Observations on the criticality of the Yvon-Born-Green equation of state

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(Received 14 September 1981)

Recent analyses of the Yvon-Born-Green equation strongly suggest that if it has a critical point, the critical correlations are, for spatial dimension less than four, negative at long range. We present here new numerical evidence that the YBG equation, in spatial dimension three, does *not* have a critical point, in contrast to the conclusions reached in previous numerical work. Our evidence comes from new numerical solutions which are closer to the supposed critical point and of greater precision than was achieved in the previous work. The extrapolations inferred from the previous work are *not* followed by the new solutions. The conclusion that there is no true critical point is based on three observations. (1) None of our numerical solutions are negative at long range. (2) The inverse compressibility does not extrapolate to zero along any isochore in the vicinity of the supposed critical point. (3) The inverse correlation length does not extrapolate to zero in the vicinity of the critical point, but rather goes through a nonzero minimum at a point of maximum, but not infinite, correlation length.

I. INTRODUCTION

Green *et al.*[1–3] have solved the Yvon-Born-Green (YBG) equation, in the superposition approximation, for the pair distribution function $g(r)$ by a numerical iterative technique. The intermolecular potential used was a hard core of radius σ with an attractive square well of radius 1.85 σ and depth ϵ. They found a region of temperature and density for which $g(r)$ became long ranged, and hence the reduced compressibility

$$\kappa_T = 1 + \int_0^\infty [g(r)-1]r^2 dr$$

quite large. Natural extrapolations of their data in this region implied a critical point near $\theta = \epsilon/kT = 0.374$ and reduced density $\lambda_0 = 4\pi n \sigma^3 = 4.60$, where n is the number of molecules per unit volume. With these critical point values, they determined from above numerical data values of the critical exponents which were very close to those believed to be correct[7] for fluids.

Subsequent analytic work on the YBG equation by Jones[4] *et al.* and by Fisher and Fishman[5,6] have made the existence of critical solutions of the YBG equation for spatial dimension three less plausible. These authors have argued that if the YBG equation has solutions for which a well defined inverse correlation length $\kappa \to 0$, then ultimately the correlations $h(r) = g(r) - 1$ must become negative at intermediate and long ranges. This is certainly not plausible for a realistic critical correlation function and none of the previous[1–3] numerical solutions have shown this property.

This apparent discrepancy between the numerical and the analytical work has led us to refine the numerical solutions of the YBG equation and in particular to construct solutions closer to the supposed critical point than was previously possible. We believe the new data show that, in the vicinity of the previously supposed critical point, the inverse correlation length does not attain zero but rather goes through a positive minimum, the inverse compressibility does not attain zero, and the correlations remain positive at intermediate and long range. Our conclusion is that the YBG equation does not show true critical behavior for space dimension three but rather has a region of temperature and density for which critical behavior starts to develop but is never completely realized.

II. NUMERICAL METHOD

Since the previous work[6,1,2] and this work lead to different conclusions concerning the critical region of the YBG equation we shall, in addition to reporting the new data, discuss the relationship between the two works and the kind of numerical difficulties which arise in constructing these solutions.

The numerical method used here is basically that described in some detail in Refs. 1–3, i.e., a rather standard first-order iterative procedure. For illustrative purposes we describe the calculations done along what was supposed to be the critical isochore, $\lambda_0=4.60$, and from which the exponent γ was found. In the previous work solutions were found for several $\theta \leq 0.371$. The compressibility was then calculated at these θ and $\ln\kappa_T$ was plotted versus $\ln\epsilon$, where $\epsilon = |\theta-\theta_c/\theta\theta_c|$. Over a range of $8\times10^{-3} \leq \epsilon \leq 4\times10^{-2}$ the data points were very nearly on a straight line whose slope determined γ to have the value 1.24. It was noticed[8] that the point at $\theta=0.371$, closest to the supposed critical point, was slightly low but this was attributed to numerical difficulties. We now see this as the beginning of a systematic deviation from the critical behavior established in the interval $8\times10^{-3} \leq \epsilon \leq 4\times10^{-2}$, a deviation whose final result is the absence of any true critical point.

In the previous work solutions for $\theta > 0.371$ were not found because of two numerical difficulties; (1) as θ increases the range of $g(r)$ increases and therefore the cutoff range r_{max} for the numerical solutions must be increased; this, in turn, causes a rather rapid increase in the computer time required for an iteration (of the order of one sec per iteration). (2) The apparent convergence rate of the iterative process becomes smaller as θ increases towards θ_c requiring many more iterations to obtain solutions at a given level of accuracy. Roundoff error in the previous single precision calculations had to be contended with. This coupled with the slow rates of convergence made it unclear whether the iterative procedure was ultimately converging at all and prevented the numerical construction of reliable solutions for $\theta > 0.371$.

We report here results obtained from new numerical solutions of the YBG equation. These differ from the previous solutions in the following respects. (1) The calculations are done in double precision, effectively eliminating the problem of any accumulation of roundoff error. (2) The calculations are done to higher convergence. Iterations are continued until the difference between successive iterates of $g(r)$ is less than 10^{-10} at every r, as compared to 10^{-6} in the previous work. (3) Solutions are found for values of (λ_0,θ) closer to the supposed critical values than in the previous work. The very slow rates of convergence typically require several thousand iterations before the desired precision is reached. As in previous work the solutions are always constructed for an interval r_{max} somewhat larger than the range at which the correlations have decreased to 10^{-6}. (4) A more detailed analysis of iterative process is given, which convincingly shows the process is converging and allows an estimate of the remaining error.[9]

III. RESULTS

Figure 1 is a plot from the new data of κ_T^{-1} vs θ for the supposed critical isochore $\lambda_0=4.60$. The dotted line shows roughly the previous extrapolation of κ_T^{-1} to zero, from data at $\theta \leq 0.371$. The

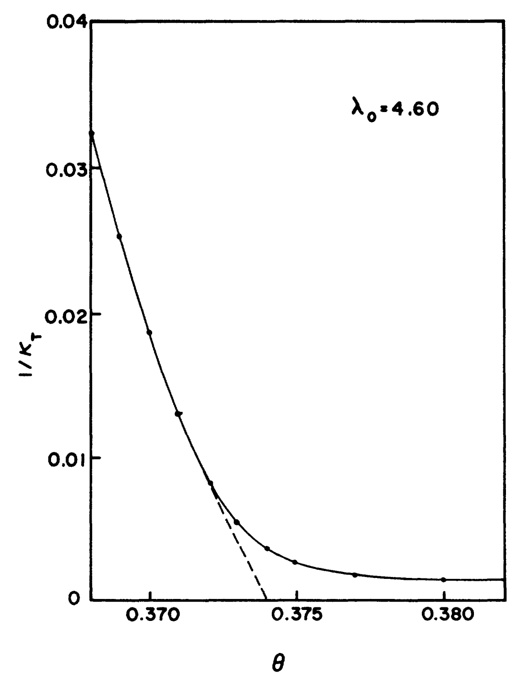

FIG. 1. Plot of κ_T^{-1} vs θ for $\lambda_0=4.60$. The dashed line is the extrapolation to $\kappa_T^{-1}=0$ of the steep portion of the locus.

data for $\theta > 0.371$ do not follow this trend and clearly do not extrapolate to zero in this region of temperature. A similar figure could be constructed for neighboring isochores. Table I presents the isothermal compressibility κ_T, the range [at which $g(r)-1 \leq 10^{-6}$] and the cutoff length r_{max} of the solutions, along several representative isochores. The range of $g(r)$ reaches a maximum along each isochore whereas the compressibility continues to increase with θ, although more slowly at the larger θ.

Another reasonable criterion for a critical point is a Kirkwood stability condition, i.e., that a certain stability function[10] $F(0,\theta,\lambda_0)$ vanish at the critical point. It has been shown[4] that this function is proportional to the square of the inverse correlation length of $g(r)$.[11] In Fig. 2 we plot $F(0,\theta,\lambda_0)$ along the isochore $\lambda_0=4.60$. The stability function does not reach zero but has a positive minimum of 0.0064 at $\theta=0.375$. This corresponds to a minimum $\kappa \simeq 0.08$ or a maximum correlation length $\xi \simeq 12.5\ \sigma$.

The numerical solutions for $g(r)$, from which the above data were constructed, were obtained by iterating until the difference Δn between the n and $n-1$ iteration was 10^{-10} at every r. This usually required several thousand iterations at the larger values of θ since Δ_n decreased very slowly with the number of iterations n. The fact that Δ_n decreases with increasing n is *not* sufficient to ensure that

TABLE I. κ_T, range, and r_{max} as a function of θ and λ_0.

λ_0	θ	κ_T	Range	r_{max}
4.55	0.368	31.33	53.00	60
	0.369	40.45	58.60	65
	0.370	54.64	65.15	70
	0.371	78.14	76.90	100
	0.372	117.32	88.40	100
	0.373	182.46	103.00	125
	0.374	274.33	115.40	150
	0.375	374.88	122.40	150
	0.377	527.95	123.35	150
	0.380	631.25	115.05	150
	0.385	685.32	103.20	150
4.60	0.368	30.79	52.85	60
	0.369	39.75	58.45	65
	0.370	53.74	66.20	75
	0.371	76.86	76.75	100
	0.372	116.17	88.50	100
	0.373	181.79	103.55	125
	0.374	276.31	116.75	150
	0.375	382.14	124.30	150
	0.377	544.96	125.65	150
	0.380	653.44	117.25	150
	0.385	708.93	104.90	150
4.65	0.368	30.09	52.55	60
	0.369	38.77	58.10	65
	0.370	52.33	65.85	75
	0.371	74.77	76.30	100
	0.372	113.19	88.20	100
	0.373	178.44	103.70	125
	0.374	275.05	117.70	150
	0.375	386.33	126.05	150
	0.377	560.75	128.05	150
	0.380	676.55	119.50	150
	0.385	732.20	106.70	150

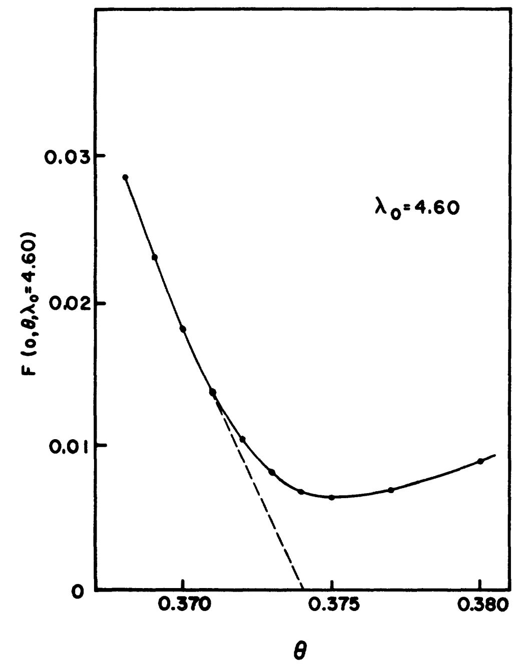

FIG. 2. Plot of $F(0,\theta,\lambda_0)$ vs θ for $\lambda_0=4.60$. The dashed line is the extrapolation to zero of the steep portion of the locus.

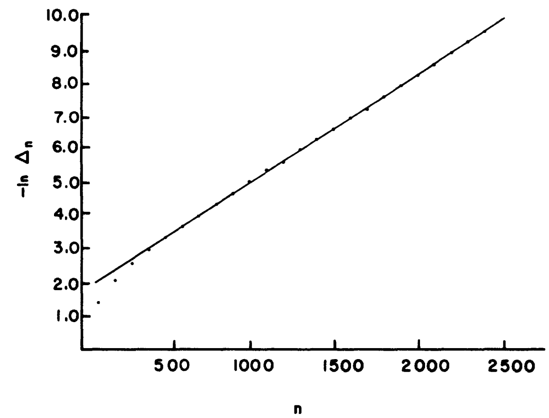

FIG. 3. Plot of $-\ln\Delta_n$ vs n for the compressibility at $\lambda_0=4.60$ and $\theta=0.375$.

the process converges. If Δ_n decreases too slowly the process may be divergent, so one must consider the possibility that the deviations from the previously extrapolated curves in Figs. 1 and 2 are due to a loss of convergence in the iterative process, i.e., that the values would continue to change slowly but ultimately by very large amounts under continued iteration. We have convincing evidence that this is not the case and can, in fact, estimate the remaining error.

A quantity X computed by a convergent first-order iterative process will *usually* approach its limit $\bar{X}$ geometrically, i.e., if X_n is the value of X at the nth iteration, then one expects for large n that the remaining error δ_n be given by $\delta_n=X_n-\bar{X}=Ac^n$, where $|c|<1$. The difference between successive iterates will be

$$\Delta_n=X_n-X_{n-1}=A(c-1)c^{n-1}.$$

So the process will converge geometrically if a plot of $\ln\Delta_n$ vs n is, for large n, a straight line whose slope ($\ln c$) is negative. This test has been applied to several of the numerical solutions where the quantity X has been chosen to be either the compressibility or the value of g at various r. A typical result is shown in Fig. 3 where, for the compressibility at $\lambda_0=4.60$, $\theta=0.375$, $-\ln\Delta_n$ vs n is plotted for $100\leq n\leq 2400$. The points fall very accurately on a straight line for $n>500$, whose slope determines a value of $c=0.9968$. So the convergence is very slow but the process shows no tendency whatsoever to lose convergence at large n. The error δ_n remaining in κ_T can be found from the successive difference Δ_n by $\delta_n=\Delta_n c/(1-c)$. For slowly converging processes ($c\simeq 1$), δ_n is much larger than Δ_n so it is important to iterate to very small Δ_n for these processes. For the compressibility example we have used here $\delta_{2400}\simeq 0.025$ which should be compared to the value of κ_T of 382.14 given in Table I. These convergence results are typical of all the data, with the convergence factor c generally closer to 1 for solutions whose range is large. It therefore appears that the large-θ solutions are as reliable as those previously found despite the slow convergence rate, and that the new conclusions based on them are warranted by the numerical evidence.

IV. CONCLUSIONS

We feel the numerical evidence supports the following conclusions concerning the critical region of the YBG equation. In the vicinity of $\lambda_0=4.60$ and $\theta=0.374$, there is no true critical point in the sense that the compressibility and correlation length of all solutions in this region remain *finite* and, in addition, the correlation function $g(r)-1$ is always positive at intermediate and long range. Thus, there is no disagreement between the numerical evidence and the analysis presented in Refs. 4–6. There is, however, a region near $\lambda_0=4.60$,

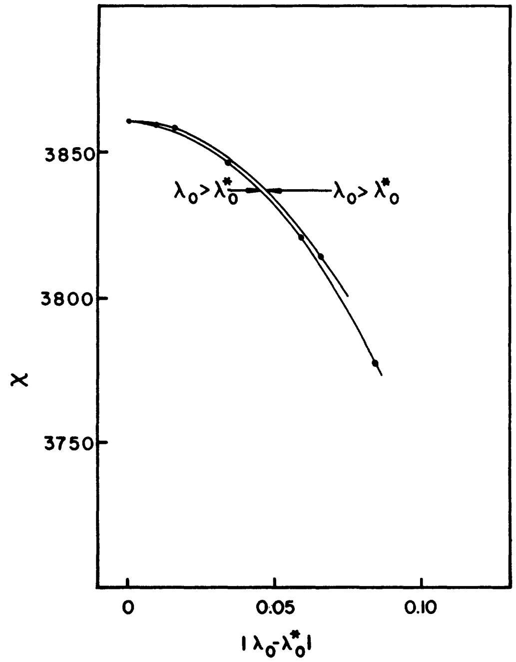

FIG. 4. Plot of χ vs $|\lambda_0-\lambda_0^*|$ for $\theta=0.373$ and $\lambda_0^*=4.634$.

$\theta=0.374$, where the solutions *appear* to be approaching a critical point. In this near critical region, the thermodynamic behavior very nearly follows the algebraic forms characteristic of true critical behavior and the exponent values are quite realistic.[1-3] This near critical region extends to perhaps $\epsilon\simeq 8\times 10^{-3}$ (i.e., to within about $\frac{1}{2}\%$ of the critical temperature) along the critical isochore. As a final example of the rather realistic properties of this region, we show in Fig. 4 a plot of the susceptibility $\chi=\lambda_0^2\kappa_T$, at $\theta=0.373$, vs $|\lambda_0-\lambda_0^*|$, where λ_0^* is the value of λ_0 for which χ is maximum on this isotherm. The behavior is nearly symmetrical as expected[12] in the neighborhood of a critical point. This symmetry becomes markedly weaker for $\theta\geq 0.375$.

ACKNOWLEDGMENTS

The authors would like to thank Professor M. E. Fisher for his helpful discussions and correspondence on this problem. K.A.G. and K.D.L. are grateful for computer time provided by Amoco Production Company, Tulsa, Oklahoma. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2272 from the Notre Dame Radiation Laboratory.

[1] K. A. Green, K. D. Luks, and J. J. Kozak, Phys. Rev. Lett. 42, 985 (1979).
[2] K. A. Green, K. D. Luks, E. Lee, and J. J. Kozak, Phys. Rev. A 21, 356 (1980).
[3] K. A. Green, K. D. Luks, and J. J. Kozak, Phys. Rev. A 24, 2093 (1981).
[4] G. L. Jones, J. J. Kozak, E. Lee, S. Fishman, and M. E. Fisher, Phys. Rev. Lett. 46, 795 (1981).
[5] M. E. Fisher and S. Fishman (unpublished).
[6] S. Fishman (unpublished).
[7] M. S. Green, M. Vincentini-Missoni, and J. M. H. Levelt-Sengers, Phys. Rev. Lett. 18, 1113 (1967); J. V. Sengers, in *Proceedings of the 1980 Cargèse Summer Institute on Phase Transitions,* edited by M. Levy, J. C. LeGuillou, and J. Zinn-Justin (Plenum, New York, 1981); A. Senger, P. Hocken, and J. V. Sengers, Phys. Today 30, 42 (1977).
[8] See footnote b, p. 986 of Ref. 1.
[9] Parts of this work were done independently by K. A. Green and by G. L. Jones. The data of the two investigators agree and lead to the same conclusions. The data reported here are that of K. A. Green for which a larger number of iterations were done. The analysis of convergence is that of G. L. Jones.
[10] W. W. Lincoln, J. J. Kozak, and K. D. Luks, J. Chem. Phys. 62, 2171 (1975).
[11] Specifically, Ref. 4 shows that $\kappa^2=1-u_0/u_2$, where u_0 and u_2 depend on g at the hard core radius and at the square-well radius. The stability function of Ref. 10 is related to this by $F=1-u_0$.
[12] J. V. Sengers and J. M. H. Levelt-Sengers, in *Progress in Liquid Physics,* edited by C. A. Croxton (Wiley, Chichester, United Kingdom, 1978), p. 103–174.