

Test of closure approximations in equilibrium classical many-body theory

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Many integral equations for numerically predicting pair correlation functions $g^{(2)}$ in classical fluids have been proposed, each based on its own "closure approximation." We have investigated a procedure for evaluating such closures, particularly their capacity to describe clustering under the influence of attractive interparticle forces. Our approach utilizes the Gaussian core model in a large closed system which, under sign change of the coupling constant λ , undergoes a collapse to form a single compact aggregate with known properties. In the infinite system limit this phenomenon causes inverse temperature (β) expansions, such as that for $g^{(2)}$, to diverge. By contrast available closures lead to convergent expansions for the Gaussian core model, but with a "critical point" on the negative real $\beta\lambda$ axis. Specific calculations have been performed illustrating this behavior for the BGYK and the PY integral equations. We suggest that the proximity of the artifactual negative-axis critical point to the origin (where the collapse singularity should actually appear) provides a measure of accuracy of closure approximations.

I. INTRODUCTION

Under conditions of thermal equilibrium the properties of classical many-body systems can be determined from the low-order spatial distribution functions for the constituent particles. These properties include all thermodynamic quantities, as well as radiation diffraction patterns. Statistical mechanical theory provides the logical connection between the spatial distribution functions of all orders and the basic interparticle interactions that operate in the material system of interest.^{1,2}

The theory of molecular distribution functions originated over half a century ago,^{3,4} and has enjoyed a rich and diverse subsequent evolution.^{1,2,5} In order to reduce formal theory to a tractable form that is capable of producing numerical results for specific model systems it has inevitably been necessary to invoke some type of closure approximation. For fluids composed of spherically symmetric particles with additive pair interactions, these closure approximations have been directed toward determining the pair correlation function $g^{(2)}(r)$ which gives the distribution of particle pair separations r .

Several tests of the accuracy of closure approximations are available. One concerns the extent to which thermodynamic consistency relations are satisfied as required, e.g., by the identity of virial and compressibility equations of state.⁶ With the advent of powerful digital computers which allow accurate and detailed simulations of models, direct comparisons have also become possible between analytical predictions and simulation results for distribution functions.⁷ It is the purpose of this paper to advocate and to apply yet another kind of test.

A large number of closure approximations can be found in the literature directed at determining $g^{(2)}(r)$. These include among many others the Kirkwood superposition approximation,^{1,8} the Percus-Yevick (PY) approximation⁹ and its extension by Verlet (PY2),¹⁰ the hypernetted chain (HNC) approximation,¹¹ and the mean spherical model

(MSM).¹² We have limited our own detailed study to the first two of these.

Our approach rests upon the existence of a catastrophic instability that develops as the coupling constant changes sign in a family of models with bounded pair interactions. The following Sec. II explains this instability for a specific case, the so-called Gaussian core model.¹³ Sections III and IV, respectively, discuss the Kirkwood superposition approximation (in connection with the Born-Green-Yvon local stress equation), and the Percus-Yevick approximation. Section V presents some numerical results for $g^{(2)}$ showing how use of either of these closures misrepresents the collapse phenomenon as a kind of critical point on the negative coupling constant axis (or equivalently on the negative axis for the inverse temperature variable $\beta = 1/k_B T$). The final discussion in Sec. VI stresses our belief that none of the other closures that have been advanced have the correct functional form to reproduce the collapse singularity.

II. GAUSSIAN CORE MODEL

The Gaussian core model¹³ possesses the following interaction potential:

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N) = \lambda \sum \exp(-r_{ij}^2), \quad (2.1)$$

where positions of the N particles are denoted by vectors \mathbf{r}_i , λ is a coupling constant, and r_{ij} is the scalar distance between particles i and j . When $\lambda > 0$ the particles are mutually repelling, and at moderate densities many of the properties of this model resemble those for models with more realistic pair interactions. In particular the Gaussian core model exhibits a conventional freezing transition as the temperature is lowered into the face-centered-cubic or the body-centered-cubic structure at low or at high density, respectively.¹³⁻¹⁵ Extensive molecular dynamics simulations have been carried out for the Gaussian core model with $\lambda > 0$.^{14,16,17}

If the number N of particles is large, changing the sign of

λ produces an instability wherein all particles mutually attract and collapse to a tightly bound and compact aggregate. In this collapsed state the usual extensive thermodynamic properties are no longer proportional to N , but to N^2 . The collapse phenomenon develops even for very small negative λ , namely of order $N^{-1} \ln N$ according to the simple argument presented in Appendix A.

A major mathematical virtue of the Gaussian core model is that exact high-temperature series can be exhibited for its thermodynamic properties and distribution functions in the large-system limit.¹⁸ The natural expansion parameter is

$\beta\lambda$, and owing to the collapse instability that occurs at $\beta\lambda = 0$ in the large-system limit, these are asymptotic series with vanishing radius of convergence. In the case of the pair correlation function we have

$$g^{(2)}(r, \beta\lambda) \sim 1 + \sum_{n=1}^{\infty} (-\beta\lambda)^n f_n(r), \quad (2.2)$$

where explicit calculation produces the following forms for the leading-order coefficient functions ($\rho = N/V$, the number density):

$$f_1(r) = \exp(-r^2); \quad (2.3)$$

$$f_2(r) = (1/2)\exp(-2r^2) + \rho(\pi/2)^{3/2}\exp(-r^2/2); \quad (2.4)$$

$$f_3(r) = (1/6)\exp(-3r^2) + \rho[(\pi/2)^{3/2}\exp(-3r^2/2) + (\pi/3)^{3/2}\exp(-2r^2/3)] + \rho^2(\pi^2/3)^{3/2}\exp(-r^2/3); \quad (2.5)$$

$$f_4(r) = (1/24)\exp(-4r^2) + \rho\pi^{3/2}[2^{-5/2}\exp(-5r^2/2) + 3^{-3/2}\exp(-5r^2/3) + (1/24)\exp(-3r^2/4) + (1/32)\exp(-r^2)] + \rho^2\pi^3[3^{-3/2}\exp(-4r^2/3) + (3/2)5^{-3/2}\exp(-2r^2/5) + 2(5^{-3/2})\exp(-3r^2/5) + (1/16)\exp(-r^2)] + \rho^3(\pi^{9/2}/8)\exp(-r^2/4). \quad (2.6)$$

For any positive density ρ one expects to be able to find pair correlation functions from any reasonable approximate theory, at least for small positive values of $\beta\lambda$. Furthermore these solutions should exhibit the qualitative characteristics expected for a stable fluid, namely, bounded and continuous short-range order that quickly decays away with increasing distance r to bring $g^{(2)}$ to its limiting value unity. However no such solutions should exist for negative $\beta\lambda$ if the approximate theory is functionally powerful enough to capture the collapse phenomenon, even if only qualitatively. Unfortunately we shall see below that this latter requirement tends not to be obeyed.

III. KIRKWOOD SUPERPOSITION APPROXIMATION

The Born–Green–Yvon integrodifferential equation for the pair correlation function has the following form¹⁹:

$$-\nabla_1 \ln g^{(2)}(r_{12}) = \beta \nabla_1 v^{(2)}(r_{12}) + \rho \beta \int d\mathbf{r}_3 [\nabla_1 v^{(2)}(r_{13})] \times g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) / g^{(2)}(r_{12}), \quad (3.1)$$

where $v^{(2)}$ represents the pair interaction, and $g^{(3)}$ is the triplet correlation function. Normally the latter is unknown just as is the desired $g^{(2)}$, but it is even more complicated.

Quite generally we can write the identity:

$$g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \equiv g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23})K(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (3.2)$$

where K is nonnegative and symmetric under interchange of particle positions. The Kirkwood superposition approxima-

tion sets K identically equal to unity.^{1,8} By using this approximation in Eq. (3.1) one obtains a nonlinear integrodifferential equation containing only the one unknown function $g^{(2)}$:

$$-\nabla_1 \ln g^{(2)}(r_{12}) = \beta \nabla_1 v^{(2)}(r_{12}) + \rho \beta \times \int d\mathbf{r}_3 [\nabla_1 v^{(2)}(r_{13})] g^{(2)}(r_{13}) g^{(2)}(r_{23}). \quad (3.3)$$

When the specific Gaussian form $\lambda \exp(-r^2)$ is inserted for $v^{(2)}(r)$, and bipolar coordinates are used for simplification, Eq. (3.3) reduces to the following form:

$$\frac{d \ln g^{(2)}(r_{12})}{dr_{12}} = 2\beta\lambda r_{12} \exp(-r_{12}^2) + (2\pi\rho\beta\lambda/r_{12}^2) \int_0^\infty dr_{13} \int_{|r_{12}-r_{13}}^{r_{12}+r_{13}} dr_{23} r_{13}r_{23} \times (r_{12}^2 + r_{13}^2 - r_{23}^2) \exp(-r_{13}^2) g^{(2)}(r_{13}) g^{(2)}(r_{23}). \quad (3.4)$$

It is straightforward to deduce (by substitution) a $\beta\lambda$ series for the solution to Eq. (3.4). The result formally has the structure displayed by the exact high-temperature series given earlier in Eq. (2.2). Indeed the coefficient functions f_1, f_2 and f_3 are again found to have the precise forms shown in Eqs. (2.3)–(2.5). However, a discrepancy (affecting only one contributing term) arises in the fourth-order coefficient, which for the Kirkwood approximation (K) becomes

$$\begin{aligned}
 f_4^{(K)}(r) = & (1/24)\exp(-4r^2) + \rho\pi^{3/2}[2^{-5/2}\exp(-5r^2/2) \\
 & + 3^{-3/2}\exp(-5r^2/3) + (1/24)\exp(-3r^2/4) + (1/32)\exp(-r^2)] \\
 & + \rho^2\pi^3[3^{-3/2}\exp(-4r^2/3) + (3/2)5^{-3/2}\exp(-2r^2/5) \\
 & + (1/3)5^{-1/2}\exp(-3r^2/5) + (1/16)\exp(-r^2)] + \rho^3(\pi^{9/2}/8)\exp(-r^2/4).
 \end{aligned} \quad (3.5)$$

IV. PERCUS-YEVICK APPROXIMATION

The direct correlation function $c(r)$ is defined implicitly in terms of $g^{(2)}$ by the Ornstein-Zernike relation:²⁰

$$g^{(2)}(r_{12}) - 1 = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13}) [g^{(2)}(r_{23}) - 1]. \quad (4.1)$$

Conventional wisdom holds that $c(r)$ has shorter range than $g^{(2)}(r) - 1$ and for that reason is more "fundamental."

The Percus-Yevick approximation takes $c(r)$ to be the following combination⁹:

$$c(r) \cong \{1 - \exp[\beta v^{(2)}(r)]\} g^{(2)}(r). \quad (4.2)$$

Hence Eq. (4.1) becomes

$$\begin{aligned}
 f_4^{(PY)}(r) = & (1/24)\exp(-4r^2) + \rho\pi^{3/2}[2^{-5/2}\exp(-5r^2/2) \\
 & + 3^{-3/2}\exp(-5r^2/3) + (1/24)\exp(-3r^2/4) + (1/32)\exp(-r^2)] \\
 & + \rho^2\pi^3[3^{-3/2}\exp(-4r^2/3) + (3/2)5^{-3/2}\exp(-2r^2/5) \\
 & + 2(5^{-3/2})\exp(-3r^2/5)] + \rho^3(\pi^{9/2}/8)\exp(-r^2/4),
 \end{aligned} \quad (4.4)$$

which differs from Eq. (2.6) only by virtue of a missing term $\rho^2(\pi^3/16)\exp(-r^2)$.

V. NUMERICAL SOLUTIONS

One of the primary tasks in the present project is to obtain numerical $g^{(2)}$ solutions for the approximate Born-Green-Yvon-Kirkwood (BGYK) and the Percus-Yevick (PY) equations. This is done first for positive values of the parameter $\beta\lambda$, followed by continuous change in this quantity toward and into negative values to see to what extent the collapse phenomenon is represented. A variety of numerical algorithms is available for this study; we have employed a Newton-Raphson technique²¹ for the BGYK case, and an iterative Fourier transform approach²² for the PY case.

Figure 1 shows a typical $g^{(2)}$ result for positive $\beta\lambda$. Specifically, this result was obtained by solving the BGYK equation for $\beta\lambda = 6.6667$, $\rho = 1.0$. Highly damped oscillatory short-range order is present, and substantial particle interpenetration is revealed by the fact that $g^{(2)}(0) \approx 0.2$. Solutions for the PY equation in this regime are quite similar to their BGYK counterparts.

As $\beta\lambda$ declines toward zero from positive values (ρ held constant), the numerical $g^{(2)}$ functions uniformly approach unity at all r . This is expected on physical grounds and is consistent with the series expansions for the two cases.

$$\begin{aligned}
 & \exp[\beta v^{(2)}(r_{12})] g^{(2)}(r_{12}) - 1 \\
 & = \rho \int d\mathbf{r}_3 \{1 - \exp[\beta v^{(2)}(r_{13})]\} \\
 & \quad \times g^{(2)}(r_{13}) [g^{(2)}(r_{23}) - 1].
 \end{aligned} \quad (4.3)$$

As in the preceding case of the Kirkwood superposition approximation, the result is a nonlinear functional equation containing only the single unknown quantity $g^{(2)}$.

As before, it is possible to generate a $\beta\lambda$ series for the solution to the Percus-Yevick integral equation. To do so it is necessary to replace $v^{(2)}$ in Eq. (4.3) with the Gaussian pair interaction $\lambda \exp(-r^2)$ and to iterate about the infinite-temperature limit. A formal series of the type (2.2) then arises. Just as was the case with the Kirkwood approximation the first three coefficient functions f_1, f_2, f_3 are exact, but the fourth-order term fails to agree with the exact form shown in Eq. (2.6). We find instead that the Percus-Yevick (PY) approximation leads to the result

We have found both for the BGYK and the PY approximations that the $g^{(2)}$ solutions smoothly continue at fixed ρ from positive $\beta\lambda$, through the origin, into the negative regime of $\beta\lambda$. Figure 2 exhibits the BGYK solution obtained

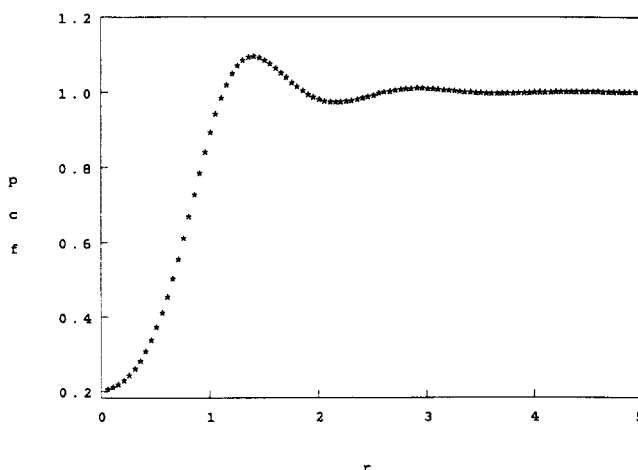


FIG. 1. Pair correlation function for the Gaussian core model, obtained by solving the BGYK equation at $\beta\lambda = 6.6667$, $\rho = 1.0$.

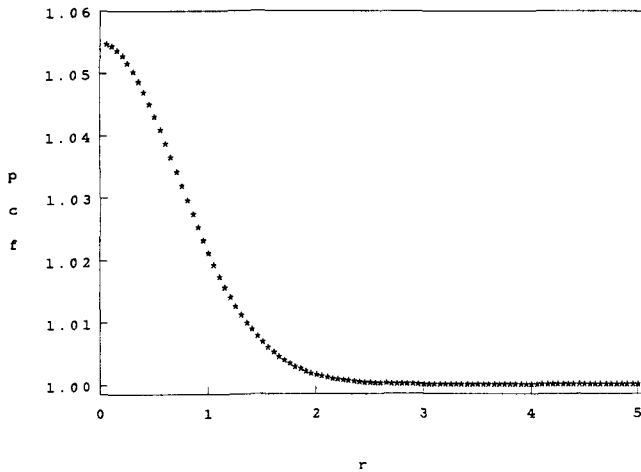


FIG. 2. Pair correlation function for the Gaussian core model, obtained by solving the BGYK equation at $\beta\lambda = -0.0500$, $\rho = 1.0$.

for $\beta\lambda = -0.0500$, $\rho = 1.0$, showing monotonic decay to unity with increasing r . Once again the PY solutions have quite similar character.

The attractive pair interactions present with $\beta\lambda < 0$ fail to produce collapse in the BGYK and PY approximations, but instead produce a modest local density enhancement. Tentatively this can be understood from the $\beta\lambda$ series for the two cases. Series results given in Secs. II–IV above indicate that $g^{(2)}(r) - 1$ is composed of Gaussian contributions with various weights and spatial ranges, both for the exact function, and for the BGYK and PY approximations. When $\beta\lambda > 0$ these contributions occur with alternating signs, and the resulting partial cancellation is r dependent in such a way as to produce damped oscillations. But when $\beta\lambda < 0$, at least through $O[(\beta\lambda)^4]$, the various Gaussian contributions all have positive signs and reinforce one another. That the BGYK and PY approximations smoothly continue from the positive to the negative $\beta\lambda$ axis indicates that the corresponding series have a nonzero radius of convergence. By

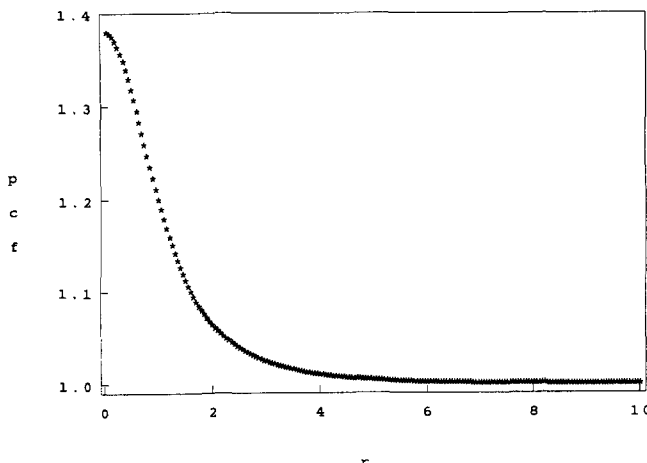


FIG. 3. Numerical pair correlation function for the BGYK equation for $\beta\lambda = -0.14599$, $\rho = 1.0$.

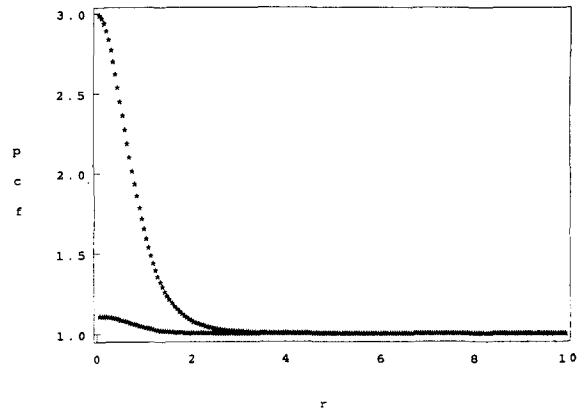


FIG. 4. Numerical pair correlation functions for the PY equation with $\beta\lambda = -0.100$ (lower curve) and -0.735 (upper curve) for $\rho = 0.1$.

contrast, the exact series for the infinite system limit must be divergent, reflecting the existence of a collapse-related essential singularity at $\beta\lambda = 0$.

As $\beta\lambda$ becomes more and more negative in the two approximations, the corresponding $g^{(2)}$ results display an increasing tendency toward local density enhancement (clustering), both regarding the magnitude of $g^{(2)}$ at $r = 0$ and the rate of monotonic decay with increasing distance. Figure 3 shows the numerical BGYK solution for $\beta\lambda = -0.14599$, $\rho = 1.0$. Comparison with Fig. 2 makes obvious the buildup both in magnitude and in range of the clustering tendency.

Figure 4 displays analogous numerical results for the PY equation, with $\beta\lambda = -0.100$ and -0.735 at the lower density $\rho = 0.1$.

Evidently the BGYK and PY approximations replace the vivid system-consuming collapse phenomenon with a pale imitation. At least for the $\beta\lambda < 0$ regime these approximations render the many-body system less cooperative than it should be.

We have been able only to obtain numerical $g^{(2)}$ solutions for the BGYK and PY equations for negative values of $\beta\lambda$ that are nearer to the origin than some negative critical limit $(\beta\lambda)_c$. This limit depends strongly on density ρ , but turns out to be nearly the same for the BGYK and PY approximations. Table I lists our estimates for these critical coupling constants.

The numerical evidence for both approximations and at the three densities considered ($\rho = 0.1, 0.4, 1.0$) indicates that $g^{(2)}(r, \beta\lambda)$ approaches a well-defined limit as $\beta\lambda$ approaches $(\beta\lambda)_c$ from above. However, the quantity

$$\frac{\partial g^{(2)}(r, \beta\lambda)}{\partial(\beta\lambda)} \quad (5.1)$$

TABLE I. Numerical estimates of the critical coupling constants for the two approximate theories.

ρ	BGYK $(\beta\lambda)_c$	PY $(\beta\lambda)_c$
0.1	-0.7312	-0.75
0.4	-0.2964	-0.305
1.0	-0.1460	-0.148

appears to diverge at $(\beta\lambda)_c$, roughly as $[(\beta\lambda) - (\beta\lambda)_c]^{-1/2}$. The critical coupling constants shown in Table I can be located by using this observation. Given this apparent branch point behavior it is then not surprising that we were unable ever to find real $g^{(2)}$ solutions for $\beta\lambda < (\beta\lambda)_c$. We suspect (but have not proved) that these critical coupling constants are the radii of convergence of the corresponding $g^{(2)}$ power series.

The isothermal compressibility κ_T is related to the pair correlation function through the well-known identity:²³

$$\rho\beta^{-1}\kappa_T = 1 + \rho \int [g^{(2)}(r) - 1] dr. \quad (5.2)$$

The integral in the right member provides a direct measure of the local clustering tendency, and so is a natural quantity to examine in the present context. Figure 5 shows a plot of $\lambda\kappa_T$ vs $\lambda\beta$ along a portion of the negative axis, for the BGYK case at $\rho = 1.0$. We see that $\lambda\kappa_T$ takes a downward plunge as $\beta\lambda$ approaches the critical value -0.1460 from above.

The data shown in Fig. 5 numerically can be fitted well with an expression of the form

$$A + B\Delta + C\Delta^{1/2}, \quad (5.3)$$

$$\Delta = \beta\lambda - (\beta\lambda)_c,$$

where A , B , and C are adjustable parameters. Analogous BGYK data for the other two densities considered (0.1, 0.4) likewise are represented well by the same form. We have not been able to improve the fits by using $\ln \Delta$ in place of $\Delta^{1/2}$ (this is a significantly poorer fit function at $\rho = 0.1$ and 1.0). In any case the compressibility seems formally to have a branch-point singularity at $(\beta\lambda)_c$.

In several respects the critical coupling constant points on the negative $\beta\lambda$ axis for the BGYK and PY approximations resemble conventional critical points. Near these points $g^{(2)}(r)$ develops relatively long-range behavior, and various thermodynamic quantities and distribution functions appear to exhibit critical singularities of branch-point character. However the specific critical singularities involved do not seem to be closely related to those that describe conventional critical phenomena, even after accounting for possible distinctions between the "mean-field" or "classical"

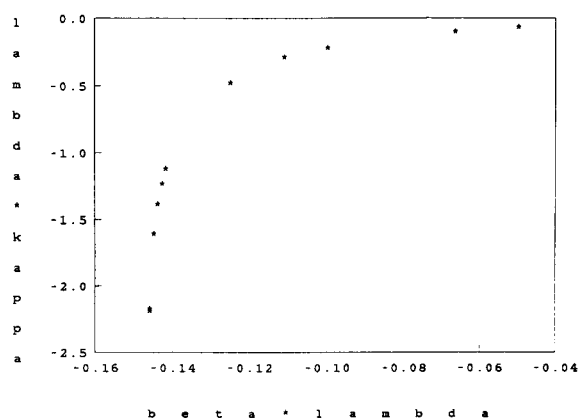


FIG. 5. Plot of the local density enhancement measure $\lambda\kappa_T$ [see Eq. (5.2)] vs $\beta\lambda$ for the BGYK approximation at $\rho = 1.0$.

values of the critical exponents, and the more realistic "non-classical" exponents.²⁴ In this context it should be emphasized that the Percus–Yevick²⁵ and the hypernetted-chain²⁶ approximations for $g^{(2)}$ are known to give qualitatively poor results at conventional critical points.

VI. DISCUSSION

Equation (B14) in Appendix B displays the explicit form of the accurate superposition correction factor K for the collapsed state, showing how drastically it differs from the constant unity proposed by Kirkwood's superposition approximation. Under the circumstances it is hardly surprising that the BGYK integral equation for $g^{(2)}$ fails to account correctly for the collapse phenomenon. It is not obvious to us that there exists an alternative functional of $g^{(2)}$ with which to approximate $g^{(3)}$ that (a) continues to be exact (as does the Kirkwood approximation) in the positive- $(\beta\lambda)$, low-density limit, (b) yields Eq. (B13) for the Gaussian core model collapsed state, and (c) leads to a numerically feasible analog to the BGYK equation.

Just as we see how badly the Kirkwood superposition approximation breaks down for the collapsed state, we can also see that the Percus–Yevick approximation is inappropriate. Starting with the Ornstein–Zernike equation (4.1), and inserting the $g^{(2)}$ expression in Eq. (B10), we find that the Fourier transform $C(k)$ of the direct correlation function $c(r)$ is

$$C(k) = \int dr \exp(ik \cdot r) c(r)$$

$$= 0 \quad (\mathbf{k} = 0)$$

$$= \frac{V \exp(-k^2/2|\beta\lambda|N)}{1 + \rho V \exp(-k^2/2|\beta\lambda|N)} \quad (\mathbf{k} \neq 0). \quad (6.1)$$

On account of the presence of the large quantity V in numerator and denominator, this function will substantially equal the constant ρ^{-1} for a wide range of nonvanishing \mathbf{k} 's around the origin.

By contrast the Percus–Yevick approximation for the direct correlation function, Eq. (4.2), leads to

$$c_{PY}(r) = V [1 - \exp(-|\beta\lambda|)] (|\beta\lambda| N/2\pi)^{3/2}$$

$$\times \exp(-|\beta\lambda|Nr^2/2). \quad (6.2)$$

In this expression we have replaced $v^{(2)}(r)$ by its value at the origin because of the extreme narrowness of the Gaussian factor. The Fourier transform is readily found to be (for all \mathbf{k})

$$C_{PY}(k) = V [1 - \exp(-|\beta\lambda|)] \exp(-k^2/2|\beta\lambda|N). \quad (6.3)$$

In stark contrast to the correct result (6.1) this is very large and positive near the origin.

Although we have only studied the two approximate theories BGYK and PY in sufficient detail to see why they fail qualitatively to describe collapse at negative $\beta\lambda$, we believe that all other currently available approximations (such as those advanced in Refs. 10–12) are analogous. In particular we expect that all will yield thermodynamic properties and particle correlation functions that are analytic in $\beta\lambda$ at

the origin. Furthermore, it seems reasonable to suppose that all will predict branch point singularities on the negative $\beta\lambda$ axis with critical point $g^{(2)}$'s similar to that shown in Fig. 3 above.

In contemplating future closure approximations for the theory of $g^{(2)}$, it may indeed be difficult to produce automatically the correct collapse singularity, located at $\beta\lambda = 0$ in the large system limit. Nevertheless at a more modest level attention should be given to generating approximations which, when applied to the Gaussian core model, manage to move the artifactual critical point closer to the origin. If this were successful it would indicate more generally that the approximations used were capable of accurately describing density fluctuations, particularly those that are associated with particle clustering under conventional physical circumstances.

APPENDIX A

Using simple arguments we now estimate the value of the coupling constant $\lambda < 0$ which will cause collapse to occur for a large fixed number N of particles with Gaussian pair interactions:

$$v^{(2)}(r_{ij}) = \lambda \exp(-r_{ij}^2). \quad (\text{A1})$$

We start with the following expression for $F^{(1)}$, the nonideal part of the Helmholtz free energy for the N particles:

$$\beta F^{(1)}(\beta, N) = -\ln \left\langle \exp \left[-\beta \sum_{i < j=1}^N v^{(2)}(r_{ij}) \right] \right\rangle. \quad (\text{A2})$$

Here $\langle \dots \rangle$ denotes an unweighted average over all possible particle positions inside the container of volume V . The transition of $F^{(1)}$ from $O(N)$ to $O(N^2)$ behavior marks the onset of collapse.

When λ is small but negative it is reasonable to suppose that the N particles fall into two categories. Generally some number $M \leq N$ will have aggregated into a more or less compact cluster, while the remainder $N - M$ are remote from the cluster and move through V in a virtually free manner. The partitioning of the N particles between bound and free is variable; taking all possibilities into account leads to

$$\begin{aligned} & \left\langle \exp \left[-\beta \sum v^{(2)}(ij) \right] \right\rangle \\ & \cong \sum_{M=L}^N \frac{N!}{(N-M)!M!V^M} \int dr_1 \cdots \int dr_M \\ & \quad \times \exp \left[-\beta \sum_{k < l=1}^M v^{(2)}(kl) \right]. \end{aligned} \quad (\text{A3})$$

In this expression the multiple integral is constrained to those positions $r_1 \cdots r_M$ which form a cluster, and L is an $O(1)$ lower limit for which the aggregate forms a recognizable cluster.

Within a compact M cluster the potential energy can be well approximated by the quadratic form:

$$\begin{aligned} \sum_{j < k=1}^M v^{(2)}(r_{jk}) & \cong \frac{1}{2} M(M-1) \lambda - \lambda \sum_{j < k}^M (r_j - r_k)^2 \\ & \cong \frac{1}{2} M(M-1) \lambda - M \lambda \sum_{j=1}^M (r_j - r_0)^2, \end{aligned} \quad (\text{A4})$$

where r_0 stands for the position of the cluster centroid:

$$r_0 = M^{-1}(r_1 + r_2 + \cdots + r_M). \quad (\text{A5})$$

This centroid of course can be located anywhere in volume V even though when $\lambda < 0$ the pair distances within the cluster are small. Consequently it makes sense to carry out a coordinate transformation which isolates the center of mass position. For this purpose we introduce the M quantities:

$$\begin{aligned} k_1 & = 0, \\ k_2 & = -2\pi/M, \quad k_3 = 2\pi/M, \\ k_4 & = -4\pi/M, \quad k_5 = 4\pi/M, \text{ etc.}, \\ k_M & = \begin{cases} 2m\pi/(2m+1) & (M \text{ odd} = 2m+1) \\ \pi & (M \text{ even}) \end{cases}. \end{aligned} \quad (\text{A6})$$

Then we have the following orthogonal transformation with unit Jacobian:

$$s_j = M^{-1/2} \sum_{i=1}^M \exp(ilk_j) r_i \quad (1 \leq j \leq M). \quad (\text{A7})$$

It is clear that $s_1 = M^{1/2} r_0$, and the other s_j are collective coordinates describing internal degrees of freedom within the cluster.

The s_j 's corresponding to $k_j \neq 0, \pi$ occur as complex conjugate pairs. It is desirable to transform each of these to a pair of real vectors. This can be effected by the transformations

$$\begin{aligned} t_{2n} & = 2^{-1/2}(s_{2n} + s_{2n+1}), \\ t_{2n+1} & = 2^{-1/2}(s_{2n} - s_{2n+1}), \end{aligned} \quad (\text{A8})$$

each of which likewise has unit Jacobian.

It is easy to show that the quadratic approximation (A4) for the cluster potential energy becomes

$$\sum_{j < k=1}^M v^{(2)}(r_{jk}) \cong \frac{1}{2} M(M-1) \lambda - M \lambda \sum_{j=2}^M t_j^2, \quad (\text{A9})$$

namely that of an isotropic oscillator in $3(M-1)$ dimensions. Consequently Eq. (A3) becomes ($t_1 \equiv s_1$):

$$\begin{aligned} & \left\langle \exp \left[-\beta \sum v^{(2)}(ij) \right] \right\rangle \\ & \cong \sum_{M=L}^N \{ N! \exp [-\frac{1}{2} M(M-1) (\beta \lambda)] / \\ & \quad [(N-M)! M! V^M] \} \\ & \quad \times \int dt_1 \cdots \int dt_M \exp \left[M \beta \lambda \sum_{j=2}^M t_j^2 \right]. \end{aligned} \quad (\text{A10})$$

The t_1 integration will give a factor $M^{3/2} V$. The condition that the M particles form a compact cluster can be taken as setting an appropriate upper limit τ_0 on the hyperradius τ in the $3(M-1)$, dimensional space:

$$\tau^2 = t_2^2 + t_3^2 + \cdots + t_M^2. \quad (\text{A11})$$

Since M is very large in our application, $O(N)$ in fact, we can suppose that the integrand in Eq. (A10) has become negligibly small at the hyperradius upper limit τ_0 . Consequently we have

$$\left\langle \exp \left[-\beta \sum v^{(2)}(ij) \right] \right\rangle \cong N! V \sum_{M=L}^N \frac{\exp \left[-\frac{1}{2} M(M-1) \beta \lambda \right]}{(N-M)! M! V^M M^{(3M-6)/2}} \times \left(\frac{\pi}{|\beta \lambda|} \right)^{3(M-1)/2}. \quad (\text{A12})$$

Evaluation of the nonideal free energy by Eq. (A2) requires taking the logarithm of expression (A12). To the order required it is then sufficient to replace the sum by its maximum term, corresponding to some $M = \bar{M}(\beta\lambda)$. Recognizing that \bar{M} is a large quantity, one obtains the following condition for its determination ($\beta\lambda < 0$):

$$0 = |\beta\lambda| \bar{M} - \frac{5}{2} \ln \bar{M} + \ln \left(1 - \frac{\bar{M}}{N} \right) + \ln \left[\rho \left(\frac{\pi}{e|\beta\lambda|} \right)^{3/2} \right]. \quad (\text{A13})$$

The structure of Eq. (A13) suggests writing

$$\bar{M} = N(1 - N^{-p}), \quad |\beta\lambda| = A \ln N/N + O(\ln \ln N/N), \quad (\text{A14})$$

so as \bar{M} increases from 0 to N , exponent p increases from 0 to infinity. Substituting these expressions into Eq. (A13) yields

$$A = 1 + p + O(\ln \ln N / \ln N). \quad (\text{A15})$$

Since p is nonnegative this result indicates a threshold magnitude of the interparticle coupling (in the large system limit):

$$(\beta\lambda)_c = -\ln N/N, \quad (\text{A16})$$

at which condensation initiates. For smaller magnitudes of $\beta\lambda$ the system is unaggregated. But as $\beta\lambda$ descends through $(\beta\lambda)_c$ in Eq. (A16) the condensation goes extremely rapidly toward completion. When the coupling doubles in magnitude to $2(\beta\lambda)_c$ the prediction is that on average all but one of the N particles will be found in the compact cluster; at $3(\beta\lambda)_c$, \bar{M} formally deviates below N only by N^{-1} .

APPENDIX B

We have established in Appendix A that the aggregation process is substantially complete when $|\beta\lambda|$ is at least a small multiple of $\ln N/N$. The objective now is to calculate low-order particle correlations in the completely aggregated state.

Utilizing the collective coordinates \mathbf{t}_j introduced in Appendix A, the normalized N -particle probability for the collapsed state is

$$P_N(\mathbf{r}_1 \cdots \mathbf{r}_N) = C_N \exp \left(-N |\beta\lambda| \sum_{j=2}^N t_j^2 \right), \quad C_N = N^{-3/2} V^{-1} (N |\beta\lambda| / \pi)^{3(N-1)/2}. \quad (\text{B1})$$

This expression can be employed to calculate distribution functions for small numbers of particles by carrying out suitable integrations. As an example, the probability $p_1(\mathbf{R}_1)$ that particle 1 is displaced by \mathbf{R}_1 from the cluster centroid position \mathbf{r}_0 is easily seen to be

$$p_1(\mathbf{R}_1) = \int d\mathbf{t}_1 \cdots \int d\mathbf{t}_N P_N \delta(\mathbf{R}_1 - \mathbf{r}_1 + \mathbf{r}_0). \quad (\text{B2})$$

This can be evaluated by introducing the formal integral representation for the Dirac delta function,

$$\delta(\mathbf{R}) = (2\pi)^{-3} \int d\mathbf{u} \exp(i\mathbf{R} \cdot \mathbf{u}), \quad (\text{B3})$$

and invoking the following relation between particle and collective coordinates (N has been assumed to be an even integer for simplicity):

$$\begin{aligned} \mathbf{r}_j - \mathbf{r}_0 = (2/N)^{1/2} [& \cos(jk_2) \mathbf{t}_2 + \sin(jk_2) \mathbf{t}_3 + \cos(jk_4) \mathbf{t}_4 \\ & + \sin(jk_4) \mathbf{t}_5 + \cdots + \cos(jk_{N-1}) \mathbf{t}_{N-1} \\ & + \sin(jk_{N-1}) \mathbf{t}_N] \quad (1 \leq j \leq N). \end{aligned} \quad (\text{B4})$$

When these identities are substituted into Eq. (B2) the resulting integrals can be carried out explicitly. One finds

$$\begin{aligned} p_1(\mathbf{R}_1) = \left(\frac{|\beta\lambda| N^2}{\pi(N-1)} \right)^{3/2} \exp \left[-|\beta\lambda| N^2 R_1^2 / (N-1) \right] \\ \cong (|\beta\lambda| N / \pi)^{3/2} \exp \left(-|\beta\lambda| N R_1^2 \right). \end{aligned} \quad (\text{B5})$$

The latter form is appropriate since N is large.

An obvious conclusion to be drawn from Eq. (B5) is that the root-mean-square displacement of the typical particle 1 from the cluster centroid is proportional to $(|\beta\lambda| N)^{-1/2}$. Because stability of the cluster requires $|\beta\lambda|$ to be at least of order $\ln N/N$ (see Appendix A), the rms displacement will be no larger in order of magnitude than $(\ln N)^{-1/2}$. Since N is assumed to be very large, this will be small compared to unity, thereby justifying use of the quadratic form (A4), (A9) for the potential.

The result (B5) has an elementary and obvious interpretation. It expresses the fact that particle 1 experiences an effective potential due to all $N-1$ other particles acting as though they all were located at a common position, virtually coincident with the centroid.

The generalization of expression (B2) is obvious to the joint probability for a pair of particles to be respectively displaced by \mathbf{R}_1 and by \mathbf{R}_2 from the centroid:

$$p_2(\mathbf{R}_1, \mathbf{R}_2) = \int d\mathbf{t}_1 \cdots \int d\mathbf{t}_N P_N \times \delta(\mathbf{R}_1 - \mathbf{r}_1 + \mathbf{r}_0) \delta(\mathbf{R}_2 - \mathbf{r}_2 + \mathbf{r}_0). \quad (\text{B6})$$

After using integral representation (B3) for both Dirac delta functions, and Eqs. (B4), the same kinds of simplifications obtain as before. The final result (in the large N limit) is exceptionally simple:

$$\begin{aligned} p_2(\mathbf{R}_1, \mathbf{R}_2) = p_1(\mathbf{R}_1) p_1(\mathbf{R}_2) \\ = (|\beta\lambda| N / \pi)^3 \exp \left[-|\beta\lambda| N (R_1^2 + R_2^2) \right]. \end{aligned} \quad (\text{B7})$$

Although the chosen particles 1 and 2 interact, their potential is virtually invariant over the small excursions permitted by the powerful cluster potential due to the remaining $N-2$ particles.

We can write

$$R_1^2 + R_2^2 \equiv \frac{1}{2} (\mathbf{R}_1 + \mathbf{R}_2)^2 + \frac{1}{2} r_{12}^2, \quad (\text{B8})$$

thereby transforming to independent centroid and relative-

configuration coordinates for the pair. After integrating over the former we obtain the distribution function $p^{(2)}$ for the scalar distance r_{12} in the collapsed state:

$$p^{(2)}(r_{12}) = (|\beta\lambda| N/2\pi)^{3/2} \exp(-\frac{1}{2}|\beta\lambda| N r_{12}^2). \quad (\text{B9})$$

For present purposes it is more useful to present this result in the form of the pair correlation function $g^{(2)}(r_{12})$. The transformation is trivial:

$$\begin{aligned} g^{(2)}(r_{12}) &= V p^{(2)}(r_{12}) \\ &= V (|\beta\lambda| N/2\pi)^{3/2} \exp(-\frac{1}{2}|\beta\lambda| N r_{12}^2). \end{aligned} \quad (\text{B10})$$

Extension to the three-particle case involves nothing fundamentally different. Not surprising, in the large N limit, the joint probability p_3 for three displacements from the cluster centroid factors into three p_1 's:

$$\begin{aligned} p_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) &= p_1(\mathbf{R}_1) p_1(\mathbf{R}_2) p_1(\mathbf{R}_3) \\ &= (|\beta\lambda| N/\pi)^{9/2} \exp[-|\beta\lambda| N (R_1^2 + R_2^2 + R_3^2)] \\ &= (|\beta\lambda| N/\pi)^{9/2} \exp[-(|\beta\lambda| N/3) \{ (\mathbf{R}_1 + \mathbf{R}_2 + \mathbf{R}_3)^2 \\ &\quad + r_{12}^2 + r_{13}^2 + r_{23}^2 \}]. \end{aligned} \quad (\text{B11})$$

The last way of writing this quantity separates the position of the three-particle centroid, which subsequently can be integrated out of the probability. The resulting probability $p^{(3)}$ for scalar distances alone becomes

$$\begin{aligned} p^{(3)}(r_{12}, r_{13}, r_{23}) &= (|\beta\lambda| N/3^{1/2}\pi)^3 \exp[-(|\beta\lambda| N/3) \\ &\quad \times (r_{12}^2 + r_{13}^2 + r_{23}^2)]. \end{aligned} \quad (\text{B12})$$

This is trivially equivalent to the three-particle correlation function:

$$\begin{aligned} g^{(3)}(r_{12}, r_{13}, r_{23}) &\equiv V^2 p^{(3)}(r_{12}, r_{13}, r_{23}) \\ &= V^2 (|\beta\lambda| N/3^{1/2}\pi)^3 \\ &\quad \times \exp[-(|\beta\lambda| N/3) (r_{12}^2 + r_{13}^2 + r_{23}^2)]. \end{aligned} \quad (\text{B13})$$

Equations (B10) and (B13) for $g^{(2)}$ and $g^{(3)}$ now permit us to calculate the Kirkwood superposition correction factor K defined in Eq. (3.2):

$$\begin{aligned} K(r_{12}, r_{13}, r_{23}) &= \frac{g^{(3)}(r_{12}, r_{13}, r_{23})}{g^{(2)}(r_{12}) g^{(2)}(r_{13}) g^{(2)}(r_{23})} \\ &= V^{-1} (8\pi/3 |\beta\lambda| N)^{3/2} \\ &\quad \times \exp[-(|\beta\lambda| N/6) (r_{12}^2 + r_{13}^2 + r_{23}^2)]. \end{aligned} \quad (\text{B14})$$

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