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Structure of hard-sphere metastable fluids

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A rational-function approximation method to analytically derive the radial distribution function $g(r)$ and the structure factor $S(q)$ of a hard-sphere fluid is revisited. The method provides a fluid structure thermodynamically consistent with a given equation of state. The Carnahan-Starling and a recently derived Padé (4,3) equations of state are considered. While the Carnahan-Starling equation leads to functions $g(r)$ and $S(q)$ even for densities larger than the crystalline close-packing density, their physical value is questionable already in the metastable fluid region. In the case of the much more reliable Padé equation of state, the method shows the existence of a threshold density, beyond which no meaningful fluid structure can be derived. This threshold value, whose signature is a diverging slope of $g(r)$ at the contact distance, coincides with the one associated in the literature with the glass transition. [S1063-651X(96)01805-3]

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I. INTRODUCTION

The radial distribution function (RDF) $g(r)$ and its close relative the (static) structure factor $S(q)=1+\rho\int d\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}[g(r)-1]$, where ρ is the density, are the basic quantities used to discuss the structure of a fluid [1]. The importance of $g(r)$ arises from the fact that, given the form of the potential of the intermolecular force, if the RDF is known as a function of ρ and the temperature T, the standard methods of statistical mechanics allow for the determination of all the equilibrium properties of the fluid. The usual approach to obtain $g(r)$ is through one of the integral equation theories. However, apart from requiring in general hard numerical labor, a disappointing aspect is that the substitution of the (necessarily) approximate values of $g(r)$ obtained from them in the (exact) statistical-mechanical formulas may lead to the so-called thermodynamic inconsistency problem. This problem appears when deriving the equation of state for the fluid using either the virial theorem or the fluctuation theorem, because both routes lead to different results. In particular, the thermodynamic relation

$$\frac{1}{\chi}=\frac{\partial}{\partial\rho}(\rho Z) \tag{1.1}$$

between the isothermal susceptibility $\chi\equiv kT(\partial\rho/\partial p)_T=S(0)$ (where k is the Boltzmann constant and p the pressure) and the compressibility factor $Z\equiv p/\rho kT$ is not satisfied. Therefore an alternative approach to the derivation of $g(r)$ avoiding this problem is certainly desirable.

Although it involves the simplest mathematical function to represent molecular interactions, a model fluid of hard spheres exhibits the most important structural features found in real fluids. This system, which has been extensively studied both within the integral equation theories and through simulation, presents a fluid-solid transition at $\eta=\eta_F\simeq0.497$, [2] where $\eta=(\pi/6)\rho\sigma^3$ is the packing fraction, σ being the hard-sphere diameter. The fluid becomes metastable beyond η_F and, at about $\eta=\eta_g\simeq0.56$, it starts to form a glass [3]. The simulation results for the glassy system are compatible with an empirical equation of state different from that of the fluid, with a diverging pressure at the random close-packing value $\eta=\eta_{\mathrm{RCP}}\simeq0.64$ [3].

The compressibility factor for a hard-sphere fluid has the very simple form

$$Z=1+4\eta g(\sigma^+), \tag{1.2}$$

involving only the contact value of the RDF. From the available exact solution of the Percus-Yevick (PY) integral equation for hard spheres [4], this contact value may be determined yielding

$$Z_{\mathrm{PY}}=\frac{1+2\eta+3\eta^2}{(1-\eta)^2}. \tag{1.3}$$

The RDF of the PY theory, $g_{\mathrm{PY}}(r)$, is in good agreement with simulation results in the stable fluid region [1]. Using this RDF, one may readily derive the result for the isothermal compressibility

$$\chi_{\mathrm{PY}}=\frac{(1-\eta)^4}{(1+2\eta)^2}, \tag{1.4}$$

which, as can be easily verified, is not thermodynamically consistent with Eq. (1.3). Nevertheless, both the equation of state derived from the isothermal compressibility as well as the one given by Eq. (1.3) yield results that compare reasonably well to the simulation data. In fact, by interpolating these two equations of state one can obtain the (phenomenological) Carnahan-Starling (CS) equation of state [5]

$$Z_{\mathrm{CS}}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{1.5}$$

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which improves the agreement with the values of numerical simulations. As far as the RDF is concerned, the improvement of the CS equation of state over the PY theory, especially near $r=\sigma$, was concluded from the results of a recent attempt [6] to derive the structural properties of a hard-sphere fluid without invoking any of the integral equation theories. The key idea of the method is to use a rational-function approximation for an auxiliary function in Laplace space and to make this function compatible with some basic physical requirements. The simplest approximation yields $g_{\rm PY}(r)$, while the next simplest one involves two free parameters that may be fixed by imposing prescribed Z and χ. This second approximation coincides precisely with the generalized mean spherical approximation [7] and of course thermodynamic consistency is easily achieved here.

It must be pointed out that an obvious unphysical feature common to both the PY and CS equations of state is that the pressure does not diverge at any packing fraction smaller than $\eta=1$. Quite recently, the computation of the eighth virial coefficient of a hard-sphere fluid [8] has led to the construction of an equation of state in the form of a Padé approximant (4,3) [cf. Eq. (2.11) below] that is presumed to be very accurate even in the *metastable* fluid region [9]. In that region, due to the fact that the Padé approximant diverges at a density near the crystalline close-packing value $\eta=\eta_0=\pi\sqrt{2}/6\simeq 0.7405$ (which is physically more reasonable than a divergence at $\eta=1$), the isothermal compressibility predicted by the CS equation is about 10% larger than that obtained from the Padé approximant. Therefore it seems natural to try to examine the effect of this recent equation of state on the structure of the metastable fluid using the method outlined above [6]. This is the main aim of the present paper.

The paper is organized as follows. In Sec. II we start by briefly describing the method to derive analytical expressions for the RDF consistent with a given equation of state. Emphasis is put on the fact that physically meaningful results cease to be obtained whenever χ becomes smaller than $\chi_{\rm PY}$. We find that the χ derived from the Padé (4,3) equation of state is only larger than $\chi_{\rm PY}$ for $\eta \lesssim 0.5604$. This value practically coincides with η_g, thus suggesting that our method is capable of predicting the presence of the glass transition. The structure of the fluid in the metastable region as obtained with this equation of state is hardly distinguishable from the one obtained from the CS equation of state, although some peculiar and subtle behavior is observed as one approaches η_g. The paper is closed in Sec. III, where we further elaborate on our findings and provide some concluding remarks.

II. RATIONAL-FUNCTION APPROXIMATION METHOD

The method we are going to use was introduced in Ref. [6] and we urge the interested reader to look for a detailed description there. Here we will restrict ourselves to quote the results required for our later development and for simplicity set $\sigma=1$ without loss of generality. First we introduce the Laplace transform of $rg(r)$:

$$G(t)=\int_0^\infty dr e^{-rt} r g(r) = \frac{t}{12\eta}[1-e^t\Phi(t)]^{-1}, \tag{2.1}$$

where the second equality serves to define the auxiliary function $\Phi(t)$. The structure factor is related to $G(t)$ by

$$S(q)=1-24\eta\, \mathrm{Re}\left.\frac{t^2G(t)-1}{t^3}\right|_{t=iq}. \tag{2.2}$$

From Eq. (2.1) it follows that

$$g(r)=\frac{1}{12\eta r}\sum_{n=1}^{\infty}\varphi_n(r-n)\Theta(r-n), \tag{2.3}$$

where Θ is the Heaviside step function and $\varphi_n(r)$ is the inverse Laplace transform of $-t[\Phi(t)]^{-n}$. As a consequence of Eq. (2.3), it is guaranteed that $g(r)$ vanishes if $r<1$ for all packing fractions and its contact value is given in terms of η by

$$g(1^+)=-\frac{1}{12\eta}\lim_{t\to\infty}\frac{t^2}{\Phi(t)}. \tag{2.4}$$

The physical requirements that ensure that Z and χ are finite [6] suggest that a simple form for the auxiliary function is the ratio of two polynomials $\Phi(t)=P_n(t)/P_m(t)$ with $n=m+2$ and $n+m\geqslant 4$. We will call this the rational-function approximation (RFA). If $n=3$ and $m=1$, the method leads to the solution of the PY equation. The next simplest approximation is $n=4$ and $m=2$, namely,

$$\Phi(t)=\frac{1+S_1t+S_2t^2+S_3t^3+S_4t^4}{1+L_1t+L_2t^2}, \tag{2.5}$$

where, due to the requirements that $\Phi(t)$ has to satisfy [6], L_1, S_1, S_2, and S_3 can be expressed as linear functions of L_2 and S_4, which remain so far as arbitrary. Now, in view of Eq. (2.4), the relation

$$L_2=-3(Z-1)S_4 \tag{2.6}$$

is satisfied for a given Z. Furthermore, prescribing a given χ leads to the equation

$$6\eta\left(\frac{1-\eta}{1+2\eta}\right)^2[L_2+3(Z_{\rm PY}-1)S_4]\left[L_2-2S_4+\frac{1-\eta}{6\eta}\right] -\frac{\chi-\chi_{\rm PY}}{24\eta}=0. \tag{2.7}$$

Substitution of Eq. (2.6) into Eq. (2.7) yields a quadratic equation for S_4. Since $g(r)$ is a positive definite quantity, $G(t)$ cannot be zero for real and positive t. Therefore, L_2 must be positive. This in turn implies [cf. Eq. (2.6)] that S_4 must then be negative and so out of the two roots of the quadratic equation one can only take the one given by

$$S_4=\frac{1-\eta}{36\eta(Z-\frac{1}{3})}\left\{1-\left[1+\frac{Z-\frac{1}{3}}{Z-Z_{\mathrm{PY}}}\left(\frac{\chi}{\chi_{\mathrm{PY}}}-1\right)\right]^{1/2}\right\}. \tag{2.8}$$

Notice that even in this case, depending on the choice of Z and χ, S_4 may be (a) indeed negative if $\chi>\chi_{\mathrm{PY}}$, (b) positive if $\chi_{\mathrm{PY}}(Z_{\mathrm{PY}}-\frac{1}{3})/(Z-\frac{1}{3})<\chi<\chi_{\mathrm{PY}}$, or (c) complex if $\chi<\chi_{\mathrm{PY}}(Z_{\mathrm{PY}}-\frac{1}{3})/(Z-\frac{1}{3})$. This takes into account the fact that $Z>Z_{\mathrm{PY}}$, which is the obvious choice. Case (b) leads to a $g(r)$, which is a real function but exhibits nonphysical features, while case (c) yields a complex RDF. The appearance of Z_{PY} and χ_{PY} in Eq. (2.8) and in the above inequalities is not fortuitous but due to the fact that the proposal (2.5) may be understood as the simplest extension of the PY theory (which corresponds to $L_2=S_4=0$).

Once S_4 has been determined, the procedure is completed upon substitution in the corresponding equations. Two additional results, not explicitly stated in Ref. [6] but that will be used below, are now given. The first one concerns the value of the derivative of the RDF at contact, a quantity that has been a subject of recent interest [10–12] and whose expression as arising in the RFA method is

$$g'(1^+)=\frac{1}{12\eta}\,\frac{L_2S_3+(L_2-L_1)S_4}{S_4^2}. \tag{2.9}$$

The other result has to do with the relation between $g(1^+)$ and $g'(1^+)$ with the short wavelength behavior of $S(q)$, namely,

$$S(q)=1+24\eta\left[g(1^+)\frac{\cos q}{q^2}-[g'(1^+)+g(1^+)]\frac{\sin q}{q^3}+\cdots\right]. \tag{2.10}$$

In order to get specific results, the method just described requires as input Z and χ. Since we want $g(r)$ to be thermodynamically consistent, it is only necessary to choose Z as χ would follow from Eq. (1.1). This was already done for the CS equation of state, Eq. (1.5), in Ref. [6]. In this paper we will consider a more refined equation of state constructed from the knowledge of the first eight virial coefficients [8, 9], namely, the Padé (4,3)

$$Z_{4,3}=\frac{1+1.024\,385\eta+1.104\,537\eta^2-0.461\,147\,2\eta^3-0.743\,038\,2\eta^4}{1-2.975\,615\eta+3.007\,000\eta^2-1.097\,758\eta^3}. \tag{2.11}$$

A comparison between the CS and the Padé equations of state shows that the differences between both equations become significant in the metastable fluid region ($\eta>\eta_F\simeq0.497$). In fact, while $Z_{4,3}$ diverges for $\eta\approx\eta_0\simeq0.7405$, Z_{CS} does it for $\eta=1$. The most important feature for our purposes is the fact that χ_{CS} is always larger than χ_{PY}, but $\chi_{4,3}$ becomes smaller than χ_{PY} for $\eta\gtrsim0.5604$. It must be pointed out that the occurrence of a threshold value for which $\chi=\chi_{PY}$ is not peculiar to the Padé equation of state, but would also happen for any equation of state yielding a diverging pressure for $\eta<1$. However, what is indeed a property of the $Z_{3,4}$, not necessarily shared by those other equations of state, is the fact that the threshold value coincides almost perfectly with the value associated [3] with the *glass transition*, namely, $\eta_g\simeq0.56$. In terms of the RFA described above, this means that such a threshold value may indicate the appearance of a different structure in the system which would then cease to be a fluid beyond $\eta\simeq0.5604$. Therefore, in the following we will identify the threshold with η_g. We will return to this point later on.

The effect of Z on the structure of the stable fluid as prescribed by the RFA outlined above may be assessed from Figs. 1 and 2. There we have plotted the difference $g(r)-g_{\mathrm{PY}}(r)$, where the different $g(r)$ have either been taken from simulation [13] or derived with the RFA method using $Z=Z_{\mathrm{CS}}$ and $Z=Z_{4,3}$. As a simple extension of the PY theory, it is satisfactory that the model proposed in Eq. (2.5) for $\Phi(t)$ succeeds in capturing the major trends observed in the simulation, providing improvements where $g_{\mathrm{PY}}(r)$ is less accurate. This is particularly noticeable close to the contact value. The improvement over the PY theory in that region may be further judged from a comparison with estimated values of $g'(1^+)$ recently obtained from Monte Carlo simulation by Smith *et al.* [12]. These authors give values of the finite-difference derivative $g'_\epsilon(1^+)\equiv g(1^+)\ln[g(1+\epsilon)/y(1-\epsilon)]/2\epsilon$, where $y(r)$ is the cavity distribution function, and they set $\epsilon=0.05$. For the sake of carrying out a consistent comparison, in Table I we give the values of the (lateral) finite-difference derivative $g'_{\epsilon+}(1^+)\equiv g(1^+)\ln[g(1+\epsilon)/g(1^+)]/\epsilon$, also with $\epsilon=0.05$, although we could provide the

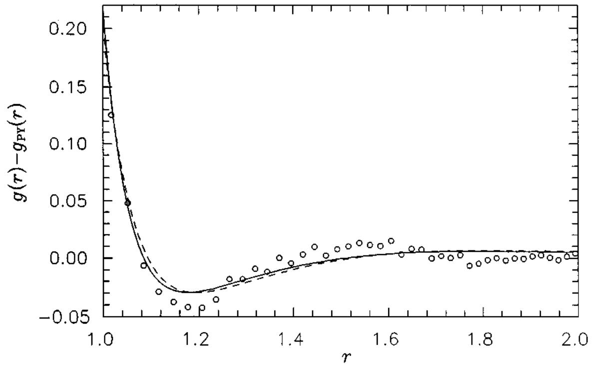

FIG. 1. Plot of the difference $g(r)-g_{\mathrm{PY}}(r)$ versus distance for $\eta=0.3403$. The solid line refers to the Padé (4,3) equation of state, the dashed line refers to the Carnahan-Starling equation of state, and the circles correspond to the simulation results [13].

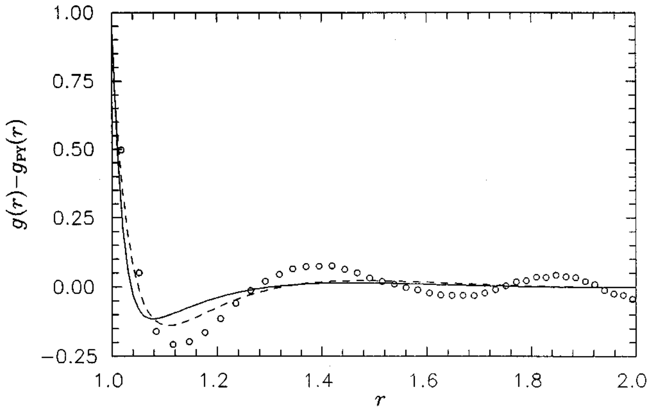

FIG. 2. Same as in Fig. 1, but for $\eta=0.4843$.

actual value of this derivative; cf. Eq. (2.9). Once again, the RFA method provides an accurate description of the structure close to the contact distance, as seen through the very good values for the slope of the RDF. This is particularly striking when using the CS equation of state. It should be stressed though that the value of the finite-difference derivative is highly sensitive to the choice of the discretization interval ϵ, especially for the higher densities. Therefore, $g'_{\epsilon+}(1^+)$ may differ appreciably from $g'(1^+)$. For instance, in the case of the CS equation of state and for $\eta=0.4712$, Eq. (2.9) yields $g'(1^+)=-49.49$.

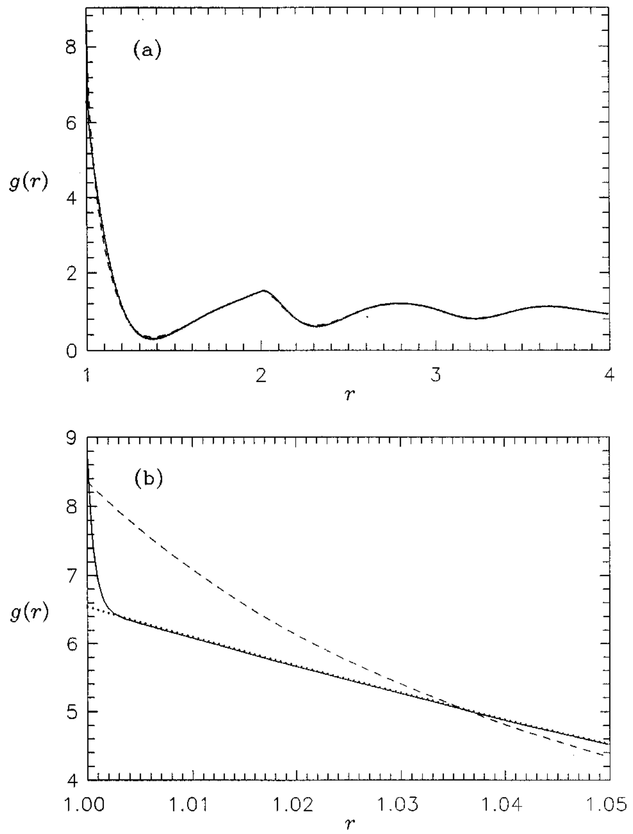

FIG. 3. Radial distribution functions $g(r)$ for $\eta=0.558$ (a) in the range $1\leqslant r\leqslant 4$ and (b) detail of the region close to the contact point. The solid lines refer to the Padé (4,3) equation of state, the dashed lines refer to the Carnahan-Starling equation of state, and the dotted lines correspond to the Percus-Yevick results.

TABLE I. Values of $g'_{\epsilon}(1^+)$ as obtained from simulation, from the Percus-Yevick (PY) theory, and from the RFA method using the Carnahan-Starling (CS) and the Padé (4,3) equations of state.

η	Simulation[a]	PY	CS	Padé (4,3)
0.1571	-1.55±0.02	-1.35	-1.53	-1.59
0.2094	-2.80±0.03	-2.30	-2.77	-2.89
0.2618	-4.89±0.07	-3.70	-4.80	-5.01
0.3142	-8.17±0.10	-5.80	-8.17	-8.55
0.3665	-13.86±0.13	-9.00	-13.88	-14.63
0.4189	-23.64±0.27	-13.97	-23.77	-25.52
0.4712	-41.26±1.34	-21.88	-41.37	-45.82

[a] Reference [12].

Now we turn to the metastable region. We have already pointed out that the Padé (4,3) equation of state is expected to be superior to the CS equation in this region because the latter predicts a finite pressure up to $\eta=1$. Therefore, one also expects that the RDF obtained from the RFA method is more reliable when using $Z_{4,3}$ than Z_{CS} and that the differences between both equations of state will be greater near the contact point. Note that as η approaches η_g from below, $\chi_{4,3}/\chi_{\mathrm{PY}}$ goes to 1. This means that S_4, as given by Eq. (2.8), goes to 0 from below. As a consequence, $g'(1^+)\sim 1/S_4\rightarrow-\infty$, as follows from Eq. (2.9). In terms of the RDF, this is translated into an abrupt change near the contact point when η is close to η_g. We illustrate this behavior in Fig. 3 for $\eta=0.5580$. In the scale of Fig. 3(a), the three different RDF's are hardly distinguishable. However, the enlargement around the contact point $r=1^+$ reveals a clear distinction between them. The features displayed in Fig. 3(b) may be understood by noticing that, while the contact values $g(1^+)$ for the CS and the Padé (4,3) equations of state are not all that different, S_4 for the latter is almost zero, so that the corresponding RDF should become very similar to $g_{\mathrm{PY}}(r)$ (which corresponds to $S_4=0$), except in the proximity of $r=1^+$. A convenient measure of this behavior is through the ''width'' δ of $g(r)$ in the neighborhood of the contact point defined by

$$\delta=\frac{g(1^+)-g_{\mathrm{PY}}(1^+)}{|g'(1^+)|} \tag{2.12}$$

and shown graphically in Fig. 4. Both equations of state yield decreasing values of δ with increasing η in the metastable region. However, in the case of $g_{4,3}(r)$, $\delta\rightarrow 0$ as $\eta\rightarrow\eta_g$. The CS equation of state would only lead to such a singularity in $g'_{\mathrm{CS}}(1^+)$ in the limit $\eta\rightarrow 1$.

To complement the above analysis, it is instructive to consider the behavior of the structure factor $S(q)$ near η_g. This is shown in Figs. 5 and 6 for $\eta=0.558$. Again, no differences are apparent in the scale of Fig. 5. Apart from this, the effect of $g'(1^+)$ as $\eta\rightarrow\eta_g$ may also be ascertained from the short wavelength behavior of $S(q)$, as given in Eq. (2.10). This becomes manifest in Fig. 6, where one can see that whereas both the result for the PY approximation and the one derived from the RFA method using the CS equation of state have already attained the ''high q'' limit for $q\simeq 250$, in

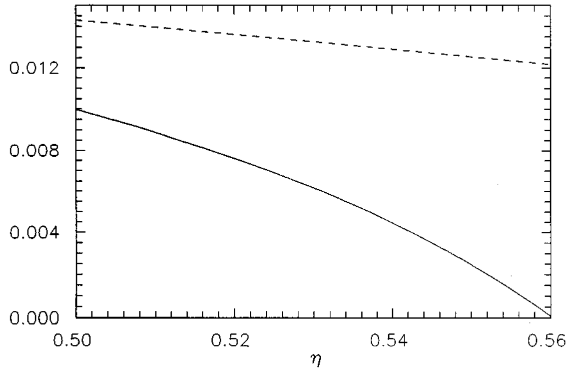

FIG. 4. ''Width'' δ as defined in Eq. (2.12) versus the packing fraction η. The solid line refers to the Padé (4,3) equation of state, while the dashed line refers to the Carnahan-Starling equation of state.

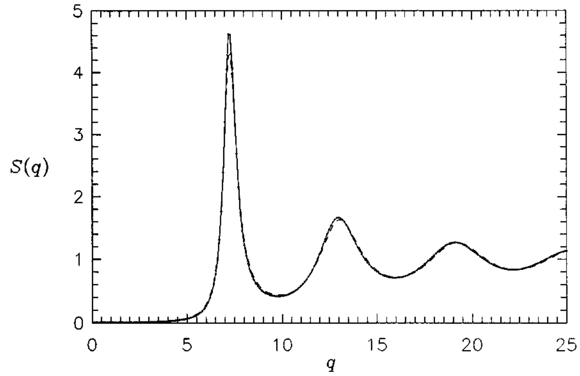

FIG. 5. Structure factor $S(q)$ versus wave number q for $\eta=0.558$. The solid line refers to the Padé (4,3) equation of state, the dashed line refers to the Carnahan-Starling equation of state, and the dotted line corresponds to the Percus-Yevick result.

the case of $Z_{4,3}$ this practically happens for $q \simeq 5000$, a value that roughly coincides with $3\delta^{-1}$. The fact that in the range $q \simeq 250$ the curves corresponding to PY and the Padé (4,3) are indistinguishable is again related to the almost zero value for S_4.

Before we close this section, some comments on the results one gets with the RFA method for $\eta > \eta_g$ are pertinent. Both in the PY approximation and using $Z_{\rm CS}$, the method would in principle lead to ''meaningful'' RDF's and structure factors up to $\eta=1$. These, however, would have the drawback (inherent in the corresponding equations of state) of missing the fact that at $\eta_0 < 1$ the system should reach a crystalline close-packed structure, so their value is questionable even in the metastable fluid region. In the case of $Z_{4,3}$, as pointed out above, if $\eta > \eta_g$, S_4 first becomes positive and then complex [when $\chi_{4,3} < \chi_{\rm PY}(Z_{\rm PY} - \frac{1}{3})/(Z_{4,3} - \frac{1}{3})$, i.e., $\eta > 0.6841$]. A positive S_4 leads to a pole in $G(t)$ [as defined in Eq. (2.1)] on the positive real axis, which in turn implies the unphysical result that the corresponding $g(r)$ grows exponentially with r. If one overlooks this feature and proceeds with the calculation of $S(q)$ through Eq. (2.2), the resulting ''structure factor'' appears to have a ''reasonable'' shape. However, taking the inverse Fourier transform of the analytical expression that one obtains for $S(q)$, yields a nonvanishing ''$g(r)$'' for $r<1$, which is again unphysical. The conclusion is then that the RFA method is clearly indicating that the Padé (4,3) equation of state is only useful for the *fluid* phase (including a *metastable* fluid region), i.e., $\eta \leq \eta_g$. It is interesting to mention that Sanchez [9] had already suggested this to be the case.

III. DISCUSSION

The results given in the preceding section lend themselves to further elaboration. First of all, it should be clear at this stage that the RFA method is particularly advantageous, as compared to the integral equation approach, in the sense that all results are analytic. It is true that the method was devised specifically for hard spheres and this might be regarded as a limitation. However, the key role played by the hard-sphere interaction in perturbation theories as well as the use of the RFA method for other closely related systems [14] provides the proper perspective to assess such limitation. So far, only the two lowest-order rational approximations of the auxiliary function $\Phi(t)$ defined in Eq. (2.1) have been considered. In principle, one could consider higher orders by fixing some extra quantities. In view of the comparison with the simulation results, one would resonably expect that the agreement between simulation and the results of the RFA method, which is already very good, could even improve on increasing the order.

In this paper we have applied the method to study the structure of the hard-sphere fluid both in the *stable* and in the *metastable* regions. We performed a comparison between the results obtained from the CS and the recently derived Padé (4,3) equations of state. In the stable fluid region both equations lead to similar RDF's that improve significantly the agreement of the PY theory with simulation, especially near the contact point. For the metastable branch, however, the two equations of state give rise to *qualitatively* different predictions. In the case of the CS equation, the RFA method provides a plausible RDF up to a packing fraction $\eta=1$, although we are fully aware that such an RDF should be meaningless beyond the crystalline close-packing value $\eta_0 = \pi\sqrt{2}/6$. On the other hand, when using the Padé (4,3), a *threshold* value $\eta_g = 0.5604$ exists, beyond which the structure of the system as predicted by the RFA method becomes *unphysical*. As pointed out earlier on, this threshold value may depend on the equation of state one uses. The question is then whether this numerical estimate will remain unaltered if a different but still accurate equation of state is considered. The recent evidence clearly indicates that the real equation of state of the hard-sphere fluid should include a divergence at the close-packing fraction η_0. Thus, by considering Alder-Hoover approximants [15], which explicitly contain a simple pole at η_0, we may attempt to answer such a question. It is rewarding that the Alder-Hoover approximants (3,3) and (4,3) yield the estimates 0.5545 and 0.5620 for η_g, respectively. The expectation is therefore that if higher-order virial coefficients were to become available in the future, the corresponding Padé approximants will not change appreciably the estimate of the threshold value. The agreement between the estimated values of η_g and the one associated in the literature with the glass transition [3] prompts us to conclude that the method is capable of not only achieving thermody-

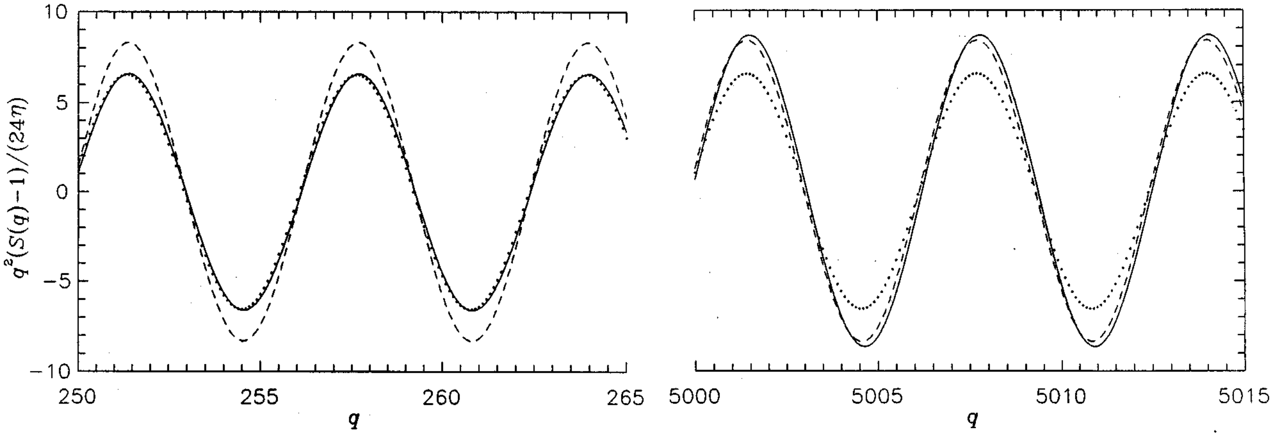

FIG. 6. Short wavelength behavior of $[S(q)-1]q^2/24\eta$ for $\eta=0.558$ and two different q intervals. The solid lines refer to the Padé (4,3) equation of state, the dashed lines refer to the Carnahan-Starling equation of state, and the dotted lines are the Percus-Yevick results.

namic consistency, but also of indicating the range of densities in which a given equation of state may represent a fluid. The key signal of the transition point is the dramatic increase of the magnitude of the slope $g'(1^+)$ as one approaches η_g. On physical grounds, this could be associated with the development of a certain effective ''stickiness'' for $\eta\to\eta_g$, a notion that has also been suggested for hard spheres in other contexts [16].

It is instructive to examine the question of whether the RFA method could also tell us something about the glass. Although admittedly not on very solid grounds, the following speculative arguments indicate that the answer may be in the affirmative sense. The equation of state of the glass is very much different than that of the fluid and (empirically) assumed to be of the general form

$$Z_{\text{glass}}=\frac{A}{1-\eta/\eta_{\text{RCP}}}. \tag{3.1}$$

Here A is a constant. It must be pointed out that the value of η_{RCP}, the random close-packing fraction, is not known precisely, although reasonable estimates are available [17]. For our purposes, the only important aspect is that it indicates the density at which Z_{glass} diverges, and we will provide our own estimate below. Since Eq. (3.1) *does not represent* the fluid phase, the method implies that S_4 as given in Eq. (2.8) cannot be negative in the range $\eta_g<\eta<\eta_{\text{RCP}}$. Therefore, in that range either it is positive or it is complex. Due to the fact that a change in the structure of the system occurs at $\eta=\eta_g$, we conjecture, guided by the previous results concerning the fluid phase, that this feature should be reflected through a change in the qualitative character of S_4. Two possibilities arise when η approaches η_g from above: either S_4 changes from positive to negative or it changes from complex to (positive) real. At $\eta=\eta_g$, the first change leads to the requirement (i) $\chi_{\text{glass}}=\chi_{\text{PY}}$ [with χ_{glass} obtained from Z_{glass} using Eq. (1.1)], while the second one implies (ii) $\chi_{\text{glass}}=\chi_{\text{PY}}(Z_{\text{PY}}-\frac{1}{3})/(Z_{\text{glass}}-\frac{1}{3})$, in agreement with conditions (a)–(c) for S_4 stated in Sec. II. The pressure should be finite and continuous at η_g, so that $Z_{\text{glass}}=Z_{4,3}$ at this packing density. On the other hand, since it has been recently suggested [3] that the pressure exhibits a change in slope on going from the fluid phase to the glass, we stick to possibility (ii). From these two conditions we find $A=2.765$ and $\eta_{\text{RCP}}=0.6448$. It is indeed striking that, as it occurred already in the case of η_g, the estimate provided by the method for η_{RCP} is in excellent agreement with those in the literature [3, 17] and the value of A is close to the one corresponding to the fit of simulation results ($A=2.67$) [3].

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