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Generalized mean spherical approximations of the dense hard-sphere fluid

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After having discussed how integral equations of the Percus-Yevick type can be generated stemming from known approximations of the direct correlation function (DCF), we show that in the case of the hard-sphere (HS) fluid they can be recast into the generalized mean spherical approximation form by using truncated Dirichlet's series. The analysis is numerically carried through by using present knowledge of second- and third-order approximations of the DCF. The virial and compressibility pressures tend to close on the Carnahan-Starling values, but improvement in the radial distribution functions is noteworthy only in the contact region, while the Waisman thermodynamical consistent approximation appears to be the most accurate one. The mechanical stability of the system is analyzed: For all the considered approximations the HS system appears mechanically stable.

I. INTRODUCTION

The thermodynamical behavior as well as the structural properties of the hard-sphere (HS) fluid are well known[1] thanks to the Monte Carlo (MC) and to the molecular-dynamics (MD) calculations carried out mainly by Wood and Jacobson[2] and by Adler and Wainwright[3] in the late 1950s. A few years later, Wertheim[4(a)] and Thiele[4(b)] solved the Percus-Yevick (PY) equation and obtained a description of the HS fluid in a much easier and clearer way. The comparison of the two descriptions shows that the PY approximation is satisfactory only for densities which are not very large, i.e., $\rho \leq 0.7$.[5,6] Moreover, the PY description does not show any indication[7,8] of phase transition, while the MC and the MD calculations strongly suggest that the HS system should freeze and melt at the densities $\rho_f = 0.94$ and $\rho_m = 1.04$, respectively.[9] In our opinion, it is interesting to follow the behavior of these discrepancies as one considers integral equations of increasing thermodynamical self-consistency.

In this paper we show how it is possible to construct integral equations of the PY type whose solutions are perturbatively exact up to a given order M (Sec. II). To this aim it is necessary to know the sum of the parallel and bridge graphs up to the Mth order. This property holds true for any fluid with a hard core. In the case of HS, by using a general theorem on Dirilchlet's series,[10] we show that the integral equation can always be formulated in terms of a generalized mean spherical approximation (GMSA) with a convenient number of Yukawa contributions (Sec. II and Appendix A, where the HS restriction is removed). In practice however, the numerical analysis can really be carried through only when the number of Yukawa terms is not large. It turns out that in the case of the HS fluid the former condition is satisfactorily fulfilled. In Sec. III we report the results obtained by explicitly performing the relevant calculations. In Sec. IV we analyze the problem of the phase transition. In fact, the former approach could give an answer to the question of the existence of a particular density value ρ_0 ($<\sqrt{2}$) beyond which the fluid phase of the HS system can no longer exist. Our argument runs as follows. On the one hand, the canonical HS ensemble, in the thermodynamical limit, does not admit metastable states.[11] On the other hand, the virial series for the grand-canonical HS ensemble has a finite radius of convergence.[12] Therefore, if we confine ourselves to the fluid phase, we are led to conclude that the analytical continuation of the sum of the virial series, relevant to a thermodynamical potential or to an n-point correlation function, should show a mathematical singularity at a particular density value ρ_s. The use of GMSA's can be particularly useful in this respect. In fact, the algebraic equations associated to GMSA's do not always admit a real solution throughout the physical range of densities, as the physical root may meet with one of the unphysical ones at a particular density value ($=\rho_s$) beyond which both roots become complex.[13-15] We find that this possibility does not take place for any of the considered approximations. It should be stressed that this conclusion contrasts with the one reported in Ref. 15, which has turned out to be incorrect.[16]

But the system may also be mechanically unstable. From our analysis also this phenomenon does not seem to take place. In fact, for all the considered approximations the HS fluid turns out mechanically stable. In Ref. 15 it has been already shown that the mechanical instability, present when the lowest $O(\rho^M)$ approximations of the direct correlation function (DCF) are used, disappears if one takes into account also the graph contributions required for restoring exactly the core condition. One could think that this conclusion depends on the fact that the involved procedure accounts for a rather unsymmetrical subset of graphs.[17] However, the former criticism does not apply to the Waisman[18] self-consistent DCF, which approximates *all* the contributing graphs. Consequently, having found that the HS system is mechanically stable also in this case makes the mechanical stability of the HS fluid almost sure. These results are reported and discussed in the conclusive section (Sec. IV).

II. GMSA-LIKE INTEGRAL EQUATIONS

By following Ref. 15 we show how it is possible to construct integral equations of the GMSA type, whose solutions are thermodynamically self-consistent up to a given perturbative order in the density parameter.

We begin by recalling the well-known expression of the DCF $[\equiv C(r,\rho)]$ and of the total correlation function $[\equiv h(r,\rho)]$, in terms of the nodal $[\equiv N(r,\rho)]$, parallel $[\equiv P(r,\rho)]$, and bridge graphs $[\equiv B(r,\rho)]$

$$C(r,\rho)=f(r)[1+N(r,\rho)]+e(r)[B(r,\rho)+P(r,\rho)] \ , \qquad (2.1)$$

$$h(r,\rho)\equiv f(r)+e(r)[N(r,\rho)+P(r,\rho)+B(r,\rho)] \ , \qquad (2.2)$$

where

$$f(r)\equiv \exp[-\beta V(r)]^{-1} \ , \qquad (2.3a)$$

$$e(r)\equiv 1+f(r) \ . \qquad (2.3b)$$

(The dependence on the inverse temperature β will be omitted throughout for greater notational simplicity.)

With the definition

$$N(r,\rho)\equiv\rho\int_{\mathbf{R}_3} C(r',\rho)h(|\mathbf{r}-\mathbf{r}'|,\rho)dv'\equiv\rho C*h \qquad (2.4)$$

the Ornstein-Zernike (OZ) equation reads

$$h=C+N \ . \qquad (2.5)$$

If we denote by $C_n(r)$, $h_n(r)$, and so on the coefficients of the term ρ^n in the density expansions of $C(r,\rho)$, $h(r,\rho)$, etc., Eqs. (2.1), (2.2), and (2.4) take on the following form:

$$C_n(r)=\delta_{n,0}f+fN_n+e(P_n+B_n) \ , \qquad (2.6a)$$

$$h_n(r)=\delta_{n,0}f+e(N_n+P_n+B_n) \ , \qquad (2.6b)$$

$$N_n(r)=\sum_{m=0}^{n-1} C_m*h_{n-1-m}, \quad \forall n\geq 1 \ . \qquad (2.6c)$$

We notice now that Eq. (2.6) can be looked at as an iterative way of constructing the solution of the OZ equation. In fact, from the topological definitions of P, B, and N, we know that $N_0=P_0=B_0=P_1=B_1=0$ and thus, from Eqs. (2.6a) and (2.6b), we derive that $C_0=h_0=f$. Now we use Eq. (2.6c) and obtain N_1. From Eqs. (2.6a) and (2.6b) we immediately get C_1 and h_1. In this way we can use Eq. (2.6c) once more and obtain N_2. At this point, C_2 and h_2 can be exactly determined only if we know the *contributions due to the second-order parallel and bridge graphs in the region external to the core.*[19] The procedure can be iterated, but at each step the determination of h_n and C_n requires the introduction of the quantity $e(P_n+B_n)$. The structure of Eq. (2.6) is such that if we assume that $e(P_n+B_n)\equiv 0$, $\forall n>M$, we obtain a solution of the OZ equation which has the following properties:

(i) it is thermodynamically self-consistent up to the Mth order;

(ii) $h(r,\rho)$ fulfills exactly the core condition;

(iii) the parallel and bridge content of DCF is exactly the one which has been put explicitly into the iterative procedure;

(iv) in the case of the HS fluid the former condition amounts to stating that the aforesaid iterative procedure does not modify $C_{\text{ext}}(r,\rho)$, i.e., the expression of the DCF in the region external to the core.

In order to translate the preceding remarks into an integral equation, let us introduce the function

$$B_M(r,\rho)\equiv e(r)\sum_{n=2}^{M}\rho^n[B_n(r)+P_n(r)] \qquad (2.7)$$

which represents the sum of the parallel and bridge graphs up to terms of the Mth order. We assume that $e(r)[P(r,\rho)+B(r,\rho)]$ can be approximated by $B_M(r,\rho)$, which by hypothesis is known. Then, by using Eqs. (2.1) and (2.2), the OZ becomes the following integral equation for $N(r,\rho)$:

$$\begin{aligned}N(r,\rho)=\rho\int_{\mathbf{R}^3}dr'\{B_M(r',\rho)+f(r')[1+N(r',\rho)]\}\\ \times[f(|\mathbf{r}-\mathbf{r}'|)+B_M(|\mathbf{r}-\mathbf{r}'|,\rho)\\ +e(|\mathbf{r}-\mathbf{r}|)N(|\mathbf{r}-\mathbf{r}'|,\rho)] \ . \qquad (2.8)\end{aligned}$$

This equation is a generalization of the PY equation (GPY), because it treats parallel and bridge graphs in a fairly symmetrical way and it reduces to the latter for $M\leq 1$. Furthermore, the solution (2.8) is thermodynamically self-consistent up to terms $O(\rho^M)$. Since Eq. (2.8) requires knowledge of $B_M(r,\rho)$, it can be useful only when one is able to obtain an accurate approximation of this quantity. We emphasize that, when the fluid has a rigid core, B_M must be evaluated only in the external region.

In the case of HS, to which we shall confine ourselves from now on, we can convert the former equation into a GMSA (Refs. 18 and 1) and thus the problem of finding the solution to Eq. (2.8) is converted into the problem of finding the numerical solutions of a system of algebraic equations. We first notice that $B_M(r,\rho)$ represents $C_{\text{ext}}^{(M)}(r,\rho)$, the Mth-order approximant of the direct correlation function external to the core. Should

$$C_{\text{ext}}^{(M)}(r,\rho)=\sum_{m=2}^{M}\rho^m\sum_{n=1}^{N}K_{m,n}\exp[-z_n(r-1)]/r \qquad (2.9)$$

the aforesaid connection between GPY's and GMSA's would be evident. In fact, the C and h, obtained by solving the GMSA defined by Eq. (2.9), can be expanded in a power series in ρ and are related by the OZ equation. Then $N_n=h_n-C_n$ is given by (2.6c). Moreover, in the external region $C_{\text{ext}}(r,\rho)$ turns out to be equal to $C_{\text{ext}}^{(M)}$ while in the internal region one finds $h(r,\rho)=-1$. These properties are exactly the same as the ones of the solution of Eq. (2.8). Thus the equivalence of (2.8) with the GMSA is proved when Eq. (2.9) holds true.

In general Eq. (2.9) is not true, but, according to a theorem on Dirichlet's series due to Müntz (Ref. 10, p. 22), one can always approximate $B_M(r,\rho)$ by a sum of Yukawa terms. More definitely, the theorem states that any function $F(x)$, continuous in the closed interval $[0,\infty]$

can be approximated by a Dirichlet polynomial $[D_M(x)]$ with an error smaller than an arbitrary positive number ϵ, namely,

$$|F(x)-D_M(x)| \le \epsilon \quad \forall x \ge 0 \tag{2.10}$$

with

$$D_M(x) \equiv \sum_{n=0}^{M} K_n \exp(-z_n x) \ . \tag{2.11}$$

In Eq. (2.11), the z_n's form an increasing sequence with $z_0=0$ and such that

$$\lim_{M\to\infty} \sum_{n=1}^{M} z_n^{-1} = \infty \ .$$

If we put $x=r-1$, $F(x) \equiv rc(r,\rho)$ and we use the continuity of $rc(r,\rho)$ in the set $[1,\infty]$; from Eq. (2.11) it follows that $C_{\text{ext}}(r,\rho)$ can always be approximate by the sum of a convenient number of Yukawa functions with an error smaller than ϵ in $[1,\infty]$, viz.,

$$C_{\text{ext}}(r,\rho) \cong \sum_{n=1}^{M} K_n \exp[-z_n(r-1)]/r \ . \tag{2.12}$$

In this way, Eq. (2.9) holds approximately true and thus one concludes that Eq. (2.8) can be made equivalent to a GMSA with a prefixed degree of accuracy.[20] The loss of accuracy, corresponding to approximation (2.12), is largely compensated for by the fact that solving GMSA equations is essentially an algebraic problem and thus we can be more confident of the correctness of the solutions as we approach the region where phase transitions may occur.[21] Of course, the aforesaid conversion can be practically useful only when approximation (2.12) turns out satisfactory with a small M value.

III. APPLICATION TO HS

This really happens in the case of the HS fluid,[15] where we know quantities

$$e(P_2+B_2) \equiv C_{2,\text{ext}}(r)$$

and

$$e(P_3+B_3) \equiv C_{3,\text{ext}}(r) \ .$$

The first, evaluated by Nijober and van Hove,[22] is algebraically known, while the second, calculated by Ree *et al.*,[23] is known numerically. Both contributions are different from zero only inside the interval [1,2] where they exhibit a smooth behavior. Thus they can be well approximated even by a single Yukawa function. The coefficients $\{K\}$ and $\{z\}$ have been determined by requiring that

$$\int_1^\infty r^2 \left\{ C_{n,\text{ext}}(r) - \sum_{j=1}^{M} K_{n,j} \exp[-z_{n,m}(r-1)]/r \right\}^2 dr \ , \quad n=2,3 \tag{3.1}$$

be as small as possible. While for $C_{3,\text{ext}}$ M has been taken equal to 1, for $C_{2,\text{ext}}$ we have considered both the case $M=1$ and $M=2$. The best K_n and z_n values are reported in Table I of Ref. 15. With these approximations, we have analyzed the following GMSA's:

$$C_{\text{ext}}(r,\rho) \cong \rho^2 C_{2,\text{ext}} \ ,$$

denoted TF1 or TF2;

$$C_{\text{ext}}(r,\rho) \cong \rho^3 C_{3,\text{ext}} \ , \tag{3.2}$$

denoted FT1; and

$$C_{\text{ext}}(r,\rho) \cong \rho^2 C_{2,\text{ext}} + \rho^3 C_{3,\text{ext}} \ ,$$

denoted TT2. These will be globally referred to later as the GM cases. The "name" has been assigned on the following basis. The first letter is T or F depending on whether contribution $C_{2,\text{ext}}$ has been accounted for or not. The second letter refers to contribution $C_{3,\text{ext}}$, while the final digit gives the total number of Yukawians used for approximating C_{ext}. Approximations TF1 and TF2 allow us to control the stability of the results with respect to small changes in the outset approximation. We notice also that thermodynamically, approximation FT1 is less consistent than TF1 or TF2, but it does not lead to any overcounting of graphs. Thus its use is legitimate and useful for examining the importance of thermodynamical consistency. Besides the GM cases, we have also considered the two following approximations, referred to later as the CT ones:

$$C_{\text{ext}}(r,\rho) \cong K_1'(\rho)\rho^2 \exp[-z_1'(\rho)(r-1)]/r \ , \tag{3.3a}$$

named CT1; and

$$C_{\text{ext}}(r,\rho) \cong K_2'(\rho)\rho^2 \exp[-z_2'(\rho)(r-1)]/r + \rho^3 C_{3,\text{ext}}(r) \ , \tag{3.3b}$$

named CT2. In Eq. (3.3b) $\rho^3 C_{3,\text{ext}}(r)$ is approximated by the same Yukawa function used in case FT1. In this way, cases CT1 and CT2 correspond to approximating the total $C_{\text{ext}}(r,\rho)$ by a single and by two Yukawian terms, respectively. Since $C_{\text{ext}}(r,\rho)$ is not known, $K_i'(\rho)$ and $z_i'(\rho)$ cannot be determined by using the aforesaid minimization procedure. In fact they will be determined by requiring that the equation of state (EOS) evaluated along the virial route and the one evaluated along the compressibility route are equal to the Carnahan-Starling EOS, which can be considered as the exact one.[24,25] One should notice that by so doing we impose thermodynamical self-consistency in a way which could rightly be called external. In fact, imposing thermodynamical self-consistency amounts to fixing the values of some unknown parameters, which have suitably been introduced into the equations by requiring that a physical quantity turns out to have the same value independently of the thermodynamical routes chosen for its evaluation. This procedure can be carried through in two ways: the internal and the external one. In the first case all the considered evaluations involve the unknown parameters, whereas in the second at least one of the evaluations does not. Clearly, in the first case one cannot be sure that the resulting outcome is really relevant to the physical model one has started from.[26] By contrast, the second case can be usefully applied only when an accurate evaluation of the physical quantity is available. For the HS fluid the last condition is fulfilled and thus we can rightly claim that, after having imposed the thermodynamical self-consistency, Eq. (3.3) does really yield an approximation of the true $C_{\mathrm{ext}}(r,\rho)$. It should also be stressed that the CT1 case was invented, solved, and, to a good extent, numerically analyzed by Waisman.[18] Before illustrating our numerical results, let us outline how they have been obtained. Cases GM and CT correspond to assuming

$$C_{\mathrm{ext}}(r,\rho) \cong \sum_{i=1}^{M} K_i \exp[-z_i(r-1)]/r ,$$

where M can be 1 or 2 and the K's account for the correct ρ dependence.

According to Ref. 27, the internal direct correlation function is given by

$$C_{\mathrm{int}}(r,\rho) = -a(1+0.5\eta r^3) - br - \sum_{i=1}^{M} \{(v_i/z_i)[1-\exp(-z_i r)]/r + (v_i/z_i)^2[\cosh(z_i r)-1]/[2rK_i \exp(z_i)]\} \tag{3.4}$$

and a, b, and $\{v_1, v_2, \ldots, v_M\}$ are the numerical solution of the following system of equations:

$$a = 1 - \rho\hat{C}(0,\rho) , \tag{3.5a}$$

$$36\eta^2 y_0^2 = -6\eta b + \sum_{i=1}^{M} q_i , \tag{3.5b}$$

$$9\eta^2(y_1^2 - 2y_0 y_2) = 9\eta^2 a - \sum_{i=1}^{M} q_i z_i^2/4 , \tag{3.5c}$$

$$9\eta^2(2y_0 y_4 - 2y_1 y_3 + y_2^2) - (36\eta^2 y_0^2)^2 = \sum_{i=1}^{M} q_i z_i^4/4 . \tag{3.5d}$$

There y_i denotes the discontinuity of the ith derivative of $rC(r,\rho)$ at the contact point, i.e.,

$$y_i \equiv \left.\frac{d^i[rC_{\mathrm{ext}}(r,\rho)]}{dr^i}\right|_{r=1^+} - \left.\frac{d^i[rC_{\mathrm{int}}(r,\rho)]}{dr^i}\right|_{r=1^-} , \tag{3.6}$$

while $\eta \equiv \pi\rho/6$,

$$q_i = 3\eta z_i^2(v_i/z_i)[1 - \tfrac{1}{2} v_i/K_i z_i \exp(z_i)] , \quad i = 1, 2, \ldots, M \tag{3.7}$$

and $\hat{C}(0,\rho)$ is the value of $\hat{C}(k,\rho)$, the Fourier transform (FT) of $C(r,\rho)$, at $k=0$. The GM cases have been analyzed by solving the corresponding numerical equations (3.5). We started from a rather small density value, i.e., $\rho = 0.05$ and we used as a starting point the approximate expressions of $\{a, b, v_1, v_2, \ldots, v_m\}$ at small ρ reported in Ref. 27. Then we determined the trajectory of the root[28] in terms of the density by letting the latter slowly increase.

The system of numerical equations corresponding to cases CT is again system (3.5), but the unknown quantities are z_1, b, and $\{v_1, v_2, \ldots, v_M\}$. In fact, a is eliminated by using the compressibility relation $a = \beta\partial p^{\mathrm{CS}}/\partial\rho$ (p^{CS} is the pressure according to the Carnahan-Starling EOS), while $K_i'(\rho)$ is eliminated by solving the equation

$$1 - (2\pi/3)\rho g(1^+) = 1 - (2\pi/3)\rho y_0 = \beta p^{\mathrm{CS}}/\rho$$

corresponding to the virial route. We can now illustrate the results.

Figure 1 represents the roots of the most typical GM and CT cases. One should notice that we have not been able to find out the roots throughout the physically accessible range of densities for the CT cases. The structure of Eq. (3.5), after the elimination of a and K_i, becomes so involved that round-off errors prevent us from going beyond $\rho = 1.11$ and $\rho = 0.7$ in the CT1 and in the CT2 cases, respectively. Actually, in both CT cases, round-off errors are amplified by the rather sharp increase of $z_i'(\rho)$'s with the density, as one can see from Fig. 2, where the $\{K_i', z_i'\}$ values, relevant to each CT case, are shown. The marked W points correspond to the solution reported by Waisman.[18]

Table I reports the contact values relevant to the considered approximations, while the osmotic coefficients in excess with respect to the Carnahan-Starling ones are shown in Fig. 3. One sees a noteworthy improvement in the thermodynamical consistency as the accuracy of C_{ext} improves. One should also notice that the virial and the compressibility values tend to bracket the CS ones.[29]

The knowledge of $\{a, b, v_1, \ldots, v_M\}$ allows us to evaluate algebraically $C(k,\rho)$ and $h(k,\rho)$ for all the considered cases. The use of a fast FT algorithm yields the radial distribution functions (RDF's). Figure 4 illustrate the changes resulting in the RDF's as we improve the accuracy. One can see that the improvement due to the inclusion of the second- and third-order corrections to C_{ext} is noticeable only in the contact region (see also the results of Table I). At larger distances, the RDF's relevant to all the considered GM approximations are practically equal to the MSA's ones. Thus, if one wants to reproduce the dip and the peak found by MC calculations one has to account for more graphs. In principle this job is done by the CT approximation. In practice, however, the resulting $C_{\mathrm{ext}}(r,\rho)$, both in the one- and in the two-Yukawa function cases, does not turn out as satisfactory as the empirical approximation worked out in Ref. 30. In this respect we notice that our main reason for considering approximation CT2 was the hope that in Eq. (3.3b) the contribution depending on $K_2'(\rho)$ would turn out small at large densities, since approximation FT1 already seems quite satisfactory (see Table I). The behavior of the resulting $K_2'(\rho)$, shown in Fig. 3, confirms this. But the sharper increase of $z_2'(\rho)$ emphasizes that $C_{\mathrm{ext}}(r,\rho)$ must be rather large only near the contact region. This result indicates that if $C_{\mathrm{ext}}(r,\rho)$ has a range longer than the one predicted by the considered CT approximations, then it must show some oscillations. In fact, the $C_{\mathrm{ext}}(r,\rho)$ evaluated by Grundke and Henderson[31] has a damped oscillatory behavior. Consequently a more accurate CT approximation cannot involve Yukawian terms with real z's only.

IV. CONCLUSIONS

From the discussion of Sec. II and Appendix A, the GMSA can describe the behavior of all real fluids with a hard core. The specificity of the fluid is reflected only in the way the K's and z's, present in the Yukawian approximation of $C_{\mathrm{ext}}(r,\rho,\beta)$, depend on ρ and β. In this way the

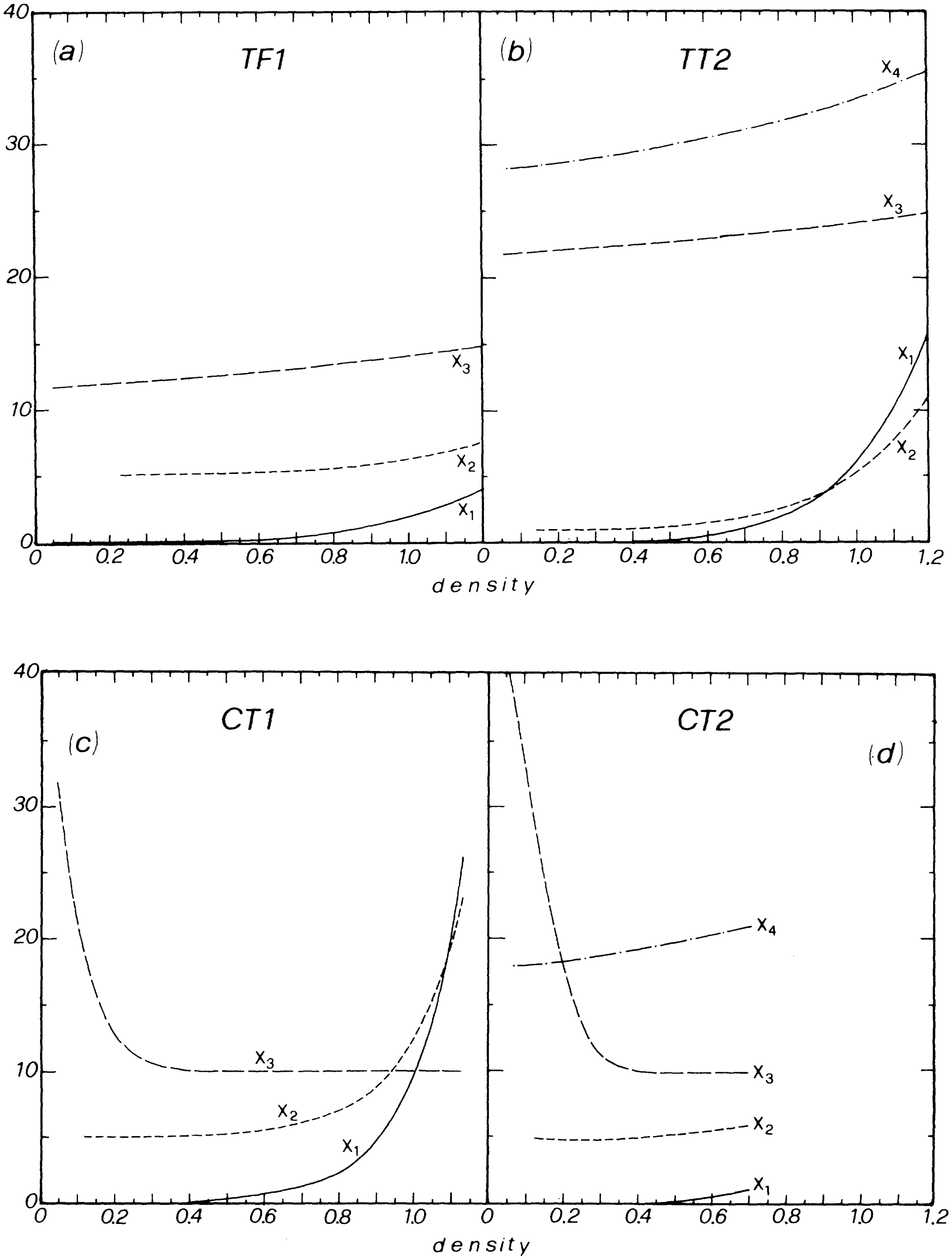

FIG. 1. The trajectories of the roots $\{x_1,x_2,\dots,x_{M+2}\}$ relevant to approximations TF1, TT2, CT1, and CT2 are shown. Quantities x_i are related to $\{a,b,v_1,\dots,v_M\}$ in the following way: $x_1=a-a_{\mathrm{MSA}}$, $x_2=-(b-b_{\mathrm{MSA}})/6$, $x_j=v_j\exp(-z_j)/(24\eta K_j z_j)$, $j\in\{1,\dots,M\}$. Moreover, in (a), (c), and (d), we have plotted x_1, $2x_2+5$, $2\times10^4x_3+10$, and 10^6x_4+15, while in (b) we have plotted x_1, $2x_2+1$, $2^4\times10x_3+20$, and 10^6x_4+25.

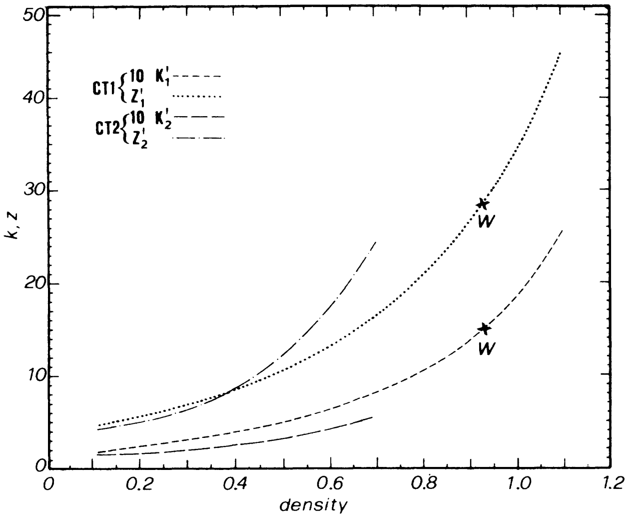

FIG. 2. Plots of $10K_i'(\rho)$ and $z_i'(\rho)$ for the CT1 and CT2 cases. The marked points coincide with the values found by Waisman at $\rho=0.936$ $(\eta=0.49)$ (Ref. 18). (Notice that $K_W=K\rho^2$). Round-off errors made the search of solutions impossible beyond the reported range.

problem of solving the integral equation yielding the RDF is converted into two numerical problems: that of approximating $C_{\text{ext}}(r,\rho,\beta)$ by finding the best $\{K\}$ and $\{z\}$ values, and that of finding the numerical solution of the GMSA system of equations. The first step is the only one which introduces an approximation whose influence on the accuracy of final results cannot be easily estimated at the outset. The results of Sec. III indicate that this effect should be rather small and thus the use of GMSA's appears quite advantageous.

After having underlined this aspect we turn to the problem of the existence of a phase transition in the HS model. As we have stressed in the introductory section, this phenomenon should be signaled by the appearance of a mathematical singularity in one of the n-point correlation functions, at a particular density value.

At the level of the two-point correlation function, the singularity can occur both in the series giving the direct correlation function and in the series giving the RDF.

The first eventuality can occur either in the series representing $C_{\text{ext}}(r,\rho)$ or in the series representing $C_{\text{int}}(r,\rho)$. In the former case, GMSA's are not useful because the nonanalyticity of $C_{\text{ext}}(r,\rho)$ with respect to ρ is washed out by the unavoidable inaccuracies due to the numerical determination of K_i's and z_i's. Oppositely, in the second case, the nonanalyticity can be safely made evident by the fact that, beyond a particular density value $(=\rho_s)$, no physically acceptable real solution exists. By contrast to Ref. 15, no ρ_s value smaller than $\sqrt{2}$ has been found for any of the considered GM approximations and thus one concludes that $C_{\text{int}}(r,\rho)$ does not become singular in the range of physical densities.

In order to see whether the second eventuality takes place, we have to look at the mechanical stability of the HS fluid.

A further advantage of GMSA is that this question can be analyzed in a safe and rather quick way since $\hat{C}(k,\rho)$, the FT of $C(r,\rho)$, can be evaluated explicitly from Eqs. (2.12) and (3.4). Then one has to look for the trajectory of the complex z root (lying in the first quadrant and closest to the origin) of the equation

$$1-\rho\hat{C}(z,\rho)=0 \tag{4.1}$$

as the density increases. If the trajectory meets the real axis at a density ρ_{MI} smaller than the close-packed density, the system is said to be mechanically unstable. The trajectories relevant to the most typical cases, i.e., MSA, TT2, and CT1, are reported in Fig. 5. The curves on the left show their behavior as the density increases up to 1.1, while those on the right complete their behaviors at higher densities. On each trajectory, each point differs from its left neighbor by a density increase of 0.1. We stress that in order to distinguish the trajectories on the left, we have vertically shifted the MSA and the TT2 curves by -0.1 and -0.05, respectively, while, on the right, only the MSA trajectory has been lowered by 0.01. However, one should note that the scales for the two sets of curves are different. In fact, the left and the bottom scales refer to the curves on the left, while the other two scales refer to the trajectory tails.

TABLE I. The contact values of the RDF, relevant to the approximations considered in this paper (columns 3—6) are compared with the corresponding values calculated by the Monte Carlo method (Ref. 6) (column 7) for different densities (column 1).

ρ	MSA	TF1	TF2	FT1	TT2	MC
0.100	1.1427	1.1442	1.1442	1.1431	1.1445	
0.200	1.3129	1.3182	1.3182	1.3156	1.3209	1.339
0.300	1.5180	1.5288	1.5285	1.5261	1.5370	1.548
0.400	1.7676	1.7857	1.7846	1.7855	1.8037	1.818
0.500	2.0753	2.1034	2.1003	2.1081	2.1364	2.116
0.600	2.4599	2.5044	2.4964	2.5149	2.5599	2.561
0.700	2.9486	3.0239	3.0055	3.0391	3.1155	3.157
0.800	3.5814	3.7198	3.6800	3.7367	3.8771	3.971
0.900	4.4194	4.6902	4.6085	4.7090	4.9836	5.147
1.000	5.5596	6.1105	5.9488	6.1529	6.7099	

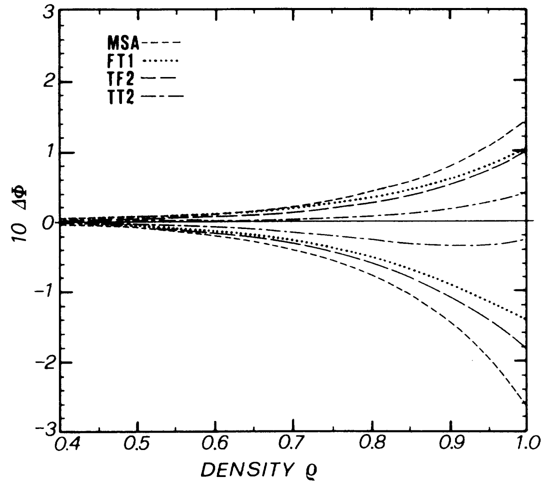

FIG. 3. The osmotic coefficients in excess with respect to the CS values, evaluated along the compressibility and the virial routes, are plotted. The former lie in the upper half-plane, while the latter lie mainly in the lower one. The improvement in the thermodynamical consistency is noticeable, as the accuracy of C_{ext} improves.

If one compares the TT2 trajectory, which actually represents all the GM cases, with those of Ref. 17, one sees that the mechanical instability, present in cases $[M,2]$ and $[N,3]$ with $M,N \in \mathbb{Z}^+$, disappears if one takes into account *all* the graphs, which are generated by $e(P_2+B_2)$ and by $e(P_3+B_3)$ in order to restore the exact core condition. In other words, the situation becomes exactly similar to the MSA case. There in fact, approximation [1,1] is mechanically unstable, while the PY solution, generated by this approximation, becomes mechanically stable. In Ref. 17 it has been suggested that, in order to have a reliable answer to the question of mechanical stability, the thermodynamical consistency of the approximation could be more important than the number of graphs accounted for. From this point of view the CT1 approximation is quite legitimate, since the CT1 expression represents a global approximation of the total $C_{\text{ext}}(r,\rho)$. Thus it is particularly interesting that the HS system turns out mechanically stable also in the CT1 case. Strictly speaking, this is true only in the density range where round-off errors have not prevented us from obtaining the numerical solutions. However, the behavior of the CT1 trajectory is such that its intersection with the real axis at a density smaller than the close-packing value

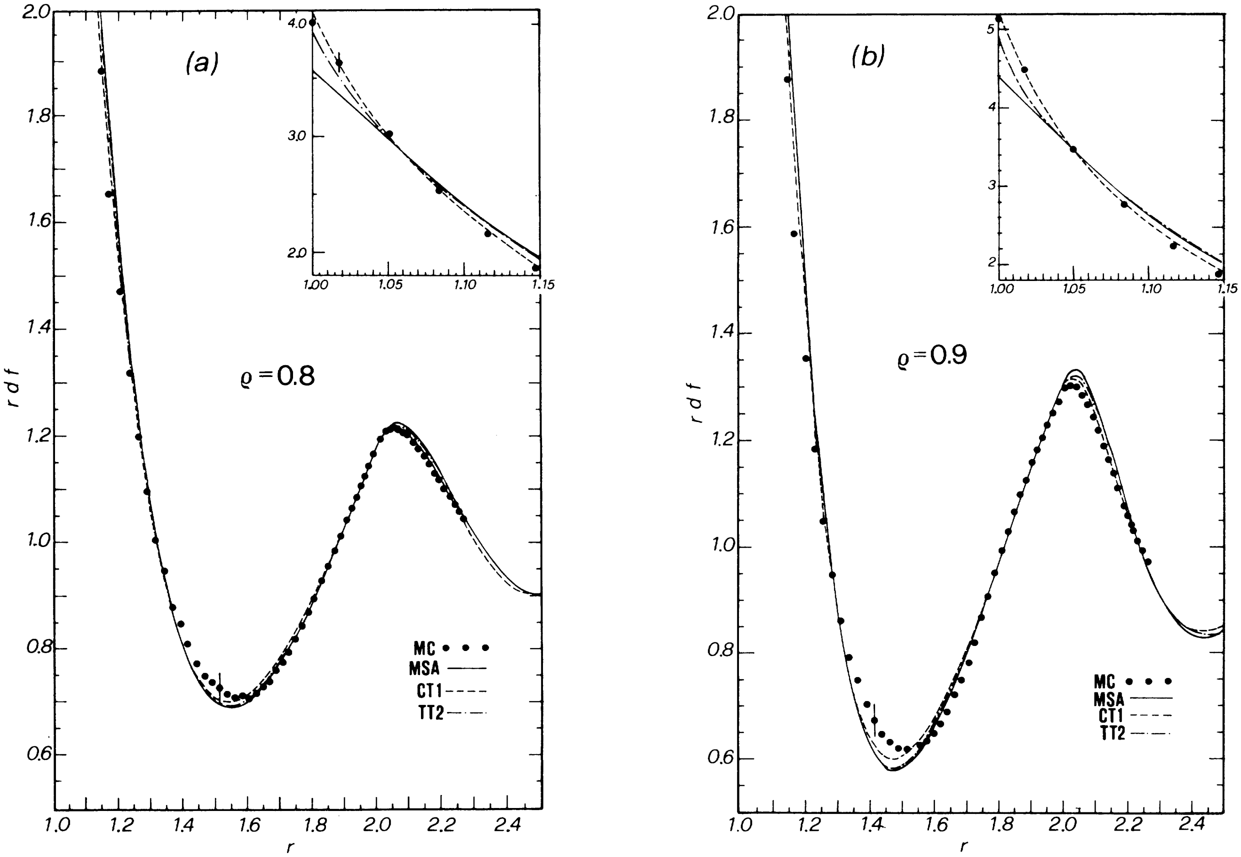

FIG. 4. Behavior of the RDF at densities $\rho=0.8$ and 0.9 according to different approximations. The dots correspond to the MC values of Ref. 6, the solid line gives the MSA values which are very close to the GM's, while the dash-dotted line represents the CT1 RDF function. The vertical bar gives the numerical uncertainty of MC results.

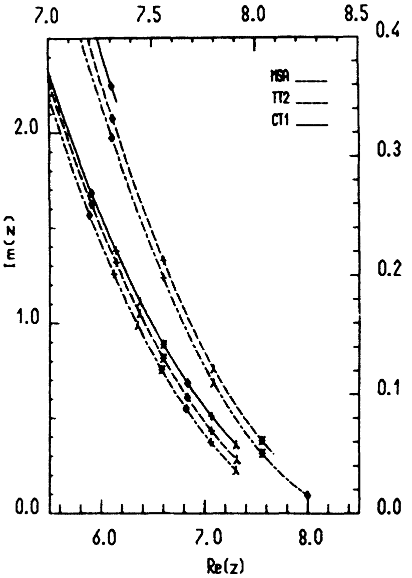

FIG. 5. The curves on the left show the trajectories of the root of Eq. (4.1) when $\hat{C}(z,r)$ is described by one of the approximations reported in the upper right of the figure. The dots correspond to density values increasing by 0.1 from the starting value $\rho=0.5$. The scales on the left and on the bottom are the appropriate ones. The curves on the right represent the continuations of the former trajectories. On each of these curves, the upper point corresponds to $\rho=1.1$ and it increases by 0.1. The relevant scales are the right and the upper ones. Finally, in order to distinguish the different trajectories, on the left, the MSA and the TT2 curves have been lowered by 0.1 and 0.05, respectively. On the right, only the MSA curve has been lowered by 0.01.

appears extremely unlikely. Therefore we can confidently conclude that the HS system is mechanically stable. Of course, this fact does not necessarily imply that the HS system can exist only in the fluid phase. One has still to analyze the equation for the one-particle correlation function[32]

$$\rho(\mathbf{r})/z=\exp\left[\sum_{N=1}^{\infty}\int C_{N+1}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_{N+1})\times\left[\prod_{i=2}^{N+1}\rho(\mathbf{r}_i)dv_i\right]\Big/N!\right], \tag{4.2}$$

where $C_N(\mathbf{r},\ldots,\mathbf{r}_N)$ denotes the N-point direct correlation function. If this does not admit the uniform solution $\rho=\text{const}$ beyond a particular density value, then this value will represent the freezing density, as is indicated by recent theoretical analyses.[33] From our analysis it appears that this is the only practicable way for determining the region of existence of the fluid phase, in the case of the HS system.

APPENDIX

The property $f(r)\equiv 0$, $\forall r>1$, is the distinctive feature of the HS model. Its main consequence is that the direct correlation function outside the core is equal to the sum of the parallel and bridge graphs. This is evident from Eq. (2.6a).

By contrast, for fluids with a rigid core, $C_{\text{ext}}(r,\rho,\beta)$ also depends on the sum of nodal graphs. One has in fact

$$C_{\text{ext}}(r,\rho,\beta)=f_{\text{ext}}(r,\beta)[1+N_{\text{ext}}(r,\rho,\beta)]+e(r,\beta)B_{\text{ext}}(r,\rho,\beta)\ . \tag{A1}$$

One can now construct GMSA's which are "exact" up to a given order, say M, by using the Mth approximant of Eq. (A1), viz.,

$$C_{\text{ext}}^{(M)}(r,\rho,\beta)=f\left[1+\sum_{n=1}^{M}\rho^n N_n\right]+e\sum_{n=2}^{M}\rho^n(P_n+B_n)\ ,\quad r>1\ . \tag{A2}$$

One expands the latter in a Dirichlet series

$$C_{\text{ext}}^{(M)}(r,\rho,\beta)=\sum_{n=1}^{\infty}K_n^{(M)}(\rho,\beta)\exp[-z_n(r-1)]/r\ ,\quad r>1 \tag{A3}$$

and one solves the GMSA, corresponding to $C^{(N,M)}(r)$, the Nth approximant of series (A3). The limit, as $N\rightarrow\infty$, of these solutions represents the GMSA solution exact up to the Mth order.

We remark that in order to construct the generalized PY (GPY) equation, exact up to the Mth order, we need to know $B^{(M)}$, while the corresponding GMSA also requires the knowledge of $N^{(M)}$.

This can hardly be considered a limitation, since the knowledge of $B^{(M)}$ in practice rests on that of all P_n's and N_n's with $n<M$. It should also be noted that the solutions of the GMSA and of the equivalent GPY, i.e., the GPY which is exact to the same order M, coincide only up to terms $O(\rho^M)$ inclusive, although both solutions fulfill exactly the core condition. In order to recover the GPY solution exactly, one should expand in a Dirichlet series the $C_{\text{ext}}(r,\rho,\beta)$ resulting from the solution of the GPY. This expression in fact differs from the right-hand side of (A2) for the quantity

$$\sum_{n=M+1}^{\infty}\rho^n f_{\text{ext}}N_n^{(\text{GPY})},\quad r>1$$

i.e., the sum of the contributions generated by Eq. (2.8) or (2.6a). This remark has some interest only in principle. Although the use of the Mth-order GMSA can be convenient only if one uses the first formulation, presently we do not know any reason for saying which of the two approximations is the most reliable.

Finally, we remark that GMSA's turn out accurate and practically convenient since one optimizes also the choice of z_n's. Actually, the considered CT cases represent an extreme case, since at each density we choose the most suitable z values. On the one hand, one could say that they turn out so suitable that a single Yukawa function yields already a good approximation. On the other hand, it is difficult to say whether this property also holds true for other simple fluids, because one cannot forget that the HS case is particularly lucky since we are essentially aware of the EOS of the system.

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