one might be able to determine the degree to which nonclassical critical behavior is exhibited by the YBG equation for the classical, square-well-potential fluid. Thus we are led to the seminal question: How accurately does the YBG equation with superposition approximation describe spatial correlations in the vicinity of the critical point?

We decided to study the behavior of $g^{(2)}(x)$ along the critical isochore specified by the reduced density $\lambda_{oc} = 4\pi n\sigma_1^3 = 4.6$, where n is the number of molecules per cubic centimeter. This value was determined by Co, Kozak, and Luks,⁶ who also established that $\theta_{oc} = \epsilon/kT_c = 0.3743$ in their study. They determined γ to be about 1.09, where

$$K_T \propto |T - T_c|^{-\gamma}$$

and

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

Incidentally, the use of the compressibility equation, as opposed to the virial theorem, is absolutely crucial here. The virial theorem, when used in conjunction with functions $g^{(2)}(x)$ for the square-well-potential fluid, collapses to an expression in which only the short-range behavior of the $g^{(2)}(x)$ is sampled. On the other hand, the compressibility representation for the pressure of a square-well-potential fluid incorporates information on the down-range behavior of the function $g^{(2)}(x)$. Thus, in delineating the coexistence region, where these down-range correlations are of the highest importance, the compressibility expression is expected to be the more appropriate equation. It is for this reason that the compressibility equation alone has been used in recent years for studies on the square-well-potential fluid.

Several refinements are made in our present computations in comparison to these of Ref. 6:

(1) x_{\max} is extended to whatever value is needed to allow $g^{(2)}(x)$ to attain $1.000\,000 \pm 10^{-6}$ at long range.

(2) The convergence criteria placed on $g^{(2)}(x)$ in the YBG equation is more stringent. Convergence is assumed to be achieved when differences between $g^{(2)}(x)$ at all x between successive iterations is 10^{-6} , as compared to the 10^{-4} used in Ref. 6.

(3) The value of θ_c is reestimated from these new $g^{(2)}(x)$ data, since the location of θ_c directly affects the value determined for γ .

(The square-well parameter $R = 1.85$, where $R = \sigma_2/\sigma_1$ is a parameter denoting well width, was

maintained in order to preserve internal consistency with our earlier study.⁶) Refinements 1 and 2 above have a direct bearing on the value of K_T , as at long range $g^{(2)}(x) - 1$ is a small number of $O(10^{-5}$ to $10^{-6})$ and is weighted by x^2 . Notice that any inaccuracy in $g^{(2)}(x) - 1$, or an approximation such as $g^{(2)}(x) \equiv 1$, would be magnified by this factor x^2 . All computer computations were performed at single precision and thus our precision is probably beginning to be affected by roundoff as $x \rightarrow x_{\max}$.

Table I lists, as a function of θ , the value of x_{\max} , the value of x where $g^{(2)}(x) = 1.000\,000 \pm 10^{-6}$, and the value of K_T along with its uncertainty. Again, the uncertainty in K_T is larger than in $g^{(2)}(x)$ because $g^{(2)}(x) - 1$ is weighted by x^2 , i.e., computer roundoff contributions can conceivably affect the value of K_T . We feel, for instance, that the value of K_T at $\theta = 0.371$ might be low by as much as 3% as a result of computer roundoff, even though the above-stated convergences on $g^{(2)}(x)$ were met. Note that, at two values of θ , different starting solutions for $g^{(2)}(x)$ were used so that the converged $g^{(2)}(x)$ was approached from two different directions. For example, to determine $g^{(2)}(x)$ at $\theta = 0.368$, initial input of converged results at $\theta = 0.366$ and $\theta = 0.369$ were employed in separate generations of the $g^{(2)}(x)$ function at $\theta = 0.368$.

Using the values of K_T in Table I, a plot of K_T^{-1} vs θ was made to determine a new value of θ_c .

TABLE I. x_{\max} , range of $g^{(2)}(x)$, and K_T as a function of θ for the YBG square-well-potential fluid at $\lambda_0 = 4.6$ with $R = 1.85$.

θ	x_{\max}	Range	K_T
0.319	15	10.85	1.76 ± 0.02
0.329	15	11.90	2.21 ± 0.03
0.339	20	15.65	2.96 ± 0.01
0.349	20	18.30	4.43 ± 0.01
0.359	30	21.40	8.29 ± 0.01
0.366	40	29.90	19.34 ± 0.01
0.368 ^a	40	34.55	28.46 ± 0.04
0.369	40	37.05	36.07 ± 0.01
0.370 ^a	45	40.35	47.77 ± 0.05
0.371	50	44.25	66.50 ± 0.05^b

^a $g^{(2)}(x)$ at these θ were calculated twice using two different starting guesses for $g^{(2)}(x)$, obtained respectively from higher and lower values of θ .

^b This value of K_T appears low despite its apparent convergence accuracy. This could be due to an accumulation of roundoff contributions at large x .

(where $1/K_T \rightarrow 0$), since it is important in a study of this kind to pin down the location of the critical point with great care. It was found that $\theta_c = 0.3741$ to four significant figures, a value slightly less than the value we reported ($\theta_c = 0.3743$) in the calculation⁶ for which x_{\max} was taken as 15. It should be stressed that in this manuscript θ_c was found by using K_T information. In Refs. 6 and 2 it was found by a different approach—that of stability analysis. It is both encouraging and interesting that the two approaches yield quite similar values of θ_c .

Using this new value of θ_c , γ was determined from a log-log plot of K_T vs $(\theta_c - \theta)/\theta\theta_c$, the latter quantity being directly proportional to $T - T_c$. Taking into account the uncertainties in the K_T values and θ_c and allowing for error in the graphical determination of γ , a value of $\gamma = 1.24 \pm 0.04$ was found. We remark that in Refs. 6 and 2 we assigned a value and uncertainty to γ of 1.09 ± 0.02 . This number, along with its uncertainty, was based on the best computations of $g(x)$ that we had made up to that time for a given truncation in the range of integration of the YBG equation. In the present study, it was decided to extend the range x_{\max} of integration of the YBG equation in order to determine better the down-range behavior and improve the computational accuracy of the functions $g(x)$ generated. The consequence was that more reliable and accurate $g(x)$ data were obtained in a region much closer to the critical point, and the use of these data led to the value of $\gamma = 1.24 \pm 0.04$ reported in the manuscript. With these highly accurate $g(x)$, the (very sensitive) function K_T could be determined at several θ to the accuracies states in Table I. In turn, θ_c could be determined from K_T to an accuracy of ± 0.0001 as reported. The uncertainties reported in both K_T and θ_c led to our estimate of ± 0.04 in γ , which we feel is a generous admission of uncertainty. (That θ_c and K_T have uncertainties of comparable magnitude is coincidental.) The value $\gamma = 1.24 \pm 0.04$ spans the Ising-model result of 1.24 and the experimental value of 1.23 ± 0.02 reported by Chu⁷ based on reliable existing data. One can conclude that extension of x_{\max} to values as high as 50 takes into account the spatial correlations needed to represent the nonclassical behavior of the YBG equation of state. It appears that the YBG equation with the Kirkwood superposition approximation offers a most realistic description of the long-ranged, interparticle correlations which begin to dominate as one approaches the critical point.

A central question at this point, of course, is whether an extended calculation of the other critical exponents would yield classical or nonclassical values. Our rationale for focusing initially on the critical exponent γ was that γ is the easiest exponent to obtain from the YBG equation; moreover, its evaluation leads to a value of θ_c in the process. From a tactical (and logical) point of view, the next exponent to evaluate would be δ (i.e., δ_G and δ_L), since a knowledge of θ_c and the critical density used to obtain γ are now available. The numerical evaluation of δ is much more difficult than that of γ . $g(x)$ is required in the vicinity of the critical point, of course, but the state points used to compute δ are closer to the two-phase coexistence region; thus, there may be a need for values of x_{\max} even larger than $x_{\max} \approx 50$. (This might explain why in Ref. 6 $\delta_L \neq \delta_G$, i.e., a poor result was obtained.) Finally, β (i.e., β_G and β_L) could be evaluated if one determined the locus of the coexistence envelope. It is important to emphasize that the determination of β reported in Ref. 6 was based not on the above program but rather was obtained by implementing the Kirkwood criterion assuming that the locus on the lower bound of stability of the fluid phase was *coincident* with the locus of the coexistence envelope; although theorems on the existence and uniqueness of solutions to nonlinear integral equations suggest such a correspondence, no formal proof establishing an exact equivalence of these loci has even been given. In fact, a principal motivation for undertaking the difficult numerical program outlined above would be to clarify the exact nature of the correspondence between these loci, and to check the earlier estimates of δ and β reported in Ref. 6.

The implications of the present study are of interest in light of on-going analytic studies of the distribution-function theories of statistical mechanics. For example, it is now known that phase transitions are characterized by singularities in certain thermodynamic functions that are otherwise analytic.⁸ Moreover, it is the nature of the singularity that determines the classical versus nonclassical behavior of the critical exponents. In studies based on the Ising model, for example, the singularity is clearly exposed and the attendant critical exponents are well characterized. In numerical studies based on integral equations derived from the BBGKY hierarchy, the singularity is disguised and its influence is felt in a more subtle way; in particular, the structure of the pair correlation function $g^{(2)}(x)$ changes as

one enters the coexistence region. In the one-phase gas regime, the $g^{(2)}(x)$ function relaxes to the mean density value after no more than a few (vis., $x_{\max} < 7$) intermolecular diameters. On the other hand, as one increases the density along a given isotherm, $g^{(2)}(x)$ lifts off the mean-density solution in a quite abrupt and dramatic way upon entering the coexistence region, and remains distinctly different from the mean-density solution even if the range of integration is extended to 50 intermolecular diameters (the present study). In numerical studies based on an integral-equation approach, this effect has been documented by several groups over the last decade, and what we have tried to do in this study is to perform our numerical experiments with an accuracy which is comparable to the best experimental studies.⁴ If one seeks an accuracy of 10^{-6} in the calculation of $g^{(2)}(x)$ (the present study), the data show that the YBG equation under the superposition approximation yields a solution for $g^{(2)}(x)$ which is certainly *not* the uniform-density solution as one approaches the critical point, even when x_{\max} is set at 50. This behavior is, of course, monitored by the function K_T whose behavior is represented in Table I.

Although a main emphasis in contemporary theories of phase transitions is on the characterization of the underlying singularity, it should also be recognized that a mathematical feature common to integral equations derived from the BBG-KY hierarchy under the superposition closure is the presence of nonlinearity, e.g., the YBG equation for $g(r)$ may be written as an integral equation of the Hammerstein type with an exponential nonlinearity. The relationship between nonlinearity and singularity in such theories is under active investigation at the present time^{9,10} and the precise determination of the critical exponent γ reported here reinforces the impression that universality at the level of a distribution-function approach to the theory of critical phenomena may be linked to rather general conditions on the existence of solutions to the hierarchy equations.

Attempts have already been made to apply fixed-point theorems and bifurcation theory to the nonlinear integral equations of statistical mechanics,^{2,9} and the more recent theory of stable mappings and their singularities may provide a general framework within which to explore this point (see the remarks in Refs. 3 and 9).

The main conclusion to be drawn from this study is that, if the calculation of $g(x)$ from the YBG theory is done meticulously enough, nonclassical results will occur. In addition to the nonclassical value of γ reported in this note, the authors strongly feel that nonclassical values of both δ and β will occur also if these calculations are done meticulously enough. Presumably this implies as well that the corresponding gas and liquid values of the exponents will *not* be unequal. The quantitative confirmation of our belief that β and δ would be nonclassical will require a very substantial effort.

¹B. Widom, *Science* **157**, 375 (1967).

²For example, see the review by K. D. Luks and J. J. Kozak, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1978), Vol. 40, pp. 139–201.

³K. U. Co, K. D. Luks, and J. J. Kozak, "Solutions of the Yvon-Born-Green Equation for a System of Square-Well Molecules at a Temperature Below the Triple Point" (to be published).

⁴A. Levelt Sengers, R. Hocken, and J. V. Sengers, *Phys. Today* **30**, No. 12, 42 (1977).

⁵B. J. Alder, D. A. Young, and M. A. Mark, *J. Chem. Phys.* **56**, 3013 (1972).

⁶K. U. Co, J. J. Kozak, and K. D. Luks, *J. Chem. Phys.* **64**, 2197 (1976).

⁷B. Chu, *Ber. Bunsenges. Phys. Chem.* **76**, 202 (1972).

⁸D. Ruelle, *Statistical Mechanics* (Benjamin, New York, 1969).

⁹For a recent review, see J. J. Kozak, "Nonlinear Problems in the Theory of Phase Transitions" (to be published).

¹⁰J. J. Kozak, "Phase Transitions as a Problem in Bifurcation Theory" (to be published).