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Stability of phases of a square-well fluid within superposition approximation

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The analytic and numerical methods introduced previously to study the phase behavior of hard sphere fluids starting from the Yvon-Born-Green (YBG) equation under the Kirkwood superposition approximation (KSA) are adapted to the square-well fluid. We are able to show conclusively that the YBG equation under the KSA closure when applied to the square-well fluid: (i) predicts the existence of an absolute stability limit corresponding to freezing where undamped oscillations appear in the long-distance behavior of correlations, (ii) in accordance with earlier studies reveals the existence of a liquid-vapor transition by the appearance of a "near-critical region" where monotonically decaying correlations acquire very long range, although the system never loses stability. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4801329]

I. INTRODUCTION

This contribution returns to a conceptual question that was addressed thirty years ago:[1]

Does the Yvon-Born-Green (YBG) equation under the Kirkwood superposition approximation (KSA) exhibit a true critical point?

Extensive analytical[2] and numerical[3] studies were carried out, and the conclusion reached was that there is no true critical point for d = 3 but rather a region of "near critical behavior." In this "near" critical region, however, earlier numerical studies of the square-well fluid based on the YBG equation under the KSA had shown convincingly that the critical exponents $[\beta, \gamma, \delta, \alpha]$ extracted from the numerical solutions had values in substantial agreement with the accepted experimental values and, further, they satisfied two of the (Griffiths) inequalities that involve all four exponents.[4–7] Anticipating a later discussion, it was also shown[8] that if one used the virial equation for the pressure, the value obtained for the critical compressibility factor z_c for a well-width $\lambda = 1.85$ was in agreement with the one reported previously by Young and Rice[9] for $\lambda = 1.5$, viz. $z_c = 0.48 \pm 0.02$, essentially the mean field value, $z_c = 0.5$. But if one used the compressibility equation for the pressure, the estimated value of the critical compressibility factor $z_c = 0.2914 \pm 0.0087$ was in accord with experimental data on inert gases.[8]

While the analytic techniques implemented in Refs. 1–3 were powerful, the theoretical question left unresolved was whether the conclusions reached regarding the critical behavior of the YBG equation remain unchanged if these techniques were extended or new techniques developed to deal with the full YBG equation. The rationale underlying the present study is that the numerical evidence on critical exponents, cited above, is sufficiently suggestive that, rather than abandon the YBG equation, perhaps a fresh approach may lead to new insights.

Recently, the authors of the present study have developed an analytic criterion to study the asymptotic decay of correlations in hard disk and hard sphere fluids[10] and in hypersphere fluids.[11] The results obtained in Ref. 10 are immediately relevant to the present study. From our analysis and complementary numerical studies, we found for hard discs that exponentially damped oscillations can occur only up to a packing fraction $\phi^* \sim 0.718$, a value which is in agreement with the packing fraction $\phi \sim 0.723$ believed to characterize the transition from the ordered solid phase to a dense fluid phase, as inferred from Mak's Monte Carlo simulations.[12] For hard spheres, the same method of analysis predicted that the exponential damping of oscillations in d = 3 becomes impossible when $\lambda_0 = 4n\pi\sigma^3[1 + H(1)] = 34.81$, where $H(1)$ 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 $\lambda_0 \geq 34.8$ first reported in a numerical study of the Kirkwood equation by Kirkwood, Maum, and Alder.[13] The method also confirmed, correctly, the absence of any structural transition in hard rods for the entire range of densities below closest packing.

Building on the studies reported in Refs. 10 and 11 here a square-well fluid will be analyzed using the same approach. We derive from the second YBG hierarchy equation a nonlinear closed equation for the radial distribution function using the Kirkwood superposition approximation. We then transform the resulting integro-differential equation into a purely integral equation under the assumption of asymptotic vanishing of correlations at large distances. The resulting integral equation is the basis of the whole subsequent analysis.

We study the physical implications of the derived integral equation both analytically and numerically. Our aim is to derive an analytic criterion for the limits of stability of the three possible phases of the system, i.e., vapor, liquid, and solid. In particular we formulate an analytic criterion

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permitting us to localize, in principle, the vapor-liquid critical point. An essential role in our approach is played by the derivation of a condition determining the complex frequencies governing the large distance decay of correlations. The structure of the asymptotic exponential modes depends on the thermodynamic state of the system, and permits us to localize the limits of stability of various phases of the system. Our analytic approach is closely related to the general program proposed in an inspiring, but largely unknown book by Fisher.[14] However, our interpretation and conclusions deviate in a number of points from those presented therein.

In order to benefit from the analytic predictions and arrive at quantitative results, we need to know the radial distribution as a function of distance, density, and temperature. We determine and report here the contact values at distances corresponding to the hard-core diameter and the range λ of the attractive square well, solving the integral equation by iterative methods. The methods used in obtaining the relevant numerical results and their reliability are an essential part of the present work.

II. YVON-BORN-GREEN EQUATION FOR A SQUARE-WELL FLUID

We consider a fluid composed of spherical particles with hard core diameter σ and an attractive square-well pair potential

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

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

The hard core excludes overlapping configurations. So, the Boltzmann factor corresponding to the assumed interaction vanishes for $r < \sigma$ and reads

$$\begin{aligned}\chi_B(r) &= \theta(r-\sigma)\exp[-\beta U(r)]\\ &= \theta(r-\lambda\sigma) + B\theta(r-\sigma)\theta(\lambda\sigma - r),\end{aligned} \tag{2}$$

where

$$B = \exp(\beta\epsilon), \tag{3}$$

and $\beta = 1/k_BT$ denotes the inverse temperature.

The two- and three-particle reduced densities are conveniently written in the form

$$n_2(r_{12}) = n^2\chi_B(r_{12})y_2(r_{12}), \tag{4}$$

$$n_3(r_{12}, r_{13}, r_{23}) = n^3\chi_B(r_{12})\chi_B(r_{13})\chi_B(r_{23})y_3(r_{12}, r_{13}, r_{23}). \tag{5}$$

Here n denotes the mean number density of the homogeneous fluid, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ are distances between points $\mathbf{r}_i$ and $\mathbf{r}_j$.

The functions $y_2(r_{12})$ and $y_3(r_{12}, r_{13}, r_{23})$ are supposed to be continuous and differentiable. They are related by the second YBG hierarchy equation,

$$\begin{aligned}&\chi_B(r_{12})\frac{\partial}{\partial\mathbf{r}_1}y_2(r_{12})\\ &= \chi_B(r_{12})n\int d\mathbf{r}_3\left[\frac{\partial}{\partial\mathbf{r}_1}\chi_B(r_{13})\right]\chi_B(r_{23})y_3(r_{12}, r_{13}, r_{23}).\end{aligned} \tag{6}$$

Putting $\mathbf{r}_{12} = \mathbf{r} = r\hat{\mathbf{r}}$, $|\hat{\mathbf{r}}| = 1$, and introducing the integration variable $\mathbf{r}_{13} = s\hat{\boldsymbol{\sigma}}$, $|\hat{\boldsymbol{\sigma}}| = 1$, we rewrite (6) as

$$\begin{aligned}\frac{d}{dr}y_2(r) = n\int d\hat{\boldsymbol{\sigma}}(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{r}})\int_0^\infty ds\,s^2\left[\frac{d}{ds}\chi_B(s)\right]\\ \times\chi_B(|s\hat{\boldsymbol{\sigma}} - \mathbf{r}|)y_3(r, s, |s\hat{\boldsymbol{\sigma}} - \mathbf{r}|),\end{aligned} \tag{7}$$

where $\int d\hat{\boldsymbol{\sigma}}$ denotes the integration over three-dimensional solid angle.

Inserting into (7) the relation

$$\frac{d}{ds}\chi_B(s) = \delta(s-\sigma)B - \delta(s-\lambda\sigma)(B-1), \tag{8}$$

we find

$$\begin{aligned}\frac{d}{dr}y_2(r) = n\int d\hat{\boldsymbol{\sigma}}(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{r}})\sigma^2[\chi_B(|\sigma\hat{\boldsymbol{\sigma}} - \mathbf{r}|)y_3(r, \sigma, |\sigma\hat{\boldsymbol{\sigma}} - \mathbf{r}|)B\\ + \lambda^2\chi_B(|\lambda\sigma\hat{\boldsymbol{\sigma}} - \mathbf{r}|)y_3(r, \lambda\sigma, |\lambda\sigma\hat{\boldsymbol{\sigma}} - \mathbf{r}|)(1-B)].\end{aligned} \tag{9}$$

The Kirkwood superposition approximation,

$$y_3(r, s, t) = y_2(r)y_2(s)y_2(t), \tag{10}$$

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 $Y(x) = y_2(\sigma x)$:

$$\begin{aligned}\frac{d}{dx}\ln Y(x) = n\sigma^3\int d\hat{\boldsymbol{\sigma}}(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{x}})[\chi_B(|\mathbf{x} - \hat{\boldsymbol{\sigma}}|)Y(1)Y(|\mathbf{x} - \hat{\boldsymbol{\sigma}}|)B\\ + \lambda^2\chi_B(|\mathbf{x} - \lambda\hat{\boldsymbol{\sigma}}|)Y(\lambda)Y(|\mathbf{x} - \lambda\hat{\boldsymbol{\sigma}}|)(1-B)],\end{aligned} \tag{11}$$

where (see Eq. (2))

$$\chi_B(x) = \theta(x-1)[1 + \theta(\lambda - x)(B-1)]. \tag{12}$$

III. INTEGRAL EQUATION

We define the correlation function

$$H(x) = Y(x) - 1, \tag{13}$$

and assume that

$$\lim_{x\to\infty} H(x) = 0. \tag{14}$$

The next step of our analysis consists in deriving from Eq. (11) a purely integral equation with the essential use of the boundary condition (14). We rewrite Eq. (11) putting $\mu = (\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{x}})$, and denoting by ϕ the volume fraction $\phi = \pi n\sigma^3/6$. The equation takes the form

$$\begin{aligned}\frac{d}{dx}\ln Y(x) = 12\phi\int_0^1 d\mu\,\mu\{Y(1)B[f(\sqrt{x^2 - 2x\mu + 1})\\ - f(\sqrt{x^2 + 2x\mu + 1})]\\ - \lambda^2 Y(\lambda)(B-1)[f(\sqrt{x^2 - 2x\mu\lambda + \lambda^2})\\ - f(\sqrt{x^2 + 2x\mu\lambda + \lambda^2})]\},\end{aligned} \tag{15}$$

where for convenience we used the notation $f(x) = \chi_B(x)Y(x)$.

Integrating both sides of Eq. (15) over the interval (x, ∞) and denoting the integration variable by y we find

$$\ln Y(x) = 2\pi n\sigma^3[-Y(1)B\, I_1(x) + \lambda^2 Y(\lambda)(B-1)\, I_\lambda(x)], \tag{16}$$

where

$$\begin{aligned} I_1(x) &= \int_x^\infty dy \int_0^1 d\mu\, \mu\{[f(\sqrt{y^2-2y\mu+1})-1] \\ &\quad - [f(\sqrt{y^2+2y\mu+1})-1]\} \\ &= \int_0^1 d\mu\, \mu \int_{x-\mu}^{x+\mu} dy\, [f(\sqrt{y^2+1-\mu^2})-1], \end{aligned} \tag{17}$$

and

$$\begin{aligned} I_\lambda(x) &= \int_x^\infty dy \int_0^1 d\mu\, \mu\{[f(\sqrt{y^2-2y\mu\lambda+\lambda^2})-1] \\ &\quad - [f(\sqrt{y^2+2y\mu\lambda+\lambda^2})-1]\} \\ &= \int_0^1 d\mu\, \mu \int_{x-\mu\lambda}^{x+\mu\lambda} dy\, [f(\sqrt{y^2+\lambda^2(1-\mu^2)})-1]. \end{aligned} \tag{18}$$

In the process of evaluation of the integrals $I_1(x)$ and $I_\lambda(x)$ we use the fact that in accordance with assumption (14) the difference $[f(s)-1]$ approaches 0 when $s \to \infty$. The detailed derivation of the final results can be found in the supplementary material.[26] It is quite remarkable that one integration in the double integral (18) can be performed analytically.

For $I_1(x)$ we get

$$I_1(x) = \frac{1}{2x}\int_{x-1}^{x+1} ds\, s f(s)[1-(s-x)^2] - \frac{2}{3}. \tag{19}$$

The evaluation of the integral $I_\lambda(x)$ requires separate consideration of the intervals $x > \lambda$, and $1 < x < \lambda$.

When $x > \lambda$, we find

$$I_\lambda(x) = \frac{1}{2x\lambda^2}\int_{x-\lambda}^{x+\lambda} ds\, s f(s)[\lambda^2-(s-x)^2] - \frac{2}{3}\lambda. \tag{20}$$

When $1 < x < \lambda$, straightforward but rather lengthy calculations (see the supplementary material[26]) yield the formula

$$\begin{aligned} I_\lambda(x) &= \frac{1}{2x\lambda^2}\int_{\lambda-x}^{x+\lambda} ds\, s f(s)[\lambda^2-(s-x)^2] \\ &\quad + \theta(\lambda-x)\frac{2}{\lambda^2}\int_0^{\lambda-x} ds\, s^2 f(s) - \frac{2}{3}\lambda. \end{aligned} \tag{21}$$

We are now ready to write down the nonlinear integral equation satisfied by the two-particle density $Y(x)$. By combining Eqs. (16), (19), (20), and (21) we get

$$\ln Y(x) = R_1(x) + R_2(x), \tag{22}$$

where

$$\begin{aligned} R_1(x) &= 12\phi\left\{-Y(1)B\left[\frac{1}{2x}\int_{x-1}^{x+1} ds\, s f(s)[1-(x-s)^2] - \frac{2}{3}\right]\right. \\ &\quad + Y(\lambda)(B-1)\left[\frac{1}{2x}\int_{|x-\lambda|}^{x+\lambda} ds\, s f(s)[\lambda^2\right. \\ &\quad \left.\left. -(s-x)^2] - \frac{2}{3}\lambda^3\right]\right\}, \end{aligned} \tag{23}$$

$$R_2(x) = 24\phi\, \theta(\lambda-x)\, Y(\lambda)(B-1)\int_0^{\lambda-x} ds\, s^2 f(s), \tag{24}$$

and

$$f(s) = \chi_B(s)\, Y(s) = [\theta(s-\lambda) + \theta(\lambda-s)\theta(s-1)\, B]\, Y(s). \tag{25}$$

The factor $\chi_B(s)$ present in the defining equation (25) imposes the condition $s > 1$. It follows that in the physically relevant region $x > 1$, the term $R_2(x)$ vanishes when $\lambda < 2$. On the other hand for $\lambda > 2$ both $R_1(x)$ and $R_2(x)$ contribute. The above analysis shows that the structure of the integral equation changes when the range of the attractive well exceeds the threshold value $\lambda^* = 2$. We find

(1) $\ln Y(x) = R_1(x)$, if $1 < \lambda < 2$

(2) $\ln Y(x) = R_1(x) + R_2(x)$, if $\lambda > 2$

In the cases of $\lambda = 1.4$ and $\lambda = 1.85$ studied here the equality (1) applies, which requires solving the integral equation,

$$\begin{aligned} \ln Y(x) &= 12\phi\left\{-Y(1)B\left[\frac{1}{2x}\int_{x-1}^{x+1} ds\, s\, \chi_B(s)\right.\right. \\ &\quad \left. \times Y(s)[1-(x-s)^2] - \frac{2}{3}\right] \\ &\quad + Y(\lambda)(B-1)\left[\frac{1}{2x}\int_{|x-\lambda|}^{x+\lambda} ds\, s\, \chi_B(s)\, Y(s)\right. \\ &\quad \left.\left. \times [\lambda^2-(s-x)^2] - \frac{2}{3}\lambda^3\right]\right\}. \end{aligned} \tag{26}$$

IV. ASYMPTOTIC DECAY OF CORRELATIONS: EXPONENTIAL MODES

Let us consider Eq. (26) in the region of $x \gg 1$. Using the fundamental assumption (14) about vanishing of correlations when $x \to \infty$ we replace on the left-hand side of (26) 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 which holds when $x \gg 1$ reads

$$\begin{aligned} xH(x) &= 6\phi\left\{-Y(1)B\int_{x-1}^{x+1} ds\, sH(s)[1-(s-x)^2]\right. \\ &\quad \left. + Y(\lambda)(B-1)\int_{x-\lambda}^{x+\lambda} ds\, sH(s)[\lambda^2-(s-x)^2]\right\}. \end{aligned} \tag{27}$$

Equation (27) 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 which makes the present approach appropriate to study predictions of the Kirkwood superposition approximation.

In this respect, our approach is different from that developed in Ref. 2. In the regime of large compressibility, Fisher and Fishman[2] proceed by inserting into the YBG equation (11) a large-distance expansion, and retain a few lowest order terms. Thus an additional approximation is introduced in their analysis. As a consequence, the equation studied in Ref. 2 is not the integral equation (27), but a second-order nonlinear differential equation which results from combining (11) 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. (27) the exponential mode

$$xH(x;\kappa) = \exp(\kappa x), \tag{28}$$

where κ is a complex number. $H(x;\kappa)$ is a solution of Eq. (27) provided the parameter κ satisfies the condition

$$1 = 24\phi\,[\,\lambda^3 Y(\lambda)(B-1)F(\lambda\kappa) - Y(1)BF(\kappa)\,], \tag{29}$$

where the function F is defined by

$$F(\kappa) = \frac{[\kappa\cosh\kappa - \sinh\kappa]}{\kappa^3}. \tag{30}$$

The series representation of $F(\kappa) = F(-\kappa)$ reads

$$F(\kappa) = \sum_{n=0}^{\infty} \frac{\kappa^{2n}}{(2n+3)(2n+1)!} = \frac{1}{3}\left[1 + \frac{\kappa^2}{10} + \frac{\kappa^4}{280} + \ldots\right]. \tag{31}$$

On 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 (28) whose frequency $\kappa = -a + ib$ has the smallest value of $a > 0$, 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 (we recall that $B = \exp(\epsilon/k_BT)$). So, let us fix the temperature, and consider solutions of Eq. (29) when the state of the system is changing along an isotherm $B = \exp(\epsilon/k_BT) = \text{const}$. Our aim is 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.[10,11]

Consider the case of vanishing of $\kappa = a + ib$. Taking the limit $\kappa \to 0$ on both sides of Eq. (29) we find the relation

$$1 + 8\phi\, Y(1)B = 8\phi\,\lambda^3 Y(\lambda)(B-1). \tag{32}$$

In fact, relation (32) follows directly if we assume the absence of exponential damping inserting into Eq. (27) correlation function of the form

$$H(x) = \frac{\text{const}}{x}. \tag{33}$$

Equation (32) shows the relevance of the quantity

$$\Gamma = 1 + 8\phi[\,Y(1)B - \lambda^3 Y(\lambda)(B-1)]. \tag{34}$$

For real $\kappa \ll 1$, relation (29) takes the asymptotic form (see the expansion (31)),

$$\Gamma = \frac{4}{5}\phi\,[\lambda^5 Y(\lambda)(B-1) - BY(1)]\,\kappa^2, \tag{35}$$

which shows that the range of the correlation function grows as $1/\sqrt{\Gamma}$ when Γ approaches zero. The vanishing of Γ defines an absolute instability line in the plane (ϕ, T), corresponding to some implicit function $T(\phi)$.

The curve $\phi \to T(\phi)$ must have a finite absolute maximum. Indeed, when the temperature increases the parameter B approaches 1, so that the right-hand side of (32) tends to zero, whereas the left-hand side remains strictly positive. It is thus clear that isotherms corresponding to sufficiently high temperatures pass above the curve representing function $T(\phi)$.

The numerical evidence shows that

$$Y(\lambda) < Y(1). \tag{36}$$

If Eq. (32) is satisfied, and (36) holds, then

$$\lambda^3 Y(\lambda)[B-1] > \frac{1}{8\phi} + Y(\lambda)B,$$

or

$$Y(\lambda)[\lambda^3[B-1] - B] > \frac{1}{8\phi},$$

which is possible only if

$$\lambda^3\left[1 - \frac{1}{B}\right] = \lambda^3[1 - \exp(-\epsilon/k_BT)] > 1. \tag{37}$$

In accordance with the previous remark, (37) represents an upper bound on temperatures for which equation $\Gamma = 0$ can be satisfied.

We can thus in principle expect the existence of a critical temperature with the corresponding isotherm touching the curve defined by $\Gamma = 0$ at a single (critical) point. The corresponding condition can be obtained by differentiating both sides of (32) with respect to ϕ, and imposing the necessary condition for a maximum. The resulting equation reads

$$-\frac{1}{8\phi^2} + B\frac{\partial Y(1)}{\partial\phi} = \lambda^3[B-1]\frac{\partial Y(\lambda)}{\partial\phi}. \tag{38}$$

Equations (32) and (38) taken together define the critical temperature and the critical volume fraction of the vapor-liquid phase transition.

Clearly, to check whether the derived equations (34) and (38) can be asymptotically satisfied by solutions of the integral equation (26), and obtain quantitative predictions, we need to know the contact values $Y(1)$ and $Y(\lambda)$ as functions of the volume fraction and temperature. This is the hardest part of our numerical study as it requires solving the full nonlinear integral equation (26).

Before discussing this point let us first present an analytic analysis concerning the behavior of the exponential mode (28) at the approach to the threshold value $\kappa = a + ib = 0$. We follow here closely the method developed in Ref. 14 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 (29) takes the form

$$1 = 24(\phi_0 + \delta\phi)\,[\,\lambda^3 Y(\lambda;\phi_0 + \delta\phi)(B-1)F(\lambda(\delta a + i\delta b)) - Y(1;\phi_0+\delta\phi)BF(\delta a + i\delta b)]. \tag{39}$$

Using the series expansion (31), and, keeping asymptotically 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. (39). The conditions read,

$$\begin{aligned} &B\left(\phi_0\frac{\partial Y(1;\phi_0)}{\partial\phi_0} + Y(1;\phi_0)\right)\delta\phi \\ &\quad + \frac{B}{10}\phi_0 Y(1;\phi_0)[(\delta a)^2 - (\delta b)^2] \\ &= (B-1)\lambda^3\left(\phi_0\frac{\partial Y(\lambda;\phi_0)}{\partial\phi_0} + Y(\lambda;\phi_0)\right)\delta\phi \\ &\quad + \frac{(B-1)}{10}\phi_0\lambda^5 Y(\lambda;\phi_0)[(\delta a)^2 - (\delta b)^2], \end{aligned} \tag{40}$$

$$BY(1;\phi_0)\delta a\delta b = \lambda^3(B-1)Y(\lambda;\phi_0)\delta a\delta b. \tag{41}$$

They have to be considered together with the threshold line equation (32),

$$\frac{1}{8\phi} + Y(1;\phi_0)B = \lambda^3 Y(\lambda;\phi_0)[B-1].$$

As $\delta a \neq 0$, Eqs. (32) and (41) 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 monotonous decay of correlations in the immediate vicinity of the critical point. This fact supports the interpretation of the threshold line (32) as representing the absolute stability limit for the fluid (liquid or vapor) phases.

Inserting $\delta b = 0$ into (40) and using Eq. (32) we derive an asymptotic relation between δa and $\delta\phi$ of the form,

$$\begin{aligned} &\left[\phi_0(B-1)\lambda^3(\lambda^2-1)Y(\lambda;\phi_0) + \frac{1}{8}\right](\delta a)^2 \\ &\quad = 10\phi_0\left[B\frac{\partial Y(1;\phi_0)}{\partial\phi_0} - (B-1)\lambda^3\frac{\partial Y(\lambda;\phi_0)}{\partial\phi_0} - \frac{1}{8\phi_0^2}\right]\delta\phi. \end{aligned} \tag{42}$$

We note that on the right-hand side there appears the expression,

$$\Psi(\phi) = B\frac{\partial Y(1;\phi)}{\partial\phi} - \lambda^3[B-1]\frac{\partial Y(\lambda;\phi)}{\partial\phi} - \frac{1}{8\phi^2}, \tag{43}$$

which vanishes at the critical point (see Eq. (38)). This fact has important consequences. Indeed, when $\Psi(\phi) \neq 0$, Eq. (42) 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 critical point at ϕ_0 is an isolated instability point.

V. CONSISTENCY QUESTIONS

If the system attains the instability line (32) the correlation function decays as $1/x$ so that the integral in the compressibility equation,

$$\begin{aligned} &n\sigma^3\int d\mathbf{x}\,[\chi_B(x)Y(x) - 1] \\ &\quad = n\sigma^3\int d\mathbf{x}\,\{[\theta(x-\lambda) + B\theta(x-1)\theta(\lambda - x)]Y(x) - 1\} \\ &\quad = k_BT\frac{\partial n}{\partial p} - 1 = k_BTn\kappa_T - 1 \end{aligned} \tag{44}$$

diverges. The appearance of an infinite compressibility κ_T is a consequence of the vanishing of exponential damping. The compressibility equation (44) would be thus consistent with the superposition approximation if it could drive the system to the loss of stability.

However, the consistency disappears when we turn to the virial equation of state,

$$\frac{\beta p}{n} = 1 + \frac{2}{3}n\pi\sigma^3[\,BY(1) - \lambda^3(B-1)Y(\lambda)]. \tag{45}$$

Indeed, from (45) we find

$$\begin{aligned} \beta\frac{\partial p}{\partial n} &= 1 + \frac{4}{3}n\pi\sigma^3[BY(1) - \lambda^3(B-1)Y(\lambda)] \\ &\quad + \frac{2}{3}n^2\pi\sigma^3\left[B\frac{\partial Y(1)}{\partial n} - \lambda^3(B-1)\frac{\partial Y(\lambda)}{\partial n}\right]. \end{aligned} \tag{46}$$

Recalling the definition of the volume fraction $6\phi = \pi n\sigma^3$ we find that on the instability line (32),

$$\begin{aligned} &1 + \frac{4}{3}n\pi\sigma^3[BY(1) - \lambda^3(B-1)Y(\lambda)] \\ &\quad = 1 + 8\phi[BY(1) - \lambda^3(B-1)Y(\lambda)] = \Gamma = 0, \end{aligned} \tag{47}$$

so that Eq. (46) takes the form

$$\beta\frac{\partial p}{\partial n} = \frac{2}{3}n^2\pi\sigma^3\left[B\frac{\partial Y(1)}{\partial n} - \lambda^3(B-1)\frac{\partial Y(\lambda)}{\partial n}\right]. \tag{48}$$

The right-hand side of (48) does not vanish. For instance, the condition (38) localizing the critical point implies that at such a point the equality,

$$\frac{2}{3}n^2\pi\sigma^3\left[B\frac{\partial Y(1)}{\partial n} - \lambda^3(B-1)\frac{\partial Y(\lambda)}{\partial n}\right]$$
$$= 4\phi\left[B\frac{\partial Y(1)}{\partial \phi} - \lambda^3(B-1)\frac{\partial Y(\lambda)}{\partial \phi}\right] = \frac{1}{2\phi} > 0 \quad (49)$$

must hold. According to the virial equation of state the compressibility would remain thus finite on the instability line (and, in particular, at the critical point) which shows that this equation is inconsistent with the superposition approximation. It follows that the equation of state compatible with the superposition approximation should be derived from the compressibility relation (44). A similar suggestion can be found in Ref. 2.

The above remarks are important because they show the inadequacy of the virial equation to predict physical properties of fluids whose states are described within the superposition approximation. There exists some confusion in the literature on this point. For instance, I. Z. Fisher assumes the vanishing of the right-hand side of (48); see Ref. 14. As this does not follow from the basic integral equation (22) 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 instability line (32) cannot contain a critical point, a statement with which we disagree.

Moreover, we wish to stress that on the instability line (32), and in particular at the critical point, the relation

$$\frac{p}{nk_BT} = \frac{1}{2} \quad (50)$$

invoked by some authors (see, e.g., Refs. 14 and 15) cannot be justified because it is obtained by combining the virial equation (45) with the relation $\Gamma = 1 + 8\phi[Y(1)B - \lambda^3 Y(\lambda)(B-1)] = 0$ which results from the superposition approximation. Such a combination is not allowed because of the described above inconsistency. Equation (50) does not follow from the superposition approximation which is also illustrated by the fact, already mentioned in the Introduction, that the critical compressibility factor calculated numerically on the basis of YBG equation does not exceed 0.35.

VI. ITERATIVE SOLUTION OF THE INTEGRAL EQUATION

Similarly to the previous work,[10,11] we solve the integral equation for $H(x)$ resulting from (26),

$$H(x) = -1 + \exp\Bigg\{12\phi\Bigg(-Y(1)B\left[\frac{1}{2x}\int_{x-1}^{x+1} ds\, s\, \chi_B(s)\, Y(s)\right.$$
$$\left.\times\,[1-(x-s)^2] - \frac{2}{3}\right]$$
$$+\,Y(\lambda)(B-1)\left[\frac{1}{2x}\int_{|x-\lambda|}^{x+\lambda} ds\, s\, \chi_B(s)\, Y(s)\right.$$
$$\left.\times\ [\lambda^2-(s-x)^2] - \frac{2}{3}\lambda^3\right]\Bigg)\Bigg\}, \quad (51)$$

where $Y(x) = H(x) + 1$, by a standard Neumann method with successive over-relaxation.[20] The iterative solutions are then given by

$$H_n = (1-\alpha)H_{n-1} + \alpha\mathcal{L}(H_{n-1}), \quad (52)$$

where $\mathcal{L}$ is the operator appearing in the RHS of Eq. (51). Due to the slow convergence of the iterations, it was necessary to use a relatively small value of the relaxation parameter $\alpha = 0.05$. The convergence was particularly slow at low temperatures and moderate to large volume fractions. We have studied two values of the square-well potential range, $\lambda = 1.4$ and $\lambda = 1.85$, and found the results in these two cases to be significantly different.

Let us begin our analysis by considering a square well of a width $\lambda = 1.85$, the system previously considered, e.g., in Refs. 3–5, and 8. Several important conclusions can be drawn from the analysis of the shapes of the correlation functions, as presented in Figs. 1 and 2 as well as in Table I. First, at high temperatures $B \leq 1.4$, the situation is reminiscent of that for a hard-sphere system:[11] with increasing volume fraction the decay of correlations becomes slower, and a pronounced peak structure appears. Examples of correlation functions in this parameter range (B = 1.2, $\lambda = 1.85$) are presented in

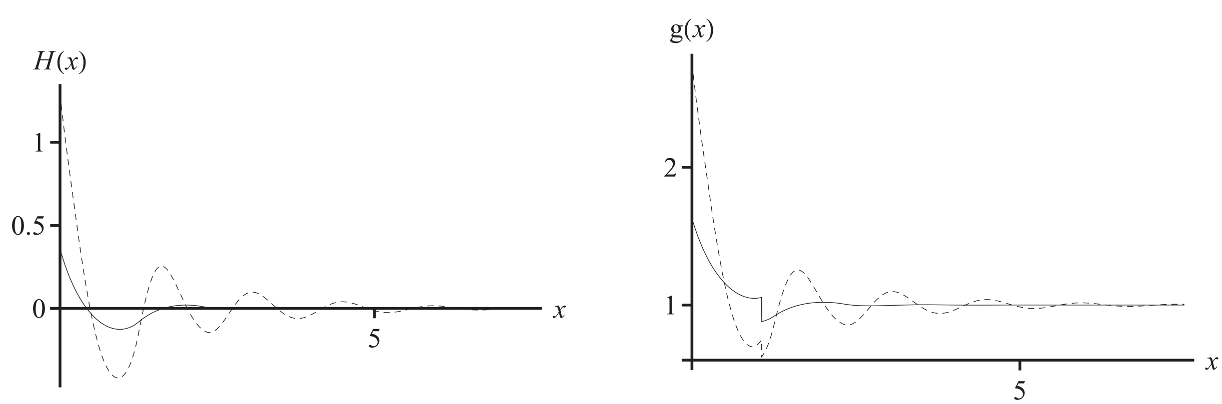

FIG. 1. Left panel: correlation function $H(x)$ for $\lambda = 1.85$, $B = 1.2$, and $\phi = 0.2$ (solid) and $\phi = 0.5$ (dashed). Right panel: the corresponding pair distribution functions $g(x) = \chi(x)(1 + H(x))$.

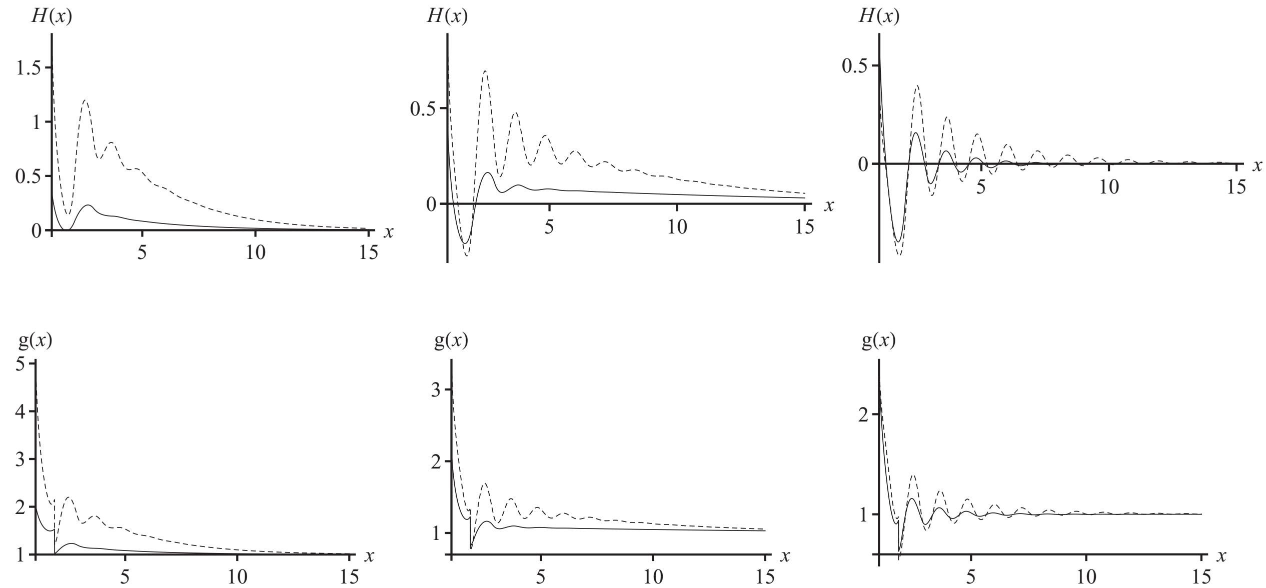

FIG. 2. Upper panel: correlation function $H(x)$ for $\lambda = 1.85$, $B = 1.5$ (solid), and $B = 1.8$ (dashed) for $\phi = 0.1$ (left), $\phi = 0.25$ (center), and $\phi = 0.45$ (right). Lower panel: the corresponding pair distribution functions $g(x) = \chi(x)(1 + H(x))$.

Fig. 1. Besides $H(x)$, we also plot the pair distribution $g(x) = \chi_B(x)[1 + H(x)]$. Note that the latter has a discontinuity at the boundary of the potential well, i.e., at $x = \lambda$. As it is observed, both functions attain a slowly decaying oscillatory tail as the volume fraction is increased. The oscillatory character of the decay is confirmed by the mode analysis, in which one represents $xH(x)$ as a linear combination of exponential modes $\exp(\kappa x)$ where κ is a complex number, a solution of Eq. (29). In the high temperature range the slowest decaying mode (κ_0) has a nonzero imaginary part, except in the region of small volume fractions (cf. the left panel of Fig. 3). The dominant oscillatory mode manifests itself in the oscillatory behavior of the correlation functions. As the density is increased the real part of this mode approaches zero, whereas the imaginary part changes by a relatively small amount: for the case presented in Fig. 3 the frequencies change from $\kappa_0 = -2.48978 \pm 4.61493I$ at $\phi = 0.05$ to $\kappa_0 = -0.221575 \pm 5.59814I$ at $\phi = 0.5$. Finally, at $\phi \approx 0.52$ the real part of κ_0 vanishes, which announces the change in the nature of correlations and thus implies a structural change in the fluid. The similarities between the present case and the hard-sphere system analyzed in Ref. 11 imply that the transition can be interpreted as freezing of the fluid into the crystalline structure. Indeed, it is known that the steric repulsion plays a determining role in the freezing process, hence one expects that a square well fluid and hard-sphere fluid will behave in an analogous manner in this transition.

At a smaller temperature, corresponding to $B = 1.5$ (solid lines in Fig. 2), the decay of the correlation functions becomes much slower, and is non-oscillatory in character up to $\phi \approx 0.37$. The magnitude of $\mathrm{Re}(\kappa_0)$ quickly decreases with increasing ϕ: from $\kappa_0 = -1.02$ at $\phi = 0.05$ to $\kappa = -0.075$ at $\phi = 0.25$. Notably, as observed in Fig. 3 in the range $0.1 \leq \phi \leq 0.3$ the value of κ_0 changes only slightly, staying at a level of $0.05-0.2$, even though the shape of $H(x)$ dependence for small x does change significantly over this density range. For larger volume fractions the magnitude of $\mathrm{Re}(\kappa_0)$ begins to increase again, the oscillatory mode becomes dominant (cf. the right panels of Fig. 2) and finally, at $\phi \approx 0.52$, there is a freezing transition, similar to the one observed at $B = 1.75$. As the

TABLE I. Contact values of the correlation functions at $\lambda = 1.85$.

	$B = 1.45$		$B = 1.6$		$B = 1.8$	
	$H(1)$	$H(\lambda)$	$H(1)$	$H(\lambda)$	$H(1)$	$H(\lambda)$
$\phi = 0.05$	0.0648572	−0.0389442	0.209986	0.0303177	2.35631	0.604497
$\phi = 0.10$	0.129762	−0.0745082	1.20609	0.231001	1.75796	0.199533
$\phi = 0.15$	0.19894	−0.108402	0.998016	0.0483199	1.3445	−0.0152117
$\phi = 0.20$	0.234583	−0.155135	0.815456	−0.0771737	1.06157	−0.150923
$\phi = 0.25$	0.257577	−0.202365	0.669675	−0.168302	0.854621	−0.246122
$\phi = 0.30$	0.336735	−0.237536	0.551809	−0.237994	0.695745	−0.317308
$\phi = 0.35$	0.458241	−0.271999	0.454293	−0.293386	0.569615	−0.372817
$\phi = 0.40$	0.593454	−0.312394	0.425349	−0.338726	0.46711	−0.417458
$\phi = 0.45$	0.704467	−0.362874	0.49653	−0.387397	0.38211	−0.456379

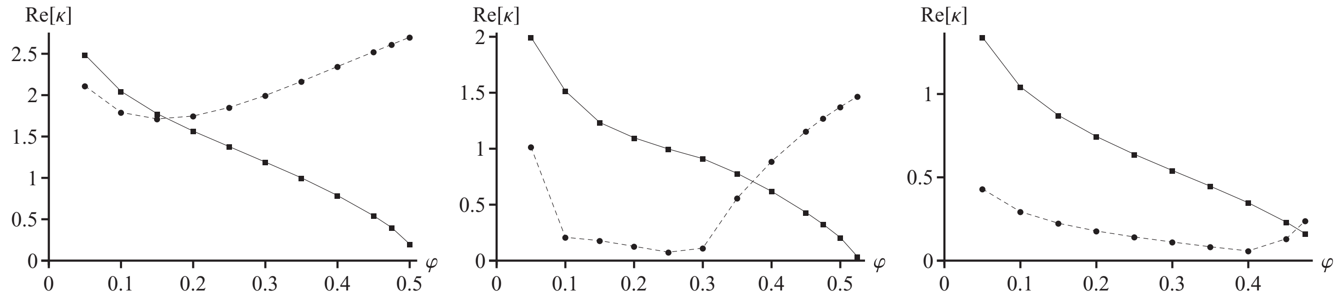

FIG. 3. The magnitude of the purely real root (dashed) and the smallest (in terms of $Re(\kappa)$) root with nonzero imaginary part (solid) for $\lambda = 1.85$ and $B = 1.2$ (left), $B = 1.5$ (center), and $B = 1.8$ (right).

temperature is further decreased, at $B = 1.8$ (dashed lines in Fig. 2), the value of volume fraction at which the oscillatory mode begins to dominate shifts towards even larger densities.

A good test of self-consistency of the theory is to compare the frequencies calculated using Eq. (29) with the actual asymptotic behaviour of $H(x)$. To this end, one can analyze the function $\kappa_{eff}(x)$, as proposed by Jones *et al.*[3] (note, however the typo in sign of $1/x$ term in the original definition),

$$\kappa_{eff}(x) = \frac{1}{H(x)}\frac{dH(x)}{dx} + \frac{1}{x}. \qquad (53)$$

For $H(x)$ asymptotically of the form $e^{\kappa x}/x$ (with κ real) one gets $\kappa(x) \to \kappa$ as $x \to \infty$. A typical form of $\kappa_{eff}(x)$ dependence is shown in the left panel of Fig. 4, as observed, after initial oscillations $\kappa_{eff}(x)$ relatively quickly attains the asymptotic value.

Figure 5 compares the values of κ obtained from the solution of Eq. (29) and those from the asymptotic analysis. As observed, there is a reasonable agreement between the two; with the systematic difference of about 5%–10%.

A further insight into the character of "critical" regions can be obtained by analysis of the parameter Γ defined in Eq. (34). For relatively large temperatures (e.g., $B = 1.2$ in Fig. 6) the dependence $\Gamma(\phi)$ is a monotonically increasing function. However, as the temperature is decreased, a minimum appears in $\Gamma(\phi)$ dependence, the depth of which increases with a decreasing temperature. Finally, at about $B = 1.455$, Γ comes closely to the zero line, with $\Gamma(\phi_{min} = 0.19) \approx 0.0065$. At even smaller temperatures the minimum widens but, notably, the curve never touches nor crosses the $\Gamma = 0$ axis. With a further decrease of temperature, the minimum continues to widen, but at the same time its bottom rises slightly in the small density region. This results in ϕ_{min} shifting to the right; however the minimal value continues to be very close to zero (for $B = 1.6$ we get $\Gamma_{min} \approx 0.001$ at $\phi_{min} \approx 0.35$ whereas at $B = 1.8$ we get $\Gamma_{min} \approx 0.008$ at $\phi_{min} \approx 0.4$).

Let us now turn to the case of $\lambda = 1.4$ (Figs. 7–9). The potential well is now more narrow thus one needs to go to significantly lower temperatures than at $\lambda = 1.85$ to reach the regions of small Γ values. At $B = 2.15$, the plateau again appears on $\Gamma(\phi)$ curve, extending between $\phi = 0.2$ and $\phi = 0.35$ with the corresponding value of $\Gamma_{min} \approx 0.03$ (Fig. 9). Unexpectedly however, and in contrast to the behavior at $\lambda = 1.85$, at even smaller temperatures the minimum of $\Gamma(\phi)$ dependence rises again above $\Gamma = 0$ line, reaching, e.g., $\Gamma_{min} \approx 0.09$ for $B = 2.5$. As a result, the region around $\phi = 0.25$, $B = 2.15$ seems to constitute a global minimum of $\Gamma(\phi, B)$. Further differences between $\lambda = 1.8$ and $\lambda = 1.45$ case are observed in analysis of mode frequencies (cf. Figs. 3 and 8). Whereas for $\lambda = 1.85$, the region of non-oscillatory decay progressively shifts towards larger ϕ as the temperature decreases (at least in the temperature range studied); the situation at $\lambda = 1.4$ is more complex, with the non-oscillatory region first increasing but then decreasing as the temperature is lowered. In other words, as the temperature is decreased below the "near-critical" region, the ordering of the fluid becomes progressively more solid-like, with the oscillatory correlation function.

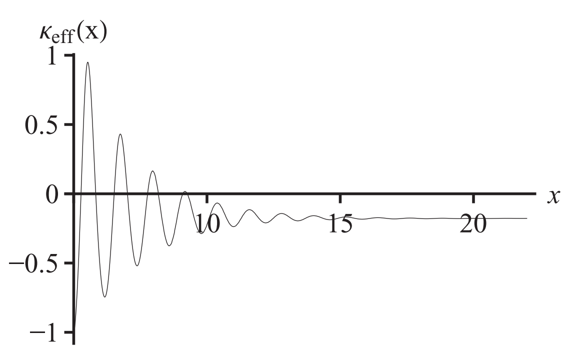

FIG. 4. The function $\kappa_{eff}(x)$ for $\lambda = 1.85$, $\phi = 0.25$, and $B = 1.8$.

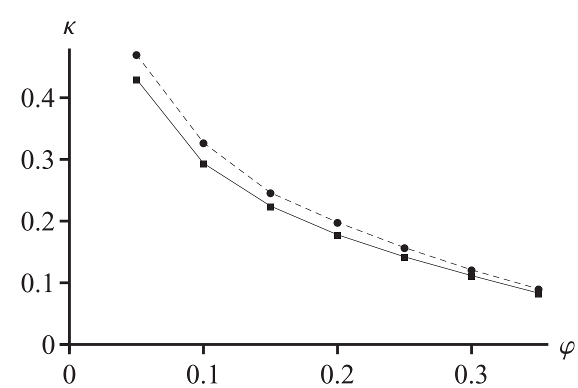

FIG. 5. The magnitude of the purely real root κ calculated from the solution of Eq. (29) (solid) and from the asymptotic values of $\kappa_{eff}(x)$ (dashed) for $\lambda = 1.85$ and $B = 1.8$.

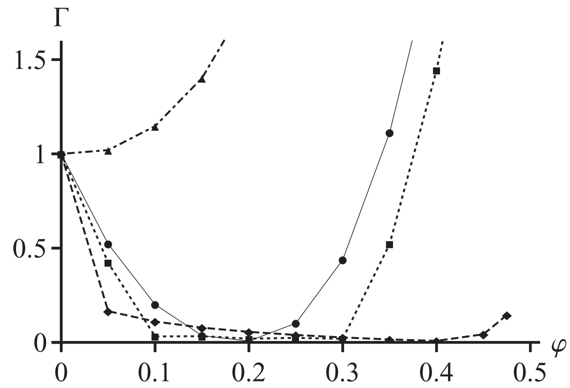

FIG. 6. The parameter Γ as a function of volume fraction for $\lambda = 1.85$ for different temperatures corresponding to B = 1.2 (dotted-dashed), B = 1.45 (solid), B = 1.5 (dotted), and B = 1.8 (dashed).

One way to understand some aspects of this behavior is to relate it to the results of Liu *et al.*[21] The authors of this study found that short-range square well fluids behave in a fundamentally different way from the long-ranged ones. In particular, liquid-vapor transition in short-range fluids was found to overlap with the freezing transition, with the vapor-liquid coexistence curve enclosed within the vapor-solid coexistence curve, and no triple point present.

Most importantly, for all studied values of B and ϕ the iteration procedure is convergent and the resulting Γ is positive. In the small Γ range, the results show the dependence on the integration interval, but increasing the interval leads invariably to the slight increase of both Γ and the magnitude of the frequency of the dominating mode; thus it seems unlikely that a further increase of the integration interval will bring the system into the instability region. The results thus seem to be consistent with the findings of Jones *et al.*,[3] who reported the existence of the "nearly-critical" region in the (T, ϕ) diagram, in which the mode frequencies remain negative, albeit very small in the magnitude.

VII. DISCUSSION AND CONCLUSIONS

In this paper, we continue our study of the consequences of introducing the Kirkwood superposition approximation as a closure in the Yvon-Born-Green equation. Whereas our previous studies[10,11] have focused on particles interacting via purely repulsive forces, here we consider in addition the role of attractions. Our analytic methods can be adapted most straightforwardly to the case of the square-well fluid, a model for which there exists an extensive literature.[16] Of particular relevance for the present work are the treatises of Rice and Gray[17] and Cole,[18] the reviews of Barker and Henderson[19] and Caccamo,[22] and the more recent contributions of Yuste and co-workers.[23–25]

The fundamental question raised in the paper is that of the limits of stability of various phases of a square-well fluid as predicted by the Yvon-Born-Green equation under the Kirkwood superposition approximation. 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 (26) derived under the assumption of integrability of the correlation function $H(x)$. It implied the asymptotic decay of the form

$$H(x) \sim \frac{\exp(-ax)}{x} \cos b, \quad a > 0, \tag{54}$$

and was corroborated numerically in our study. When a vanishes, the correlation function ceases to be integrable, the phase looses 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, consists in 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

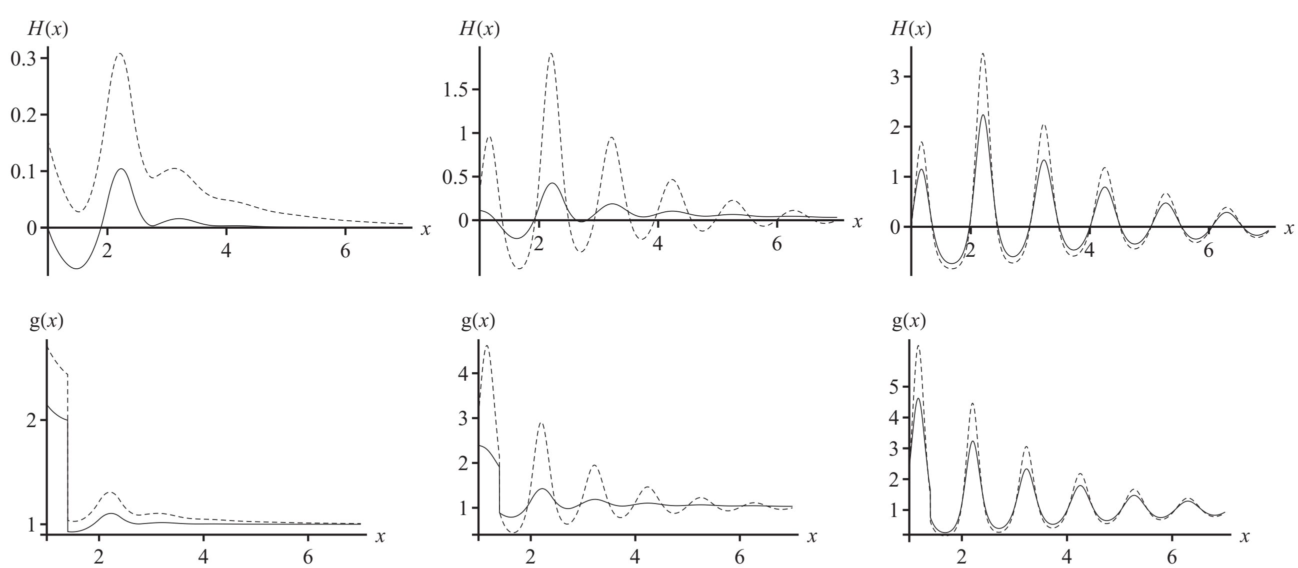

FIG. 7. Upper panel: correlation function $H(x)$ for $\lambda = 1.4$, $B = 2.15$ (solid), and $B = 2.35$ (dashed) for $\phi = 0.1$ (left), $\phi = 0.25$ (center), and $\phi = 0.4$ (right). Lower panel: the corresponding pair distribution functions $g(x) = \chi(x)(1 + H(x))$.

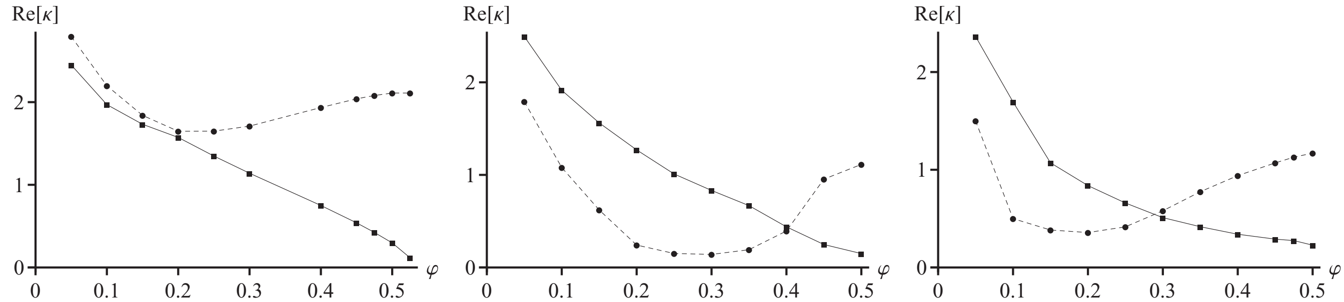

FIG. 8. The magnitude of the purely real root (dashed) and the smallest (in terms of $Re(\kappa)$) root with nonzero imaginary part (solid) for $\lambda = 1.4$ and $B = 1.75$ (left), $B = 2.15$ (center), and $B = 2.35$ (right).

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. It has been clearly illustrated for a square well of range $\lambda = 1.85$ on the isotherm $B = \exp(\beta\epsilon) = 1.2$ (see Fig. 1): the damping of oscillations becomes weaker and weaker with increasing volume fraction ϕ to disappear at the threshold value $\phi_0 \sim 0.52$. We thus conclude that the superposition approximation predicts for square-well fluids the existence of an absolute stability limit corresponding to freezing.

While the freezing transition is also expected to occur at lower temperatures, we find that, before arriving at freezing, there appears a new phenomenon which can be looked upon as a manifestation of the existence of liquid-vapor stability limit.

This new phenomenon is related to the second possibility of loosing mechanical stability: *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 (28)) approaches zero. Using the type of analysis elaborated in Ref. 14 we could show analytically that the approach of κ to zero is possible only along the real axis, i.e., with $b = 0$. The numerical evidence confirms this result. As illustrated in Fig. 3 for $\lambda = 1.85$, the purely real root κ governs the decay of correlations at temperature $B = \exp(\beta\epsilon) = 1.6$ up to $\phi \sim 0.35$, contrary to what was the case at a higher temperature ($B = 1.2$), where the oscillatory decay takes over already at $\phi \approx 0.15$.

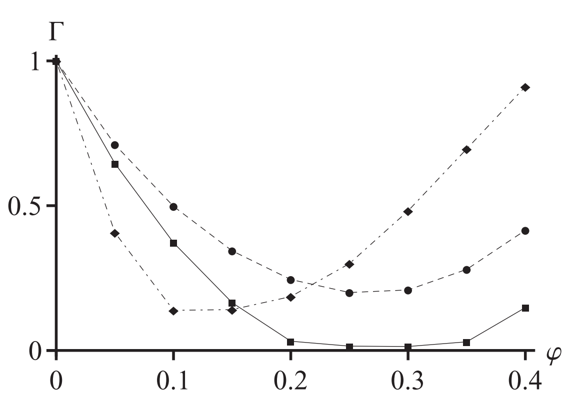

FIG. 9. The parameter Γ as a function of volume fraction and temperature for $\lambda = 1.4$ and B = 2.05 (dashed), B = 2.15 (solid), and B = 2.5 (dotted-dashed).

The fundamental question in our study of the square-well fluid is whether one can actually reach the absolute stability limit where $\kappa = 0$, implying asymptotically a non-integrable power law decay $H(x) \sim 1/x$. As shown in Sec. IV, this question includes in particular the problem of existence of a critical isotherm containing the critical point.

In our analytic considerations based on the integral equation (26) there appears the quantity $\Gamma = 1 + 8\phi[Y(1)B - \lambda^3 Y(\lambda)(B - 1)]$, the vanishing of which was shown to be equivalent to reaching the absolute stability limit 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 turned out to be sensitive to the temperature.

Along high temperature isotherms Γ increases with ϕ, staying away from zero (see, e.g., the case of $\lambda = 1.85$, $B = 1.2$ presented in Fig. 6). 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 towards the loss of stability. The approach to zero occurs already along the isotherm $B = 1.455$ on which the minimum attained by Γ equals 0.0065. The minimum then widens and also becomes deeper. It has been established that the curve $\phi \to \Gamma(\phi, 1.6)$ decreases to a value of the order 10^{-3}. At the same time, for $B > 1.45$ a plateau appears where Γ stays very close to zero over intervals whose length grows 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" which marks the appearance of the plateau for lower temperatures would correspond thus for $\lambda = 1.85$ to $B = 1.455$, and the "critical volume fraction" where the minimum of Γ is attained was found numerically to be $\phi_0 = 0.19$. The plateau itself, although corresponding to stable uniform states, may well signal the existence of two-phase states. Consequently, increasing the volume fraction beyond the plateau region should mark the entrance into a pure liquid phase. This is consistently reflected by the increase of Γ driving the system away from the absolute stability line (32). Further increase of the volume fraction leads to freezing signaled by the approach to undamped oscillatory behavior of correlations.

The behavior of the system at $\lambda = 1.4$ is intriguing. Apparently, the region of small Γ values in the (ϕ, T) phase space is limited, with a global minimum at $\phi = 0.25$, $B = 2.15$. Again, however, 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 absolute stability line $\Gamma = 0$, and in particular the conditions for the critical point, cannot be exactly satisfied by the solutions of the integral equation (26). However, within the adopted interpretation of the numerical results, the position of the "absolute stability line," and of the "critical isotherm" can be approximately localized.

It should be said at this point that the analysis of the critical behavior presented in Ref. 2 (see also Ref. 3) led to a similar conclusion: in three dimensions the YBG equation cannot predict a "true criticality." However, the basis for this conclusion was the nonlinear differential equation whose derivation required an additional approximation superposed on the KSA.

Here we studied the consequences of the integral equation (26) representing exactly the KSA, without additional approximations. Whereas our study does not rule out decisively the possibility of reaching the absolute stability line $\Gamma = 0$, the analytic and numerical results presented here suggest that solutions of (26) will always be stable, and thus lie outside this line. However, a rigorous analytic argument supporting this suggestion has not been found up to now.

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