DISTRIBUTION FUNCTION APPROACH TO THE STABILITY OF FLUID PHASES

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I. INTRODUCTION

"It has been said that there exists no general theory of liquids because it is impossible to utilize the simplifying conditions either of the kinetic theory of gases [1] where the density is small, or the theory of solids [2] where a high degree of spatial order may be assumed. Yet a mathematical formulation of the problem should be possible, without making such an assumption, since only the general laws of mechanics and statistics are involved; though the solution itself may be extremely difficult."

With this introduction, Born and Green [3] began their formulation of what has since been termed the "BBGKY hierarchy". Historically, the acronym is

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correct only if the letters are read right to left. Yvon's development [4] and that of Kirkwood [5] appeared in 1935, whereas the Born–Green paper [3] and the article of Bogoliubov [6] (see also Ref. 7) appeared in 1946 . Indeed, as noted in 1967 by Rushbrooke in his Spiers Memorial Lecture [8], not only did Yvon derive the "BBGKY hierarchy," stating explicitly the first and second equations [9], but he also discussed the factorized structure of the equilibrium reduced distributions, and derived the first two equations of "YBG theory [10]." Born and Green were apparently unaware of Yvon's earlier contribution (his work was not cited), and obtained the same results a decade later.

Born and Green continue: "In the following we shall give a set of equations which describes not only the equilibrium of a statistical assembly of molecules — this could be done equally well by the methods of statistical mechanics —- but also the dynamical properties. Our method consists of the introduction of not a single distribution function as in the kinetic theory of gases, but a complete set of such functions for singlets, doublets, triplets, and so on, of molecules in the assembly, and depending not only on position and velocity, but also on higher derivatives with respect to the time."

For pairwise additive interactions, the functions being described, distributions of singlets, doublets, triplets, and so on, are linked, for example, the doublet distribution function satisfying an integral equation in which the triplet distribution function must be specified, the triplet distribution function satisfying an integral equation in which the distribution function for a quartet of particles must be specified, and so on, leaving us ultimately with only one equation for the N-particle distribution function. As noted by Kirkwood in his formulation of the hierarchy equations [5], unless some closure is introduced to truncate the hierarchy, "we are driven back to the many dimensional phase integrals with which we started."

To address this problem, Kirkwood [5] suggested a closure appropriate for gases at moderate density, and then one more appropriate for a dense fluid; today, the latter closure is referred to as the Kirkwood superposition approximation. An extensive literature has grown up assessing the consequences of adopting this closure (as will be referenced later in this section). Some authors simply regard the KSA as a convenient mathematical simplification, a "working hypothesis" to obtain solutions to the derived nonlinear integral equation(s).

Lost in this characterization is Kirkwood's rationale for introducing the closure. It was inspired by Onsager's 1933 paper [11] on the theory of concentrated electrolyte solutions, which advanced a method for taking into account fluctuating forces in calculating thermodynamic functions.

Drawing on insights presented in earlier contributions of Maxwell [12], Gibbs [13], Boltzmann [14], Einstein [15], and Smoluchowski [16], Onsager [11] defined a potential "which (for the case of fluctuating forces) replaces the energy in the Maxwell–Boltzmann distribution," a potential he identified as "the potential of average force." In the literature, this potential W_n, also referred to as the "potential of mean force," is defined as follows:

$$W_n = -kT \ln g_n,$$

Here g_n is the n-particle reduced distribution function.

To obtain the potential of mean force for a subset of molecules of an N-particle system, we are back to the problem of solving a set of $N-1$ simultaneous integral equations in which the number of fixed molecules $i, j, \ldots, l$, ranges from 1 to $N-1$. Kirkwood, arguing by analogy (see later), proposed that in condensed systems: "An obvious and simple approximation may be obtained by assuming superposition in the potentials of mean force."

Thus, for example, the three-body potential of mean force W_3 is expressed as the sum of three two-body potentials W_2,

$$W_3(i,k,s) = W_2(i,k) + W_2(i,s) + W_2(k,s),$$

with the equivalent statement in terms of three-particle distribution functions being

$$g_3(i,k,s) = g_2(i,k)g_2(i,s)g_2(k,s).$$

Before introducing this closure, Kirkwood [5] commented on the assumption of pairwise additivity in representing the potential of intermolecular forces V_N, noting that this assumption "in no way excludes the simultaneous interaction of groups of more than two molecules. It simply states that in such a group, the mutual potential energy of any pair is independent of the presence of other molecules." In a similar spirit, on introducing the additivity assumption for the potential of mean force, Kirkwood again emphasized that for three particles i, k, and s, this assumption "holds for the direct action of i and k on s," but "it cannot hold exactly for their indirect action on s through their effect on the distribution of the remaining $N-3$ molecules." He then outlined an approach based on the theory of fluctuations to assess the magnitude of the discrepancy introduced (by calculating "third-order fluctuations"), and gave physical arguments to suggest where the approximation would be acceptable, for example, if "s and k are situated at some distance from each other so that their spheres of influence on the distribution of a third molecule l, do not overlap appreciably."

Comprehensive summaries of the distribution function approach to calculate the properties and stability of fluid phases have been presented in monographs by Green [17], I. Z. Fisher [18], Rice and Gray [19], Cole [20], Croxton [21], and Baus and Tejero [22] and in the reviews of Rushbrooke [8], Barker and Henderson [23], Caccamo [24], and Grouba et al. [25].

Representative of this body of work are the foundational analytic and numerical studies of Kirkwood, Alder, and their colleagues [26–31] on the first equations of the hierarchy under the Kirkwood closure. These led to unexpected insights on the behavior of dense fluids, for example, that a system of particles interacting via purely repulsive forces could exhibit a phase transition.

Subsequently, Rice et al. [32–34] calculated corrections to the KSA for potentials having both repulsive and attractive parts and, on analyzing the sign and magnitude of these corrections, suggested that [19] "it is entirely possible that with realistic potentials and densities the cancellation among the terms correcting the superposition value of $g_3(1, 2, 3)$ may be almost complete." Of immediate relevance to the problem considered in this review, for both the simple and modified forms of the YBG equation, Young and Rice [34] obtained the equation of state for the square-well fluid, characterized the fluid–solid transition, and showed numerically that there was a region where the isothermal compressibility exhibited a pronounced maximum, with the range of pair correlations extremely long.

As one consequence of finding that loss of stability of the fluid phase could be studied using a distribution function approach, Rice and others [35–39] used theorems drawn from bifurcation theory to analyze the first and second hierarchy equations (nonlinear integral equations) under the KSA. Necessary conditions were established to determine whether increase in an order parameter (e.g., the density) might lead to the emergence of multiple solutions, thus signaling the onset of a new phase.

In the late 1970s, reports that numerical solution of the YBG equation using Kirkwood's closure for a system of particles interacting via the square-well potential led to critical exponents with values in substantial agreement with experiment [40–46] triggered new analytic studies, which led to valuable insights on the stability of the fluid phase in the neighborhood of the critical point [47–50].

This review summarizes a new analytic approach to study the stability of fluid phases, with the results obtained supported by numerical studies (also summarized here). We comment first on the choice of intermolecular potential adopted, the square-well potential. Both Yvon and Kirkwood chose this potential to "test drive" their theory, the former to calculate the second virial coefficient with application to nitrogen and helium and the latter to illustrate the form of the pair distribution function g_2. Although only a many-parameter potential function can adequately represent the subtle interactions between atoms or molecules, there is a belief, articulated by Widom [51], that if such a potential function were idealized as a square-well potential, but "the statistical mechanical consequences of such a potential were then determined without further approximations, there would undoubtedly result 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."

This insight provides a conceptual rationale for our choice of the square-well potential. Given the emphasis on the square-well potential in previous studies, this choice of potential also has the pragmatic advantage that it allows us to contrast and distinguish our results from those reported earlier. From an analytic point of view, the significant advantage gained is that the square-well potential can be represented in terms of Heaviside step functions allowing a number of calculations to be performed analytically that would be impossible to carry out for a more realistic, many-parameter potential.

An integrated, self-contained presentation of our analytic approach, proceeding from the BBGKY hierarchy equations, and including insights drawn from the Baxter hierarchy, is presented in Sections II–VII and in Appendices A and B. In Section VII, the principal results obtained are summarized, and we highlight several outstanding questions in the theory that remain unresolved.

II. YBG EQUATION FOR A SQUARE-WELL FLUID

The program introduced by Yvon, Kirkwood, Born, Green, and Bogoliubov was formulated to account for both nonequilibrium and equilibrium properties of the states of matter. Accordingly, we include in Appendix A the dynamical description of the square-well fluid based on the hierarchy of equations for the multiparticle distribution functions. From this, we derive therein the second BBGKY hierarchy equation for a square-well fluid at thermal equilibrium. Although the equilibrium hierarchy can be deduced directly from the structure of the equilibrium Gibbs ensemble, its most fundamental derivation is that from the dynamical hierarchy, where it appears as describing a stable-state invariant under the microscopic evolution. Hopefully, the derivation presented in Appendix A will be useful for studies of nonequilibrium transport processes in square-well fluids.

We begin our study of the second BBGKY hierarchy equation at thermal equilibrium drawing upon analytic methods developed and numerical results obtained in Refs. [52–55]. We thus consider a fluid composed of spherical particles with hard-core diameter σ and an attractive square-well pair potential

$$U(r) = -E\theta(\lambda\sigma - r), \tag{1}$$

where $E > 0$, $\lambda > 1$, and θ is a unit Heaviside step function.

At equilibrium, the reduced spatial distributions $n_2(\mathbf{r}_1, \mathbf{r}_2)$ and $n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ representing number densities of pairs and of triplets of particles, respectively, can be conveniently written as

$$\begin{aligned} n_2(\mathbf{r}_1, \mathbf{r}_2) &= n^2\, \chi_B(r_{12})\, y_2(r_{12}), \\ n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= n^3\, \chi_B(r_{12})\chi_B(r_{13})\chi_B(r_{23})\, y_3(r_{12}, r_{13}, r_{23}) \end{aligned} \tag{2}$$

where n is the number density, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the particles situated at points $\mathbf{r}_i$ and $\mathbf{r}_j$, and χ_B is the Boltzmann factor corresponding to the square-well interaction

$$\chi_B(r_{ij}) = \theta(r_{ij} - \sigma)\theta(\lambda\sigma - r_{ij})\, B + \theta(r_{ij} - \lambda\sigma), \tag{3}$$

where

$$B = \exp\left(\frac{E}{k_B T}\right). \tag{4}$$

The dimensionless functions y_2 and y_3 are supposed to be continuous and differentiable.

Starting from the dynamical BBGKY theory, we derived (see Appendix A) the second YBG hierarchy equation (A.28), which can be simply written using the Dirac δ-distributions

$$\begin{aligned} \frac{d}{dr} y_2(r) = n \int d\hat{\boldsymbol{\sigma}}\, (\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{r}}) \int_0^\infty ds\, s^2 \left[\delta(s-\sigma)B + \delta(s-\lambda\sigma)(1-B)\right] \\ \times \chi_B(|s\hat{\boldsymbol{\sigma}} - \mathbf{r}|) y_3(r, s, |s\hat{\boldsymbol{\sigma}} - \mathbf{r}|), \end{aligned} \tag{5}$$

where $\int d\hat{\boldsymbol{\sigma}}$ denotes the integration over three-dimensional solid angle, and $\hat{\boldsymbol{r}}$ is a unit vector defined by $\mathbf{r} = r\hat{\boldsymbol{r}}$.

The KSA

$$y_3(r, s, t) = y_2(r) y_2(s) y_2(t) \tag{6}$$

leads then to a closed nonlinear equation for the radial distribution $y_2(r)$. Putting $\mathbf{r} = \sigma\mathbf{x}$, we write this equation for the dimensionless function $Y(x) = y_2(\sigma x)$

$$\begin{aligned} \frac{d}{dx} \ln Y(x) = n\sigma^3 \int d\hat{\boldsymbol{\sigma}}\, (\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{x}}\,) \left[\chi_B(|\mathbf{x} - \hat{\boldsymbol{\sigma}}|) Y(1) Y(|\mathbf{x} - \hat{\boldsymbol{\sigma}}|) B \right. \\ \left. - \lambda^2 \chi_B(|\mathbf{x} - \lambda\hat{\boldsymbol{\sigma}}|) Y(\lambda) Y(|\mathbf{x} - \lambda\hat{\boldsymbol{\sigma}}|)(B-1)\right], \end{aligned} \tag{7}$$

where the Boltzmann factor (see (3)) takes the form

$$\chi_B(x) = \theta(x-1)\left[1 + \theta(\lambda - x)(B-1)\right]. \tag{8}$$

We next define the correlation function

$$H(x) = Y(x) - 1, \tag{9}$$

subject to the condition

$$\lim_{x\to\infty} H(x) = 0. \tag{10}$$

We now derive from Eq. (7) an integral equation making essential use of the boundary condition (10). Putting $\mu = (\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{x}}\,)$, and denoting by ϕ the volume fraction

$$\phi = \frac{\pi n \sigma^3}{6} \tag{11}$$

we get

$$\begin{aligned}\frac{d}{dx}\ln Y(x) = 12\phi \int_0^1 d\mu\, \mu \Big\{ & Y(1)B\Big[f(\sqrt{x^2-2x\mu+1}) - f(\sqrt{x^2+2x\mu+1})\Big] \\ & -\lambda^2 Y(\lambda)(B-1)\Big[f(\sqrt{x^2-2x\mu\lambda+\lambda^2}) - f(\sqrt{x^2+2x\mu\lambda+\lambda^2})\Big]\Big\},\end{aligned} \tag{12}$$

where for convenience we used the notation

$$f(x) = \chi_B(x)\, Y(x). \tag{13}$$

Integrating both sides of Eq. (12) over the interval (x, ∞), we derived [54] the integral equation for $Y(x)$. Our analysis revealed an interesting fact that the structure of the equation changed when the range of the attractive well crossed the threshold value $\lambda^* = 2$. In the two cases $\lambda = 1.4$ and $\lambda = 1.85$ studied here, the equation acquires the form

$$\begin{aligned}\ln Y(x) = 12\phi \Big\{ & -Y(1)B\left[\frac{1}{2x}\int_{x-1}^{x+1} ds\, sf(s)[1-(x-s)^2] - \frac{2}{3}\right] \\ & + Y(\lambda)(B-1)\left[\frac{1}{2x}\int_{|x-\lambda|}^{x+\lambda} ds\, sf(s)[\lambda^2-(s-x)^2] - \frac{2}{3}\lambda^3\right]\Big\}.\end{aligned} \tag{14}$$

Equation (14) is the starting point of our subsequent analysis.

III. ASYMPTOTIC DECAY OF CORRELATIONS: EXPONENTIAL MODES

Historically, several analytic methods have been introduced to determine the limits of stability of fluid phases [18, 26, 27, 35–39]. We present here a method based on studying the large-distance behavior of correlations between the density fluctuations. The loss of stability of a given phase is signaled then by the qualitative change in the law governing the decay of the pair correlation function. For instance, in the case of an approach toward the liquid–vapor critical point along the critical isotherm, the exponentially damped monotonic decay is replaced by a nonintegrable power law implying the divergence of the isothermal compressibility.

To implement this approach, we consider Eq. (14) in the region of $x \gg 1$. Using the fundamental assumption (10) about vanishing of correlations when $x \to \infty$, we replace on the left-hand side of Eq. (14) the function $\ln Y(x) = \ln[H(x)+1]$ by $H(x)$. On the right-hand side, we use the fact that in the region $s > \lambda$ the function $\chi_B(s) \equiv 1$. The resulting integral equation that holds when $x \gg 1$ reads

$$xH(x) = 6\phi \left\{ -Y(1)B \int_{x-1}^{x+1} ds\, sH(s)[1-(s-x)^2] \right. \\ \left. +Y(\lambda)(B-1) \int_{x-\lambda}^{x+\lambda} ds\, sH(s)[\lambda^2-(s-x)^2] \right\}. \tag{15}$$

Equation (15) is an exact consequence of the superposition approximation valid asymptotically at large distances provided the correlation function is integrable. No additional approximations have been introduced making the present approach more suitable to study the consequences of adopting the Kirkwood closure than other analyses in the literature. For example, our approach is different from that developed in Ref. 47, and developed extensively in Refs. 48 and 49. In the regime of large compressibility, the analyses presented in Refs. 47–49 proceed by inserting into the YBG equation (7) a large-distance expansion, retaining a few lowest order terms. Thus, an *additional* approximation was introduced in the analysis. The equation studied by Fisher and Fishman [48, 49] is not the integral equation (15), but a second-order nonlinear differential equation, which results from combining (7) with the constructed moment expansion, terminated at the second-order term.

In order to pursue our study of the asymptotic decay of the correlation function $H(x)$, we insert into Eq. (15) the exponential mode

$$xH(x;\kappa) = \exp(\kappa x), \tag{16}$$

where κ is a complex number. $H(x;\kappa)$ is a solution of Eq. (15) provided the parameter κ satisfies the condition

$$1 = 24\phi\,[\,\lambda^3 Y(\lambda)(B-1)F(\lambda\kappa) - Y(1)BF(\kappa)], \tag{17}$$

where the function F is defined by

$$F(\kappa) = \frac{[\kappa\cosh\kappa - \sinh\kappa]}{\kappa^3} = \sum_{n=0}^{\infty} \frac{\kappa^{2n}}{(2n+3)(2n+1)!} \\ = \frac{1}{3}\left[1 + \frac{\kappa^2}{10} + \frac{\kappa^4}{280} + \cdots\right]. \tag{18}$$

On the real axis, $F(\kappa)$ attains its absolute minimum at $\kappa = 0$, where $F(0) = 1/3$.

In order to determine the actual asymptotic decay law of the correlation function $H(x)$, we have to find the exponential mode (16) whose frequency

$$\kappa = a + ib = -|a| + ib \tag{19}$$

has the smallest value of $|a|$, and represents thus exponential damping with the longest range $|a|^{-1}$.

Clearly, the value of κ depends on the volume fraction ϕ, and on the temperature via $B = \exp(E/k_B T)$. So, we fix the temperature and consider solutions of Eq. (17) when the state of the system is changing along an isotherm $B = \exp(E/k_B T) =$ const. We wish to study the possibility of a loss of stability of a given phase of the system reflected by asymptotic vanishing of the real part a of the slowest decaying mode. Here, two cases can occur. It may happen that when the volume fraction approaches some value ϕ_0, both real and imaginary parts of κ tend to zero. Another possibility is that only the real part vanishes, but the imaginary part b remains different from zero. The latter case has been already discussed in our studies of hard-sphere systems [52, 53].

Consider the case of vanishing of κ. Introducing the quantity

$$\Gamma = 1 + 8\phi\,[\,Y(1)B - \lambda^3 Y(\lambda)(B-1)] \tag{20}$$

and taking the limit $\kappa \to 0$ on both sides of Eq. (17), we find the relation

$$\Gamma = 0. \tag{21}$$

We also note that for real $\kappa \ll 1$, Eq. (17) takes the asymptotic form (see the series expansion in (18))

$$\Gamma = \frac{4}{5}\phi\,[\lambda^5 Y(\lambda)(B-1) - BY(1)]\,\kappa^2. \tag{22}$$

The range of the correlation function grows thus as $1/\sqrt{\Gamma}$ when Γ approaches zero.

For a given λ, Γ is a function of volume fraction and temperature. Its vanishing defines a line of absolute stability in the plane (ϕ, T). Crossing the line (21) makes the exponential damping disappear, leading to a diverging spatial integral of $H(x)$.

When the temperature increases, the parameter B approaches 1, so that the term involving $(B-1)$ in (20) tends to zero, yielding a strictly positive value of Γ. It is thus clear that isotherms corresponding to sufficiently high temperatures do not cross the line of stability $\Gamma = 0$.

The numerical evidence shows that

$$Y(\lambda) < Y(1). \tag{23}$$

If (23) holds, then Eq. (21) can be satisfied only if

$$\lambda^3\left[1 - \frac{1}{B}\right] = \lambda^3\left[1 - \exp\left(\frac{-E}{k_B T}\right)\right] > 1. \tag{24}$$

In accordance with the previous remark, (24) imposes an upper bound for temperatures for which equation $\Gamma = 0$ can be satisfied.

In order to identify the critical point on the curve $\Gamma = 0$, we present an analysis of the behavior of the exponential mode (16) as the threshold value $\kappa = a + ib = 0$ is approached. We follow here closely the method developed by I. Z. Fisher [18] supposing that on an isotherm at some volume fraction ϕ_0 the exponential damping vanishes, so that $a(\phi_0) = b(\phi_0) = 0$. Therefore, when ϕ approaches ϕ_0, we write

$$\phi = \phi_0 + \delta\phi, \quad \kappa = \delta a + i\delta b,$$

where $\delta\phi \ll 1$, $\delta a \ll 1$, and $\delta b \ll 1$.

Equation (17) then takes the form

$$\begin{aligned} 1 = 24(\phi_0 + \delta\phi)\,[\,\lambda^3 Y(\lambda; \phi_0 + \delta\phi)(B-1)F(\lambda(\delta a + i\delta b)) \\ - Y(1; \phi_0 + \delta\phi) B F(\delta a + i\delta b)]. \end{aligned} \tag{25}$$

Using the series expansion (18) of function F, and, retaining terms up to the second order in deviations δa and δb, we obtain two conditions by considering the real and the imaginary part of Eq. (25). The conditions read

$$\begin{aligned} & B\left(\phi_0 \frac{\partial Y(1;\phi_0)}{\partial \phi_0} + Y(1;\phi_0)\right)\delta\phi + \frac{B}{10}\phi_0 Y(1;\phi_0)[(\delta a)^2 - (\delta b)^2] \qquad (26) \\ & \quad = (B-1)\lambda^3\left(\phi_0 \frac{\partial Y(\lambda;\phi_0)}{\partial \phi_0} + Y(\lambda;\phi_0)\right)\delta\phi \\ & \qquad + \frac{(B-1)}{10}\phi_0 \lambda^5 Y(\lambda;\phi_0)[(\delta a)^2 - (\delta b)^2] \\ & BY(1;\phi_0)\delta a \delta b = \lambda^3 (B-1) Y(\lambda;\phi_0)\delta a \delta b. \qquad (27) \end{aligned}$$

These have to be considered together with the threshold line equation $\Gamma(\phi_0) = 0$.

As $\delta a \neq 0$, Eqs. (21) and (27) are compatible only if $\delta b = 0$. We thus arrive at an interesting conclusion that *the asymptotic approach to the* $\kappa = 0$ *instability can occur only along the real axis*. In particular, the theory predicts monotonic decay of correlations in the immediate vicinity of the critical point. *This fact supports the interpretation of the line of stability (21) as representing the absolute stability limit for the fluid (liquid or vapor) phases.*

Inserting $\delta b = 0$ into (26) and using Eq. (21), we derive an asymptotic relation between δa and $\delta\phi$ of the form

$$\left[\phi_0 (B-1)\lambda^3(\lambda^2 - 1) Y(\lambda;\phi_0) + \frac{1}{8}\right](\delta a)^2 = 10\phi_0\,\Psi(\phi)\,\delta\phi, \tag{28}$$

where

$$\Psi(\phi) = B\frac{\partial Y(1;\phi)}{\partial \phi} - \lambda^3[B-1]\frac{\partial Y(\lambda;\phi)}{\partial \phi} - \frac{1}{8\phi^2}. \tag{29}$$

We note that when $\Psi(\phi) \neq 0$, Eq. (28) can be satisfied only if $\delta\phi$ has the same sign as $\Psi(\phi)$. This means that on the corresponding isotherm, the point

ϕ_0 separates stable states from unstable states. But when $\Psi(\phi_0)=0$, the relation between δa and $\delta\phi$ changes its nature because then the lowest order term in the expansion in $\delta\phi$ is proportional to $(\delta\phi)^2$. So, if a solution with $\delta\phi>0$ exists, there is also a solution with $\delta\phi<0$. A principal conclusion of this study is that if $\Psi(\phi_0)=0$, *the neighborhood of ϕ_0 on the isotherm is composed of stable states with exponentially decaying correlations reflecting the fact that the point at ϕ_0 is an isolated point where the exponential damping responsible for the monotonic decay of correlations disappears.* Such a characterization of the critical point was proposed already in 1964 by I. Z. Fisher in his monograph [18].

Noting that

$$\begin{aligned}\frac{\partial\Gamma}{\partial\phi} &= \frac{\Gamma-1}{\phi}+8\phi\left[B\frac{\partial Y(1)}{\partial\phi}-\lambda^3[B-1]\frac{\partial Y(\lambda)}{\partial\phi}\right] \\ &= \frac{\Gamma}{\phi}+\phi\Psi(\phi),\end{aligned} \tag{30}$$

we see that at the point ϕ_0 on the limit of stability line $\Gamma=0$, the relation $\Psi(\phi)=0$ takes the form

$$\frac{\partial\Gamma}{\partial\phi}|_{\phi=\phi_0}=0. \tag{31}$$

Equations $\Gamma(\phi_0)=0$, and (31) taken together define the critical temperature and the critical volume fraction of the vapor–liquid phase transition. There remains now to answer the fundamental question of whether these equations can be satisfied by solutions of the integral equation (14) allowing the critical behavior. And to answer this question, the contact values $Y(1)$ and $Y(\lambda)$ as functions of the volume fraction and temperature are needed, which requires solving the full nonlinear integral equation (14).

IV. CONSISTENCY QUESTIONS

Before presenting in Section V numerical solutions of the integral equation (14), we discuss here an important conceptual problem related to the use of the radial distribution determined within the KSA in the derivation of the equation of state. In particular, to calculate the pressure we have to choose between the virial and compressibility pressures, as these two cease to be consistent with each other once an approximate distribution is used. We give in the following arguments in favor of the compressibility equation.

If the system attains the limit of stability line (21), the correlation function decays as $1/x$ so that the integral in the following compressibility equation diverges:

$$k_BT\frac{\partial n}{\partial p}=k_BTn\mathcal{K}_T=1+n\sigma^3\int d\mathbf{x}\,[\chi_B(x)Y(x)-1]. \tag{32}$$

The appearance of an infinite compressibility $\mathcal{K}_T$ is a consequence of vanishing of the exponential damping. Equation (32) would thus lead to physically satisfactory predictions within the KSA if the latter could drive the system to the loss of stability: at the critical point, the compressibility would become infinite.

It is significant that this important prediction disappears when we consider the virial equation of state

$$\frac{p}{nk_BT} = 1 + \frac{2}{3}n\pi\sigma^3\Big[BY(1) - \lambda^3(B-1)Y(\lambda)\Big]. \tag{33}$$

In terms of the function Γ defined in Eq. (20), it simply reads

$$\frac{p}{nk_BT} = \frac{1+\Gamma}{2}. \tag{34}$$

Differentiating with respect to n yields the relation

$$\frac{1}{k_BT}\frac{\partial p}{\partial n} = \frac{1}{2}\left(1 + \Gamma + n\frac{\partial \Gamma}{\partial n}\right). \tag{35}$$

The virial pressure on the limit of stability line satisfies the relation

$$\left(\frac{p}{k_BTn}\right)_{\Gamma=0} = \frac{1}{2}. \tag{36}$$

Equation (36) should hold in particular at the critical point, yielding a classical, unsatisfactory value of the critical ratio. Moreover, when the condition for the occurrence of the critical point (31) is satisfied, we find

$$\left(\frac{1}{k_BT}\frac{\partial p}{\partial n}\right)_{\Gamma=0,\partial\Gamma/\partial\phi=0} = \frac{1}{2}. \tag{37}$$

So, we are led immediately to the conclusion that, according to the virial equation of state, the compressibility would remain finite at the critical point that is rather unphysical. Clearly, within the KSA, the virial equation is inconsistent with the compressibility equation. And it follows at once that to derive an equation of state that properly characterizes criticality within the KSA, the compressibility relation (32) should be used. A similar suggestion can be found in Refs. 48 and 49.

An analogous situation was encountered in the study by Baxter [56] of the thermodynamic properties of a fluid of hard spheres with surface adhesion, where the Percus–Yevick approximation was solved analytically for a special limit of a square-well potential with infinite depth and vanishing range. The system was shown to suffer a first-order phase transition with a critical point. Whereas the compressibility equation led to the behavior "very reminiscent of a Van der Waals gas," with diverging compressibility at the critical point, it was found that "the virial pressure does not correspond to an infinite compressibility at the critical point, and below the critical temperature there is a range of values of the pressure for which each isotherm does not exist. Such behavior is quite unphysical." In an earlier paper, [57] Baxter presented convincing arguments in favor of "the suggestion of Percus and Yevick that in the context of their approximation it is appropriate to obtain the pressure from the compressibility relation, rather than the virial theorem." We arrived here at the same conclusion in the study of the KSA.

These comments raise the general question of "consistency" between the virial equation of state and the compressibility equation, one that can be addressed if one uses the exact YBG hierarchy in concert with the exact hierarchy introduced by Baxter [58]

$$\begin{aligned}&\left\{k_B T n^2 \mathcal{K}_T \frac{\partial}{\partial n} - k\right\} n^k\, h_k(\mathbf{r}_1, \ldots, \mathbf{r}_k) \\ &\quad = \int d\mathbf{r}_{k+1} n^{k+1} h_{k+1}(\mathbf{r}_1, \ldots, \mathbf{r}_{k+1}) \qquad k = 1, 2, 3, \ldots.\end{aligned} \tag{38}$$

Here, h_k is the k-particle dimensionless correlation function, and $\mathcal{K}_T$ denotes the isothermal compressibility. We present the proof of consistency in Appendix B.

These remarks are important because they show the inadequacy of the virial equation to predict physical properties of fluids whose states are described within the KSA. There exists some confusion in the literature on this point. For instance, I. Z. Fisher [18] assumes the vanishing of the right-hand side of (35). As this does not follow from the basic integral equation (14), he has to go beyond the superposition approximation and invoke the mean field theory, all this to force consistency of the virial equation with the divergence of compressibility. Such a reasoning led Fisher to conclude that the limit of stability line (21) cannot contain a critical point, a statement with which we disagree.

Moreover, we wish to stress that on the line (21), and in particular at the critical point, the relation (36) invoked by some authors (see e.g., Refs. 18 and 59) cannot be presented as the result of the Kirkwood closure. It is the result of combining the relation $\Gamma = 0$ (see (20)), which results from the KSA with the virial equation (33). Such a combination should be abandoned because of the earlier described inconsistency of the virial equation with the divergence of compressibility at the critical point. That Eq. (36) does not follow from the KSA when the compressibility pressure is used rather than the virial pressure is illustrated by the fact that the critical ratio calculated numerically on the basis of YBG equation [41] does not exceed then 0.35.

V. FREEZING, THE CRITICAL REGION AND THE CRITICAL POINT

The fundamental question raised in this review is that of the limits of stability of various phases of a square-well fluid as predicted by the YBG equation under the KSA. Our analytic approach consisted in studying changes in the long-distance decay of correlations occurring when the volume fraction is increased at fixed temperature. The basis of the analysis was the integral equation (14) derived under the assumption of integrability of the correlation function. It implied the asymptotic decay of the following form, as corroborated numerically:

$$H(x) \sim \frac{\exp(-ax)}{x} \cos b, \qquad a > 0 \tag{39}$$

When a vanishes, the correlation function ceases to be integrable, the phase loses completely its mechanical stability, and a structural phase transition follows. There are two possibilities for the arrival at the absolute stability limit. The first, already known from the study of hard-sphere systems [52, 53], consists in the vanishing of the damping factor a with, however, $b \neq 0$. In this case, we observe the approach to long-distance undamped oscillations, which we interpret as the occurrence of a freezing transition. In the study of square-well systems, we anticipated this behavior when increasing the volume fraction along relatively high-temperature isotherms. And indeed, the numerical solution of the integral equation confirmed the existence of a freezing transition, reminiscent of the behavior of hard-sphere fluids [52, 53]. This transition was clearly illustrated for a square well of range $\lambda = 1.85$ on the isotherm $B = \exp(E/k_B T) = 1.2$ (see Fig. 1): the damping of oscillations becomes weaker and weaker with increasing volume fraction ϕ, disappearing at the threshold value $\phi_0 \sim 0.52$. We conclude that *adopting the Kirkwood closure in the second equation of the BBGKY hierarchy for a fluid at equilibrium predicts for square-well fluids the existence of an absolute stability limit which may signal freezing*.

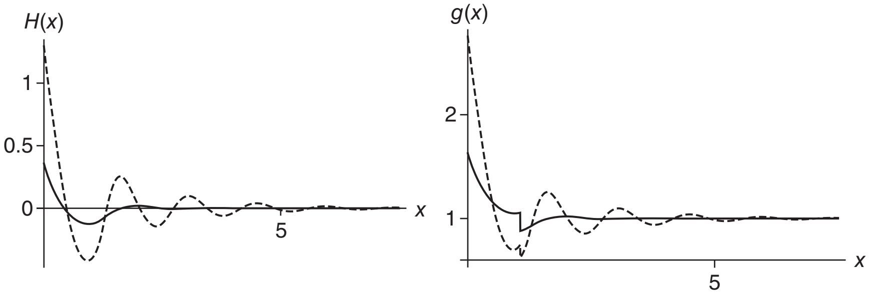

Figure 1. Left panel: correlation function $H(x)$ for $\lambda = 1.85$, $B = 1.2$, and $\phi = 0.2$ (solid) and $\phi = 0.5$ (dashed). Right panel: the corresponding pair distribution functions $g(x) = \chi(x)(1 + H(x))$.

As the temperature is decreased, at $B = 1.5$ and $B = 1.8$ (see Fig. 2), the region in which the decay of the correlation functions is non-oscillatory in character shifts toward smaller densities. At the same time, the characteristic length scale on which the correlation functions decay increases dramatically, particularly in the region of intermediate densities. This is a manifestation of a new phenomenon, related to the second possibility of losing mechanical stability where the *asymptotic decay of the correlation function $H(x)$ becomes purely monotonic, without oscillations*. This is the case where moving along an isotherm, we find that the parameter $\kappa = a + ib$ (see (17)) approaches zero. Using the type of analysis elaborated by I. Z. Fisher [18], we proved analytically that the approach of κ to zero is possible only along the real axis, that is, with $b = 0$. The numerical evidence presented in Ref. 54 confirms this result. As illustrated in Fig. 3 for $\lambda = 1.85$, the purely real root κ governs the decay of correlations at temperature $B = 1.6$ up to $\phi \sim 0.37$, contrary to what was the case at a higher temperature $B = 1.2$ where oscillatory decay takes over already at $\phi_0 \sim 0.15$. At the same time, the magnitude of the real root is very weakly dependent on the density in the range $0.1 < \phi < 0.3$, staying at a level of $0.05 - 0.2$, which is consistent with the observation of a very slow decay of the correlation functions in this range, interpreted by us as the manifestation of the existence of liquid–vapor stability limit. For higher densities, the magnitude of the purely real root increases again and finally becomes larger than the smallest root with a nonzero imaginary part. Next, as the temperature is further decreased (at $B = 1.8$, see the solid curves in Fig. 2 and the right panel of Fig. 3), the region of non-oscillatory decay shifts toward even larger densities.

The interesting question is whether, for the square-well fluid, one can actually reach the absolute stability limit where $\kappa = 0$, implying an asymptotic, non-integrable power-law decay $H(x) \sim 1/x$. As shown in Section VI, this question includes the problem of existence of a critical isotherm containing the critical point.

In our analytic considerations based on the integral equation (15), there appears the quantity

$$\Gamma = 1 + 8\phi[BY(1) - \lambda^3(B-1)Y(\lambda)],$$

the vanishing of which was shown to be equivalent to reaching the limit of stability with $\kappa = 0$. We thus directed the numerical analysis to a systematic study of Γ as a function of temperature and volume fraction for square wells of ranges $\lambda = 1.85$ and $\lambda = 1.4$. From its definition, $\Gamma(\phi = 0, B) = 1$. The behavior for increasing volume fraction is sensitive to the temperature.

Along high-temperature isotherms, Γ increases with ϕ, never reaching zero (see, e.g., the case of $\lambda = 1.85$, $B = 1.2$, presented in Fig. 4). However, at lower temperatures there occurs an important *qualitative change*: along isotherms $B = 1.45$, $B = 1.5$, and $B = 1.8$ (still at $\lambda = 1.85$), the function $\Gamma(\phi, B)$ decreases, with the initial slope becoming steeper at lower temperatures. This marks the beginning of an approach toward the loss of stability. The approach to zero occurs already

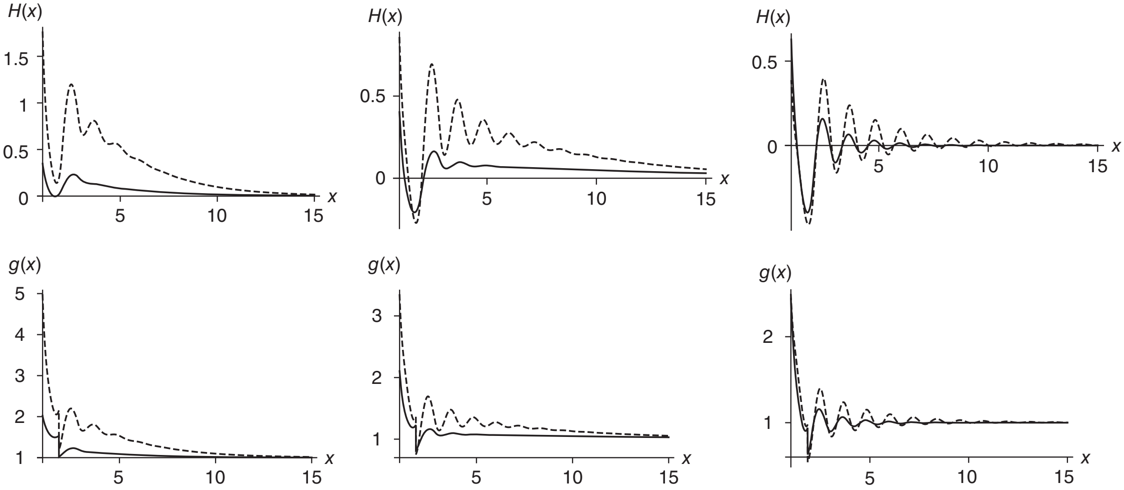

Figure 2. Upper panel: correlation function $H(x)$ for $\lambda = 1.85$, $B = 1.5$ (solid) and $B = 1.8$ (dashed) for $\phi = 0.1$ (left), $\phi = 0.25$ (center), and $\phi = 0.45$ (right). Lower panel: the corresponding pair distribution functions $g(x) = \chi(x)(1 + H(x))$.

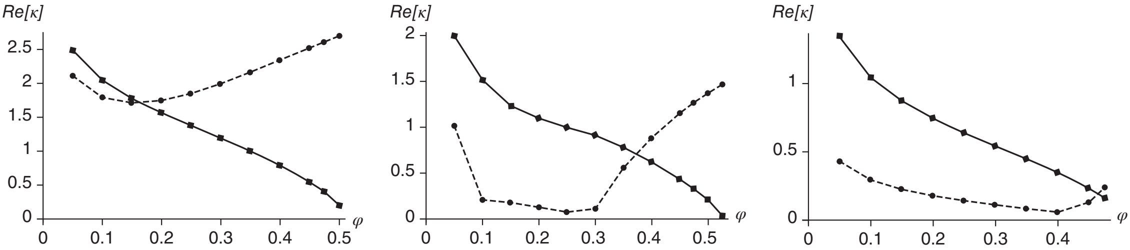

Figure 3. The magnitude of the purely real root (dashed) and the smallest (in terms of $Re(\kappa)$) root with nonzero imaginary part (solid) for $\lambda = 1.85$ and $B = 1.2$ (left), $B = 1.5$ (center), and $B = 1.8$ (right).

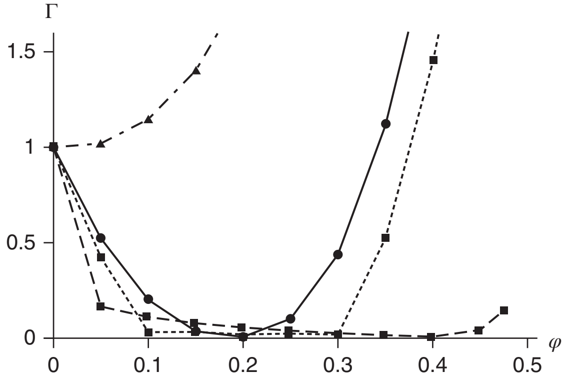

Figure 4. The parameter Γ as a function of volume fraction for $\lambda = 1.85$ for different temperatures corresponding to $B = 1.2$ (dot-dashed), $B = 1.45$ (solid), $B = 1.5$ (dotted), and $B = 1.8$ (dashed).

along the isotherm $B = 1.45$ on which the minimum attained by Γ equals 0.0126. The minimum then widens and also becomes deeper. It has been established that the curve $\phi \to \Gamma(\phi, B = 1.6)$ decreases to a very small value of the order of 10^{-3}. For $B = 1.45$, a plateau appears where Γ remains very close to zero over intervals whose width broadens with decreasing temperature.

We interpret the appearance of such a widening plateau where Γ, although positive, stays very close to zero as the way in which the YBG equation under the KSA reveals the existence of the liquid–vapor transition. The "critical isotherm" that marks the appearance of the plateau for lower temperatures would thus correspond to $B = 1.45$ for $\lambda = 1.85$, and the "critical volume fraction" where the minimum of Γ is attained was determined numerically to be $\phi = 0.19$. It is reasonable to assume that the plateau itself, although corresponding to stable uniform states, may well signal the onset of a two-phase region. In this interpretation, increasing the volume fraction beyond the plateau region should mark the entrance into a pure liquid phase, behavior reflected by an increase of Γ driving the system away from the absolute stability line (21). Further increase of the volume fraction leads to freezing, as signaled by the approach to undamped oscillatory behavior of correlations. The behavior of the system at $\lambda = 1.4$ is discussed in Ref. 54 where, once again, the values of Γ found from the numerical analysis are always positive.

The overall picture emerging from the numerical analysis suggests the conclusion that the line of stability $\Gamma = 0$, and in particular the conditions for the critical point, cannot be exactly satisfied by the solutions of the integral equation (14). However, based on our interpretation of the numerical results, the position of the "absolute stability line," and of the "critical isotherm" can be approximately localized.

The analysis of the critical behavior presented by Fisher and Fishman [48, 49] led to a similar conclusion: in three dimensions, the YBG equation cannot predict a "true criticality." However, their conclusion was based on analysis of a nonlinear differential equation derived by invoking an additional approximation beyond the KSA.

Here, we studied the consequences of the integral equation (14) representing exactly the KSA, without additional approximations. Whereas our study does not rule out decisively the possibility of reaching the line of stability, the analytic and numerical results presented in Ref. 54 and reviewed here suggest that solutions of (14) will be always stable, and thus lie outside this line.

Nonetheless, exploring this "near-critical" region reveals some fascinating results. Already by the late 1970s, it was known that the values of the critical exponents $[\alpha, \beta, \delta, \gamma]$ extracted from numerical solutions to the YBG equation under the KSA had values in substantial agreement with accepted experimental values, and further, they satisfied two of the (Griffiths) inequalities that involve all four exponents [40–46]. Our more recent calculations have corroborated that although the adoption of the Kirkwood closure appears to preclude the identification of a "true" critical point, essentially correct values of the critical exponents can be recovered via analysis of the compressibility in the regime of "intermediate" distances from the "quasi" critical point. In extracting values of the critical exponents, one must not go too far from the "quasi" critical point (else a power-law behavior will no longer be observed), or not too close (since the dependencies "flatten out" and cease to diverge as we approach the "near-critical" region).

It was also noted earlier [46] that if one used the virial equation for the pressure, the value obtained for the critical ratio z_c for a well-width $\lambda = 1.85$ was in agreement with the one reported in Ref. 34, namely, for $\lambda = 1.5$, namely, $z_c = 0.48 \pm 0.02$, essentially the mean field value, $z_c = 0.5$. Significantly, however, if one used the compressibility equation for the pressure [46], the estimated value of the critical ratio $z_c = 0.2914 \pm 0.0087$ was in near agreement with experimental data on the inert gases.

Given these analytical and numerical results, we are left with the question of whether the nonexistence of a critical point can be proved rigorously starting from the YBG equation under the Kirkwood closure. This remains an open question. As we shall show in the following section, a different strategy can be adopted to explore this question by applying the KSA within the Baxter hierarchy [58] (see also Ref. 60).

VI. PROOF OF NONEXISTENCE OF A CRITICAL POINT: THE KIRKWOOD CLOSURE APPLIED TO THE BAXTER HIERARCHY

We present an analytic argument to show that the application of the KSA to the second equation of the Baxter hierarchy (38) precludes the existence of a "true" critical point. Owing to the structure of the hierarchy the argument holds irrespective of the dimension of the system and the specific form of the interaction potential. Of course, this does not answer the question stated at the end of Section V because the radial distributions obtained from the Kirkwood closure applied to different exact hierarchy equations are different.

Of central importance is the radial distribution function $g(r) = h(r) + 1$. To proceed, we consider the cluster decomposition of the three-particle number density

$$n_3(r_{12}, r_{13}, r_{23}) = n^3[\, h_3(r_{12}, r_{13}, r_{23}) + h_2(r_{12}) + h_2(r_{13}) + h_2(r_{23}) + 1], \quad (40)$$

which defines three-particle correlation functions h_3. Using our earlier notation, in the recent equations n is the density of a homogeneous fluid, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between points $\mathbf{r}_i$ and $\mathbf{r}_j$. We assume here that the potential of interaction is spherically symmetric.

The correlation functions h_2 and h_3 satisfy the nonlinear equation

$$\int d\mathbf{r}_3\, h_3(r_{12}, r_{13}, r_{23}) = 2\left[\int d\mathbf{r} h_2(r)\right] h_2(r_{12}) + \left[1 + n\int d\mathbf{r} h_2(r)\right] \frac{\partial h_2(r_{12})}{\partial n}, \quad (41)$$

involving the isothermal compressibility $\mathcal{K}(n, T)$ through the compressibility equation (B.3). Equation (41) is the second equation of the hierarchy (38).

The superposition closure

$$n_3(r_{12}, r_{13}, r_{23}) = n^3[1 + h_2(r_{12})][1 + h_2(r_{23})][1 + h_2(r_{31})], \quad (42)$$

when compared with (40), implies an approximate expression for the three-particle correlation function

$$\begin{aligned} h_3(r_{12}, r_{13}, r_{23}) = {} & h_2(r_{12})h_2(r_{13})h_2(r_{23}) + h_2(r_{12})h_2(r_{13}) \\ & + h_2(r_{13})h_2(r_{23}) + h_2(r_{12})h_2(r_{23}). \end{aligned} \quad (43)$$

Upon inserting (43) into the integral relation (41) and integrating over the variable $\mathbf{r}_{12}$, we find

$$\int d\mathbf{r} \frac{1}{1 + h_2(r)} \frac{\partial h_2(r)}{\partial n} = \frac{\left[\int d\mathbf{r}\, h_2(r)\right]^2}{1 + n\int d\mathbf{r}\, h_2(r)}. \quad (44)$$

Analysis of Eq. (44) allows us to prove that the critical point cannot be attained within the KSA by showing that assuming the existence of a critical isotherm leads to a contradiction.

Suppose there exists an isotherm $T = T_c$ such that when the density n approaches some critical value n_c, the isothermal compressibility $\mathcal{K}_T(n, T_c)$ defined in (32) diverges. This happens because at $n = n_c$, the function $h_2(r)$ becomes non-integrable, showing a slow power-like decay at infinity. A necessary condition is that both sides of Eq. (44) should diverge in the same manner.

As $h_2(r) \to 0$ when $r \to \infty$, the large distance decay of the integrand on the left-hand side of Eq. (44) coincides with that of the derivative $\partial h_2(r)/\partial n$. So, when $n \to n_c$, the dominant (supposed diverging) contribution to the left-hand side behaves like

$$\frac{\partial}{\partial n}\left(\int d\mathbf{r}\, h_2(r)\right)_{T=T_c} = \frac{\partial}{\partial n}\left[k_B T_c \mathcal{K}_T(n, T_c) - \frac{1}{n}\right]. \tag{45}$$

In other words, the left-hand side of (44) diverges like the derivative of the compressibility.

Now, the diverging contribution to the right-hand side has the form

$$\frac{1}{n}\int d\mathbf{r} h_2(r) = \frac{1}{n^2}[nk_B T \mathcal{K}_T(n, T_c) - 1],$$

and behaves thus (up to a factor) like the compressibility. Equation (44) thus requires that the derivative with respect to the density of the compressibility at the approach to the critical density diverges exactly in the same way as the compressibility itself. This is however not possible. If one assumes the power-law divergence for the critical behavior, $\mathcal{K}(n, T_c) \sim (n - n_c)^{-\gamma}, \gamma > 0$, then the left-hand side of (44) diverges as $(n - n_c)^{-(\gamma+1)}$, whereas the right-hand side diverges as $(n - n_c)^{-\gamma}$, which is incompatible. Hence, there is a contradiction with the assumed divergence of the compressibility, leading to the conclusion that the existence of a critical isotherm, and thus of a critical point, is ruled out when the KSA is applied to the general relation (41).

The analysis presented before has been based on the relation (41) between the two- and three-particle correlation functions involving compressibility. This relation generalizes the compressibility equation (32) to higher order correlations, and is therefore particularly well suited to study the possibility of attaining a critical point, where the compressibility becomes infinite. As we stressed earlier, the relation is general, valid in any dimension. It does not depend on any specific form of interaction. Rather, the relation (41) follows directly from the structure of the equilibrium Gibbs ensemble.

The result obtained is consistent with conclusions reached in analytical and numerical studies of the three-dimensional square-well fluid based on the YBG hierarchy equations assuming the KSA. In Refs. 49 and 54, the authors concluded that within the superposition approximation, no true criticality could be attained. However, mean-field criticality in dimension $d > 4$ was predicted in Ref. 49. Our analytic result, which was derived starting from exact relations between the correlation functions, rules out the possibility of a critical point in *any* dimension. Thus, the predictions of the mean-field criticality in dimensions $d > 4$ obtained in Ref. 49 would appear to be a consequence of applying KSA to the YBG hierarchy, rather than to the Baxter hierarchy, and possibly also, of using an approximation beyond the KSA to derive the nonlinear differential equation on which the analysis in Ref. 49 was based.

Similarly, in numerical studies of the YBG integral equation under KSA, the presence of a critical point in dimensions $d = 5$ and $d = 6$ seemed to be implied by the numerical evidence (see Ref. 50). However, as the authors comment, a numerical proof of the critical point can never be rigorous, inasmuch as numerical solutions cannot be constructed arbitrarily close to the critical point, and one must rely on the extrapolation procedures instead.

In summary, we have shown that the KSA applied directly to the spatial integral of the three-particle correlation function leads to a result incompatible with the existence of a critical point.

VII. DISCUSSION, CONCLUSIONS, AND OPEN QUESTIONS

The analytic approach taken here was introduced in our earlier studies on a system of particles interacting via purely repulsive forces, namely, the hard-disk and hard-sphere fluids [52], and hard hyperspheres [55]. There, a new method for studying the asymptotic decay of correlations, first described in Ref. 61, was presented. Specifically, for the hard-sphere fluid [52], we found that exponential damping of oscillations becomes impossible when $\lambda = 4n\pi\sigma^3[1 + H(1)] \leq 34.81$, where again $H(1)$ is the contact value of the correlation function, n is the number density, and σ is the sphere diameter, in exact agreement with the condition $\lambda \leq 34.8$, first reported in a numerical study of the Kirkwood equation [28]. Adapting our analytic method to the case of a system of molecules interacting via both repulsive and attractive forces, the square-well fluid, we have shown conclusively that the YBG equation under the Kirkwood closure can account for the existence of limits of stability corresponding to both the fluid–solid transition and the fluid–gas transition [54], with the near-critical region characterized by essentially correct values of the critical exponents (see Refs. 40–46 and discussion later).

It is intriguing that the YBG equation under the Kirkwood closure can describe the unusually strong growth of the correlation length in the near-critical region, leading to a significant increase in the fluid compressibility. Moreover, as noted earlier, our results show that critical-like behavior is captured to such an extent that one can extract from numerical solutions of the YBG equation under the KSA exponents characterizing the behavior in the near-critical region.

The calculated exponents are quite close to those characterizing real critical behavior for the inert gases, and predicted by the group renormalization approach. Beyond the evidence reported in Refs. 40–46, we presented in Fig. 5 a plot of the isothermal compressibility $\mathcal{K}_T$ as a function of the volume fraction ϕ in the vicinity of a critical point. Fitting values of $\mathcal{K}_T$ to the functional form $\mathcal{K}_T(\phi) = |\phi - \phi_c|^{(\delta-1)}$ yields $\delta = 4.65 \pm 0.2$, a value congruent with the result reported earlier [42], and close to the Ising exponent ($\delta \sim 4.8$). Thus, the YBG equation under the Kirkwood closure not only predicts the loss of stability corresponding to a fluid–crystal transition but also informs us about a region of thermodynamic

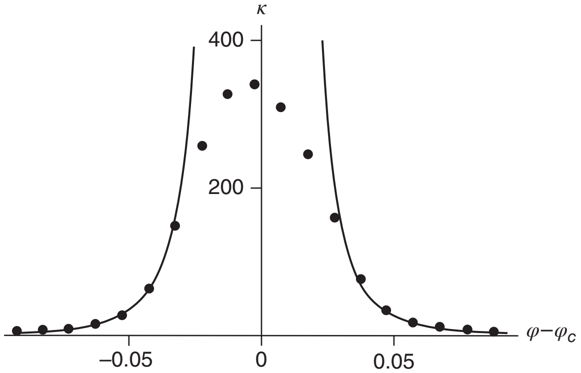

Figure 5. The isothermal compressibility, κ, as a function of the volume fraction, φ, in the neighborhood of a critical point. Filled circles: the values of κ obtained from the iterative solution of the integral equation along the isotherm $B = 1.455$. Solid line: a fit to the functional form $\kappa(\varphi) = |\varphi - \varphi_c|^{\delta-1}$ yields $\delta = 4.65 \pm 0.2$, a value congruent with the result reported earlier (32), and close to the Ising exponent ($\delta \approx 4.8$). The fit is performed in the range $|\varphi - \varphi_c| < 0.09$ excluding the regions in the immediate neighborhood of the critical point, where the function becomes concave.

parameter space where an important structural change appears, one characterized by a strong growth in the range of correlations, a fact that is observed experimentally.

In order to assess the consequences of the KSA, we also analyzed the predictions of the Baxter hierarchy (38) under the Kirkwood closure. The most important result obtained along these lines is the nonexistence theorem proved in Ref. 55 (see Section VI). There, an analytic argument was given to show that application of the KSA to the description of fluid correlation functions precludes the existence of a critical point irrespective of the dimension of the system and the specific form of the interaction potential. The essence of the proof was to show that the superposition approximation is inconsistent with the existence of a singularity of the isothermal compressibility, and thus of a critical point. It would appear, therefore, that in adopting the Kirkwood closure, correlations will never acquire a non-integrable power-law decay. We note that the Baxter hierarchy (38) has been used recently to reveal the fundamental role of multiparticle correlations in the appearance of a critical point [62].

It is important to realize that the KSA applied to the YBG equation generates a radial distribution different from that obtained by using the same approximation to close the Baxter hierarchy. From an analytic point of view, there is a fundamental difference between the results obtained using these two exact hierarchies. Assuming a divergent compressibility leads to a contradiction when the radial distribution satisfies the Baxter equation under KSA. In contradistinction, when the same closure is applied to the YBG equation, no obvious contradiction is found. Instead, there result conditions for the existence of a critical point (Eqs. 21 and 31) to be satisfied by the solution of the integral equation, and, up until now, there exists no analytic argument to answer the question of whether a solution satisfying such conditions exists.

Yet, in three dimensions, both approaches agree qualitatively in the sense that both indicate that the application of the Kirkwood closure to the description of fluid correlation functions precludes the existence of a critical point. In the case of the Baxter hierarchy, we could prove this conclusion analytically. For the YBG hierarchy, we have up to now only the numerical evidence.

In Section IV, we presented arguments showing that the use of the compressibility equation gives satisfactory results within KSA, whereas the virial formula for the pressure yields unphysical results and should not be used. In particular, the virial pressure led to a reported value [34] of $z_c = 0.48 \pm 0.02$, essentially the mean-field value, whereas the use of the compressibility equation for the pressure gave a result [36], $z_c = 0.2914 \pm 0.0087$, in substantial agreement with experiment. The analysis presented in Appendix B addressed this discrepancy, and we proved that the virial equation of state (33) and the compressibility equation (32) are, in fact, consistent provided the correlation function $h_2(r, n, T)$ is related to the three-particle correlation function h_3 both by the Baxter equation (B.6) and by the second YBG hierarchy equation (B.7).

In the course of our studies, we encountered a number of fundamental open and challenging problems whose solution would mark important progress in understanding the distribution function approach to the stability of fluid phases. Among these open questions, we highlight the following:

1. Find an analytic argument that would show whether the YBG equation under the Kirkwood closure applied to square-well fluids can or cannot account for a critical point in $d = 3$ dimensions. An even more ambitious problem would be to find an analytic answer to this question in arbitrary dimension, especially in light of predictions made by Fisher and Fishman [48, 49].
2. Derive exact analytic predictions of the KSA for the special case of the square-well fluid corresponding to the case of adhesive spheres.

   This case corresponds to the special limit where the range of the well shrinks to zero $(\lambda - 1) \to 0$, its depth approaches infinity $B = \exp(E/k_B T) \to \infty$, but the product $(\lambda - 1)B = \alpha$ stays constant. The last condition assures the existence of a well-defined asymptotic equation of state.

   The fluid of adhesive spheres was successfully studied by Baxter within the Percus–Yevick approximation where a rigorous solution for the radial distribution could be found [56]. It would be of great value to perform the same program within the KSA, or, at least, explore rigorously the possibility of a critical point.
3. Derive the properties of the radial distribution solving the second equation of the Baxter hierarchy within the KSA.

Performing this program would extend substantially our knowledge of the consequences of the KSA. One of them is the nonexistence theorem presented here. However, it would be very interesting to explore the properties of the resulting equation of state, and to check in particular whether it also predicts the quasi-critical region discovered when using the YBG equation (and whether the critical exponents calculated are classical or nonclassical).

4. Investigate analytically and numerically solutions of the YBG equation strictly within the KSA in dimensions $d > 4$.

   The problem of verifying the correctness of the prediction of mean-field criticality in $d > 4$ by Fisher and Fishman is most challenging, especially in the light of our nonexistence theorem. The real question here is to find a way of solving the problem using exclusively the Kirkwood closure of YBG without any additional approximations.

5. Following the original strategy applied by Alder to hard spheres [63], evaluate numerically the radial distribution under KSA for square-well fluids directly from the three-particle distribution without using any integral equations. This program has been announced in Ref. 63, but to our knowledge the planned molecular dynamics calculations were not carried out.

   Alder's paper [63] contains a remark that under KSA, the three-particle distribution y_3 (see Eq. 2) for equal-distance configurations takes the form

   $$y_3(r, r, r) = [y_2(r)]^3 \tag{46}$$

   A precise numerical evaluation of $y_3(r, r, r)$ permits thus to determine the two-particle distribution from the relation $y_2(r) = [y_3(r, r, r)]^{1/3}$. No integral equation is needed. It turned out that y_3 for hard spheres at contact "can be expressed by a triple product of the pair distribution functions ... to within a few percent accuracy." Alder concluded in particular that "The poor results previously obtained from the superposition approximation in the liquid region are due to an extreme magnification of the error by the integral equations in which it was introduced." And, referring to the fact that in the dense fluid and solid region for hard spheres the KSA turns out to be correct within a few percent, he added the remark "... it is not appropriate to judge the validity of an approximation in the liquid region by the accuracy with which the fourth virial coefficient is calculated."

   Solving the problem 5 would give the most valuable information about properties of the radial distribution within the KSA, predictions not modified by the operators acting in the integral equations.

Finally, it needs to be noted that, at present, there is no analytical proof of the existence of the critical point based on the full BBGKY hierarchy. Intriguingly, a number of authors over the years have suggested a more complicated structure of the phase diagram in the critical region. In particular, Mayer et al. [64] showed that reasonable assumptions about the behavior of the higher order virial coefficients lead to the temperature T_m below which surface tension becomes nonzero slightly lower than the temperature T_c below which a difference in densities is possible. More recently, Woodcock [65] has suggested that the critical region consists of a line of critical coexistence states of constant chemical potential. We are not suggesting that there is necessarily a connection between the "near critical" region uncovered in our study, and the structure of critical region emerging from the above-mentioned papers. But it is intriguing that different styles of analysis have led to questions on the proper interpretation of the near-critical region. Rigorous, analytical results on the existence (or non-existence) of the critical point are undoubtedly needed to get a deeper understanding of these problems.

The challenging problems formulated above show that the study of the physical properties of fluids based on the BBGKY hierarchy under the KSA remains an open research field both for analytic and for numerical studies. Clearly, this approach to the problem of stability of fluid phases needs further investigation, and it is our hope that this review will stimulate research in this direction.

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APPENDIX A: BBGKY HIERARCHY EQUATIONS FOR THE SQUARE-WELL FLUID

The square-well binary interaction consists of a hard core of diameter σ, and an attractive square well of depth E and range $\lambda\sigma$, with $\lambda > 1$. Within the square well, the potential is constant, so instantaneous collisional changes of velocities occur only when the distance between a pair of particles becomes σ or $\lambda\sigma$. In all other configurations, the motion is free. This fact allows one to study the kinetic theory of square-well fluids by analogy with the case of hard-sphere systems.

The dynamical evolution of the square-well fluid is described in the thermodynamic limit by the BBGKY hierarchy equations [66] (for the formal structure of the collision operators, see also Refs. 67 and 68). The second hierarchy equation establishes a relation between the two- and three-particle reduced distributions

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} - \overline{T}(1,2)\right) f_2(1,2;t)$$

$$= \int d3\,[\overline{T}(1,3) + \overline{T}(2,3)] f_3(1,2,3;t) \tag{A.1}$$

In writing (A.1) the shorthand notation $j \equiv (\mathbf{r}_j, \mathbf{v}_j), j = 1,2,3$, has been used.

The effects of binary collisions are described by the operator

$$\overline{T}(i,j) = \sum_{a=1}^{4} \overline{T}_a(i,j), \tag{A.2}$$

which takes into account four mutually exclusive dynamical events as follows:

$\overline{T}_1$ — hard core collisions at the distance σ
$\overline{T}_2$ — instantaneous change of velocities when the particles cross the distance $\lambda\sigma$ approaching each other
$\overline{T}_3$ — instantaneous change of velocities when the particles separate overcoming the energy barrier E at the distance $\lambda\sigma$
$\overline{T}_4$ — hard-core collision at the distance $\lambda\sigma$ when the particles get reflected by the energy barrier E

The particular role of distances σ and $\lambda\sigma$ leads to the appearance of the Dirac distributions in the structure of the collision operators.

$\overline{T}_1(i,j)$ is thus the hard-core collision operator whose action on a function $f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j)$ reads (for a clear derivation see Ref. 69)

$$\overline{T}_1(i,j) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j) \tag{A.3}$$

$$= \lim_{0<\epsilon\to 0} \sigma^2 \int d\hat{\boldsymbol{\sigma}}\, (\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}})\, \delta[\mathbf{r}_{ij} - \hat{\boldsymbol{\sigma}}(\sigma + \epsilon)]\, [\theta(\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i^*, \mathbf{r}_j, \mathbf{v}_j^*)$$
$$+ \theta(-\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j)].$$

Here, $\mathbf{r}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)$ and $\mathbf{v}_{ij} = (\mathbf{v}_i - \mathbf{v}_j)$ denote the relative position and the relative velocity of the particles, respectively, and $\hat{\boldsymbol{\sigma}}$ is a unit vector along the line passing through their centers in collisional configuration. The fact that the motion between collisions is free makes the collision frequency proportional to $|\mathbf{v}_{ij}|$ (the factor $(\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}})$).

The δ-distribution restricts the distance $|\mathbf{r}_{ij}| = r_{ij}$ between the centers of the particles to $(\sigma + \epsilon)$. The limiting procedure $0 < \epsilon \to 0$ permits to avoid ambiguities related to the action on a function containing the excluded volume factor $\theta(r_{ij} - \sigma)$. It reflects the fact that hard spheres approach each other always from outside.

The velocities $\mathbf{v}_i^*, \mathbf{v}_j^*$ are related to $\mathbf{v}_i, \mathbf{v}_j$ by the elastic collision law satisfying the kinetic energy conservation

$$(\mathbf{v}_i^*)^2 + (\mathbf{v}_j^*)^2 = \mathbf{v}_1^2 + \mathbf{v}_2^2. \tag{A.4}$$

The operator $\overline{T}_2(i,j)$ describing the process of entering of the particles into the attractive well acts according to the following formula:

$$\begin{aligned}
&\overline{T}_2(i,j)f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j) \\
&\quad = \lim_{0<\epsilon\to 0} (\lambda\sigma)^2 \int d\hat{\boldsymbol{\sigma}}\, (\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}})\, [\delta(\mathbf{r}_{ij} - \hat{\boldsymbol{\sigma}}(\lambda\sigma - \epsilon))\, \theta(\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i^{**}, \mathbf{r}_j, \mathbf{v}_j^{**}) \\
&\qquad + \delta(\mathbf{r}_{ij} - \hat{\boldsymbol{\sigma}}(\lambda\sigma + \epsilon))\theta(-\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j)].
\end{aligned} \tag{A.5}$$

The limit $\epsilon \to 0$ takes here into account the fact that the particles with velocities $\mathbf{v}_i^{**}, \mathbf{v}_j^{**}$ move already inside the well ($|\mathbf{r}_{ij}| < \lambda\sigma$), whereas they approach each other from outside
where $|\mathbf{r}_{ij}| > \lambda\sigma$.

The conservation of energy requires here the following relation:

$$(\mathbf{v}_i^{**})^2 + (\mathbf{v}_j^{**})^2 - \frac{2E}{m} = \mathbf{v}_1^2 + \mathbf{v}_2^2. \tag{A.6}$$

The operator $\overline{T}_3(i,j)$ describes the collisional effect of the separation of particles that cross the end point of the potential well at the distance σ_2 moving away from each other. This process can occur only if

$$\mathbf{v}_1^2 + \mathbf{v}_2^2 > \frac{2E}{m}, \quad \text{or} \quad |\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}|^2 > \frac{4E}{m}. \tag{A.7}$$

We thus find

$$\begin{aligned}
&\overline{T}_3(i,j)f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j) \\
&\quad = \lim_{0<\epsilon\to 0} (\lambda\sigma)^2 \int d\hat{\boldsymbol{\sigma}}\, (-\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}})\, [\delta(\mathbf{r}_{ij} + \hat{\boldsymbol{\sigma}}(\lambda\sigma + \epsilon)) \\
&\qquad \times \theta(-\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i^{***}, \mathbf{r}_j, \mathbf{v}_j^{***}) \\
&\qquad + \delta(\mathbf{r}_{ij} - \hat{\boldsymbol{\sigma}}(\lambda\sigma - \epsilon))\theta(\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j)]\theta\left(\mathbf{v}_1^2 + \mathbf{v}_2^2 - \frac{2E}{m}\right).
\end{aligned} \tag{A.8}$$

The conservation of energy takes the following form:

$$\mathbf{v}_1^2 + \mathbf{v}_2^2 - \frac{2E}{m} = (\mathbf{v}_i^{***})^2 + (\mathbf{v}_j^{***})^2. \tag{A.9}$$

Finally, when

$$\mathbf{v}_1^2 + \mathbf{v}_2^2 < \frac{2E}{m}, \quad \text{or} \quad |\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}}|^2 < \frac{4E}{m}, \tag{A.10}$$

the particles cannot separate and suffer a hard-core collision. The operator $\overline{T}_4(i,j)$ thus reads

$$\begin{aligned} &\overline{T}_4(i,j) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j) \\ &\quad = \lim_{0<\epsilon\to 0} (\lambda\sigma)^2 \int d\hat{\boldsymbol{\sigma}}\, (-\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}})\, \delta[\mathbf{r}_{ij} - \hat{\boldsymbol{\sigma}}(\lambda\sigma - \epsilon)]\, [\theta(-\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i^*, \mathbf{r}_j, \mathbf{v}_j^*) \\ &\qquad + \theta(\mathbf{v}_{ij} \cdot \hat{\boldsymbol{\sigma}}) f(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j, \mathbf{v}_j)]\, \theta\left(\frac{2E}{m} - \mathbf{v}_1^2 - \mathbf{v}_2^2\right). \end{aligned} \tag{A.11}$$

where the velocities $(\mathbf{v}_i^*, \mathbf{v}_j^*)$ satisfy the kinetic energy conservation law (A.4).

Our objective now is to derive the form of the second BBGKY hierarchy equation (A.1) in the case of an invariant equilibrium state. The reduced distributions then factorize into products of Maxwell velocity distributions and spatial distributions invariant under translations and rotations

$$f_s(1, 2, \ldots, s) = n_s(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_s)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) \ldots \phi(\mathbf{v}_s). \tag{A.12}$$

Here,

$$\phi(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right). \tag{A.13}$$

In order to perform the calculation, we thus need the result of the action of the collision operators $\overline{T}_a(i,j), a = 1, \ldots, 4$, on distributions that involve the velocities via the kinetic energy only. Indeed,

$$\phi(\mathbf{v}_i)\phi(\mathbf{v}_j) = \left(\frac{m}{2\pi k_B T}\right)^3 \exp\left[\frac{-m(\mathbf{v}_i^2 + \mathbf{v}_j^2)}{2k_B T}\right].$$

Taking into account the conservation laws (A.4), (A.6), (A.9), and the relations

$$\lim_{0<\epsilon\to 0} \chi_B(\sigma + \epsilon) = \lim_{0<\epsilon\to 0} \chi_B(\lambda\sigma - \epsilon) = B, \qquad \lim_{0<\epsilon\to 0} \chi_B(\lambda\sigma + \epsilon) = 1, \tag{A.14}$$

we find

$$\overline{T}_1(1,2) n_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) = n^2 B \delta(r_{12} - \sigma)(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) y_2(\sigma) \tag{A.15}$$

$$\overline{T}_2(1,2) n_2(\mathbf{r}_1, \mathbf{r}_2)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) = n^2 \delta(r_{12} - \lambda\sigma)(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) y_2(\lambda\sigma) \tag{A.16}$$

$$\overline{T}_3(1,2)n_2(\mathbf{r}_1,\mathbf{r}_2)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) = -n^2 B\delta(r_{12}-\lambda\sigma)(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2)y_2(\lambda\sigma) \times\theta\left(\mathbf{v}_1^2+\mathbf{v}_2^2-\frac{2E}{m}\right) \tag{A.17}$$

$$\overline{T}_4(1,2)n_2(\mathbf{r}_1,\mathbf{r}_2)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) = -n^2 B\delta(r_{12}-\lambda\sigma)(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2)y_2(\lambda\sigma) \times\theta\left(\frac{2E}{m}-\mathbf{v}_1^2+\mathbf{v}_2^2\right) \tag{A.18}$$

In these equations, the dimensionless functions y_s, $s = 1, 2, \ldots$ have been introduced (see Eq. 2) and the notation $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$ has been used.

Adding up all four terms (A.15) – (A.18) yields the following relation:

$$\sum_{a=1}^{4}\overline{T}_a(1,2)n_2(\mathbf{r}_1,\mathbf{r}_2)\phi(\mathbf{v}_1)\phi(\mathbf{v}_2) \tag{A.19}$$

$$= n^2(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2)\{B\,[\delta(r_{12}-\sigma)-\delta(r_{12}-\lambda\sigma)] + \delta(r_{12}-\lambda\sigma)\}y_2(r_{12}).$$

Noting that

$$\hat{}\left\{\mathbf{v}_1\cdot\frac{\partial}{\partial\mathbf{r}_1}+\mathbf{v}_2\cdot\frac{\partial}{\partial\mathbf{r}_2}\right\}\chi_B(r_{12}) = (\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\{[\delta(r_{12}-\sigma)-\delta(r_{12}-\lambda\sigma)]B+\delta(r_{12}-\lambda\sigma)\}, \tag{A.20}$$

we find that in the case of an equilibrium state the term (A.19) involving the Dirac distributions cancels out and the left-hand side L of the BBGKY equation (A.1) reduces to

$$L = n^2\chi_B(r_{12})(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2)\frac{dy_2(r_{12})}{dr_{12}} \tag{A.21}$$

The right-hand side R of Eq. (A.1) involves the integration on the phase $(\mathbf{r}_3, \mathbf{v}_3)$ of particles of the medium interacting with the pair situated at $\mathbf{r}_1$ and $\mathbf{r}_2$. Owing to the δ-distributions, the spatial integration can be performed in a straightforward way. Also, the velocity integration is simple. In order to illustrate the calculation, we present here in some detail the evaluation of the term involving the $\overline{T}_1$ operators.

Using the defining Eq. (A.3), we find

$$\int d3\,\overline{T}_1(1,3)f_3(1,2,3;t) = n^3\int d\mathbf{r}_3\int d\mathbf{v}_3 \lim_{0<\epsilon\to 0}\sigma^2\int d\hat{\boldsymbol{\sigma}}\,(\mathbf{v}_{13}\cdot\hat{\boldsymbol{\sigma}})\,\delta[\mathbf{r}_{13}-\hat{\boldsymbol{\sigma}}(\sigma+\epsilon)] \tag{A.22}$$

$$
\begin{aligned}
&[\theta(\mathbf{v}_{13}\cdot\hat{\boldsymbol{\sigma}})\phi(v_1^*)\phi(v_2)\phi(v_3^*) + +\theta(-\mathbf{v}_{13}\cdot\hat{\boldsymbol{\sigma}})\phi(v_1)\phi(v_2)\phi(v_3)]\\
&\qquad \times \chi_B(r_{12})\chi_B(r_{13})\chi_B(r_{23})y_3(r_{12}, r_{13}, r_{23})\\
&\quad = n^3\sigma^2 B\,\chi_B(r_{12})\phi(v_1)\phi(v_2)\\
&\qquad \times \int d\hat{\boldsymbol{\sigma}}\;(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_1)\chi_B(|\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|)y_3(r_{12}, \sigma_1, |\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|).
\end{aligned}
$$

Proceeding along the same lines, we obtain the following relation:

$$
\begin{aligned}
&\int d3\,\overline{T}_1(2,3)f_3(1,2,3;t)\\
&\quad = n^3\sigma^2 B\chi_B(r_{12})\phi(v_1)\phi(v_2)\\
&\qquad \times \int d\hat{\boldsymbol{\sigma}}\;(-\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_2)\chi_B(|\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|)y_3(r_{12}, \sigma, |\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|).
\end{aligned}
\tag{A.23}
$$

Using then the symmetry of function y_3, we eventually find the total contribution from hard-core collisions at $r_{12} = \sigma$

$$
\begin{aligned}
&\int d3\,[\overline{T}_1(1,3) + \overline{T}_1(2,3)]f_3(1,2,3;t)\\
&\quad = n^3\sigma^2 B\chi_B(r_{12})\phi(v_1)\phi(v_2)\\
&\qquad \times \int d\hat{\boldsymbol{\sigma}}\;(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_{12})\chi_B(|\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|)y_3(r_{12}, |\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\sigma|, \sigma).
\end{aligned}
\tag{A.24}
$$

In the same way, one can derive contributions to the right-hand side R of (A.1) coming from collisions occurring at the distance $r_{12} = \lambda\sigma$

$$
\begin{aligned}
&\int d3\,[\overline{T}_2(1,3) + \overline{T}_2(2,3)]f_3(1,2,3;t)\\
&\quad = n^3(\lambda\sigma)^2\chi_B(r_{12})\phi(v_1)\phi(v_2)\\
&\qquad \times \int d\hat{\boldsymbol{\sigma}}\;(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_{12})\chi_B(|\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\lambda\sigma|)y_3(r_{12}, |\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\lambda\sigma|, \lambda\sigma)
\end{aligned}
\tag{A.25}
$$

and

$$
\begin{aligned}
&\int d3\,[\overline{T}_3(1,3) + \overline{T}_3(2,3) + T_4(1,3) + \overline{T}_4(2,3)]f_3(1,2,3;t)\\
&\quad = -n^3(\lambda\sigma)^2 B\chi_B(r_{12})\phi(v_1)\phi(v_2)\\
&\qquad \times \int d\hat{\boldsymbol{\sigma}}\;(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_{12})\chi_B(|\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\lambda\sigma|)y_3(r_{12}, |\mathbf{r}_{12}-\hat{\boldsymbol{\sigma}}\,\lambda\sigma_2|, \sigma).
\end{aligned}
\tag{A.26}
$$

The results obtained so far permit us to write the second BBGKY equation in the form

$$\begin{aligned} & n^2\chi_B(r)(\mathbf{v}_{12}\cdot\hat{\mathbf{r}})\phi(\mathbf{v}_1)\phi(\mathbf{v}_2)\frac{dy_2(r)}{dr} \\ &= n^3\chi_B(r)\phi(v_1)\phi(v_2)\mathbf{v}_{12}\cdot\int d\hat{\boldsymbol{\sigma}}\,\hat{\boldsymbol{\sigma}}\{B\sigma^2\,\chi_B(|\mathbf{r}-\hat{\boldsymbol{\sigma}}\sigma|)\,y_3(r,|\mathbf{r}-\hat{\boldsymbol{\sigma}}\sigma|,\sigma) \\ &\quad + (\lambda\sigma)^2\,[1-B]\,\chi_B(|\mathbf{r}-\hat{\boldsymbol{\sigma}}\lambda\sigma|)\,y_3(r,|\mathbf{r}-\hat{\boldsymbol{\sigma}}\lambda\sigma|,\lambda\sigma)\} \end{aligned} \tag{A.27}$$

where we put $\mathbf{r}_{12} = \mathbf{r}$.

Equation (A.27) must hold for any value of the relative velocity $\mathbf{v}_{12}$. Taking this fact into account, we arrive at the final form of the second BBGKY hierarchy equation for a square-well fluid at thermal equilibrium

$$\begin{aligned} \frac{dy_2(r)}{dr} &= n\int d\hat{\boldsymbol{\sigma}}\,(\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\sigma}})\{\,B\sigma^2\,\chi_B(|\mathbf{r}-\hat{\boldsymbol{\sigma}}\sigma|)y_3(r,|\mathbf{r}-\hat{\boldsymbol{\sigma}}\sigma|,\sigma) \\ &\quad + [1-B](\lambda\sigma)^2\,\chi_B(|\mathbf{r}-\hat{\boldsymbol{\sigma}}\lambda\sigma|)y_3(r,|\mathbf{r}-\hat{\boldsymbol{\sigma}}\lambda\sigma|,\lambda\sigma)\,\}, \end{aligned} \tag{A.28}$$

where the Boltzmann factor $\chi_B(r)$ has been defined in Eq. (3).

APPENDIX B: PROOF OF CONSISTENCY BETWEEN THE VIRIAL AND COMPRESSIBILITY EQUATIONS OF STATE

On the one hand, the virial expression for the pressure p is given by the formula

$$p = n\left(k_BT - \frac{n}{6}\int d\mathbf{r}\left[\mathbf{r}\cdot\frac{\partial V(r)}{\partial\mathbf{r}}\right]g_2(r;n,T)\right), \tag{B.1}$$

where $V(r)$ is the pair potential, $g_2(r;n,T)$ is the radial distribution, related to the pair correlation function $h_2(r;n,T)$ by

$$g_2(r;n,T) = 1 + h_2(r;n,T). \tag{B.2}$$

On the other hand, the compressibility equation reads

$$k_BTn\mathcal{K}_T = k_BT\left(\frac{\partial n}{\partial p}\right) = 1 + n\int d\mathbf{r}\,h_2(r;n,T). \tag{B.3}$$

From (B.1), we get

$$\left(\frac{\partial p}{\partial n}\right) = k_BT - \frac{n}{3}\int d\mathbf{r}\left[\mathbf{r}\cdot\frac{\partial V(r)}{\partial\mathbf{r}}\right]\left(g_2(r;n,T) + \frac{n}{2}\frac{\partial}{\partial n}h_2(r;n,T)\right). \tag{B.4}$$

The consistency between (B.3) and (B.4) requires that the following equality holds:

$$k_B T = \left[1 + n \int d\mathbf{r}\, h_2(r; n, T)\right] \times \left\{k_B T - \frac{n}{3} \int d\mathbf{r} \left[\mathbf{r} \cdot \frac{\partial V(r)}{\partial \mathbf{r}}\right] \left(1 + h_2(r; n, T) + \frac{n}{2} \frac{\partial}{\partial n} h_2(r; n, T)\right)\right\} \tag{B.5}$$

The proof of (B.5), not given in the literature as far as the authors are aware, is presented below. We suppose that the two-particle correlation function satisfies the following exact equations:

1. The generalized compressibility equation (see Eq. (38) with $k = 2$)

$$\int d\mathbf{x}\, h_3(r, |\mathbf{x} - \mathbf{r}|, x) = 2\left[\int d\mathbf{x}\, h_2(x; n, T)\right] h_2(r; n, T) + \left[1 + n \int d\mathbf{x}\, h_2(x; n, T)\right] \frac{\partial}{\partial n} h_2(r; n, T). \tag{B.6}$$

2. The second YBG hierarchy equation

$$\begin{aligned} -n \int d\mathbf{x} \frac{\partial V(|\mathbf{r} - \mathbf{x}|)}{\partial \mathbf{r}} h_3(r, |\mathbf{x} - \mathbf{r}|, x) &= k_B T \frac{\partial h_2(r; n, T)}{\partial \mathbf{r}} + [1 + h_2(r; n, T)] \frac{\partial V(r)}{\partial \mathbf{r}} \\ &\quad + n \int d\mathbf{x} \frac{\partial V(|\mathbf{r} - \mathbf{x}|)}{\partial \mathbf{r}} h_2(x; n, T). \end{aligned} \tag{B.7}$$

We introduce the short-hand notation

$$\begin{aligned} W(r) &= \mathbf{r} \cdot \frac{\partial V(r)}{\partial \mathbf{r}} \\ I(n, T) &= \int d\mathbf{r}\, h_2(r; n, T). \end{aligned} \tag{B.8}$$

Multiplying equation (B.6) by $W(r)$ and integrating over the position space, we find the relation

$$\begin{aligned} &\int d\mathbf{x} \int d\mathbf{r} W(r)\, h_3(r, |\mathbf{x} - \mathbf{r}|, x) \\ &= 2I(n, T) \int d\mathbf{r} W(r) h_2(r; n, T) + [1 + nI(n, T)] \int d\mathbf{r}\, W(r) \frac{\partial}{\partial n} h_2(r; n, T). \end{aligned} \tag{B.9}$$

Taking then the scalar product of the YBG equation (B.7) with the vector **r**, and integrating with respect to $d\mathbf{r}$, we find

$$\begin{aligned}
&-n\int d\mathbf{r}\int d\mathbf{x}\,\mathbf{r}\cdot\frac{\partial V(|\mathbf{r}-\mathbf{x}|)}{\partial\mathbf{r}}h_3(r,|\mathbf{x}-\mathbf{r}|,x)\\
&=-\frac{n}{2}\int d\mathbf{r}\int d\mathbf{x}W(|\mathbf{r}-\mathbf{x}|)h_3(r,|\mathbf{x}-\mathbf{r}|,x)\\
&=k_BT\int d\mathbf{r}\ \ \mathbf{r}\cdot\frac{\partial h_2(r;n,T)}{\partial\mathbf{r}}+\int d\mathbf{r}\,W(r)\,[1+h_2(r;n,T)]\\
&\quad+n\int d\mathbf{x}\int d\mathbf{r}\ \ \mathbf{r}\cdot\frac{\partial V(|\mathbf{r}-\mathbf{x}|)}{\partial\mathbf{r}}h_2(x;n,T)\\
&=-3k_BTI(n,T)+\int d\mathbf{r}\,W(r)\,[1+h_2(r;n,T)]+nI(n,T)\int d\mathbf{x}\,W(x).
\end{aligned}\tag{B.10}$$

Multiplying equation (B.9) by $n/2$ and adding both sides to equation (B.10), we thus find the exact relation

$$\begin{aligned}
&nI(n,T)\int d\mathbf{r}W(r)h_2(r;n,T)+\frac{n}{2}[1+nI(n,T)]\int d\mathbf{r}\ W(r)\frac{\partial}{\partial n}h_2(r;n,T)\\
&\quad=3k_BTI(n,T)-\int d\mathbf{r}\,W(r)\,[1+h_2(r;n,T)]-nI(n,T)\int d\mathbf{x}\,W(x).
\end{aligned}\tag{B.11}$$

It can be readily checked that Eq. (B.11) coincides with the consistency equation (B.5). This analytic result leads to the conclusion that the virial equation of state (B.1) and the compressibility equation (B.3) are consistent *provided* the correlation function $h_2(r;n,T)$ is related to the three-particle correlation function h_3, both by the generalized compressibility equation (B.6) and by the second YBG hierarchy equation (B.7).

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