

## Effective field theory for hard-sphere fluids

Nelson Studart and Hamilton V. da Silveira

*Departamento de Física, Universidade Federal de São Carlos, São Carlos, São Paulo 13565-905, Brazil*

Umbelino de Freitas

*Departamento de Física, Universidade Federal da Paraíba, João Pessoa, Paraíba, 58051-970, Brazil*

(Received 22 May 1995)

We have developed an effective field theory based on the Singwi, Tosi, Land, and Sjölander approximation for the density-density response function to investigate the properties of hard-sphere fluids. Simple analytical expressions are provided for the effective potential, the static structure factor, the Fourier transform of the direct correlation function, and the isothermal compressibility. From the hydrodynamic theory, we have also calculated the collective modes. Our results are in good agreement with those obtained from molecular dynamics simulations at intermediate densities.

PACS number(s): 51.10.+y, 52.35.Dm, 61.20.Gy

### I. INTRODUCTION

The hard-core fluids play a fundamental role in the theory of liquids as a reference system for various perturbation theories. One well-known theory of hard-sphere fluids is that of Percus and Yevick (PY), whose analytical solution of the integral equation yields results of considerable success [1]. Another approximation is the hypernetted chain approximation, which, to a much lesser extent, gives useful results for the direct correlation function  $c(r)$  [2]. Verlet has proposed a semiphenomenological equation for the radial correlation function  $g(r)$ , which yields results with great accuracy compared to "exact" numerical results [3]. Based on a geometrical interpretation of  $c(r)$ , Baus and Colot construct a general expression of  $c(r)$ , which is consistent with previous results for any dimensions [4].

The Singwi, Tosi, Land, and Sjölander (STLS) theory [5] is one of the most successful approaches to the many-body problem. First developed to study the electron correlations of the electron gas at metallic densities, the theory has been applied to several other many-particle quantum and classical systems. Even though the majority of the calculations of the STLS scheme have been devoted to determining dielectric properties of systems with long-range potential, there are some works dealing with short-range interactions, in particular Bose and Fermi systems [6–9] and classical liquids [10]. Recently it has been applied to the investigation of a charged system with a hard core [11].

In this paper we developed a theory based on the effective mean field obtained from the decoupling of the two-particle correlation function in the Bogoliubov-Born-Green-Kirkwood-Yuon hierarchy, as originally formulated in the STLS approach, to the case of a classical hard-sphere fluid. In contrast with previous theories that give expressions for  $c(r)$ , the STLS scheme provides directly an analytical expression for its Fourier transform  $c(k)$ , or the structure factor  $S(k)$ . In Sec. II, we derive the analytical expression for  $S(k)$  in the effective-field

approximation and in Sec. III we present our numerical results for the radial correlation function  $g(r)$ , the compressibility and the collective modes of the hard-sphere fluid.

### II. STRUCTURE FACTOR IN THE EFFECTIVE-FIELD APPROXIMATION

In the STLS theory, the wave-vector- and frequency-dependent density-density response function  $\chi(\vec{k}, \omega)$  is written as

$$\chi(\vec{k}, \omega) = \frac{\chi_0(\vec{k}, \omega)}{1 - \Psi(k) \chi_0(\vec{k}, \omega)}, \quad (1)$$

where  $\Psi(k)$  is effective local field potential and  $\chi_0(\vec{k}, \omega)$  is the density-density response function of the non-interacting system, which in the classical case is given by [12, 13]

$$\begin{aligned} \text{Re}\chi_0(\vec{k}, \omega) &= -\rho\beta[1 - 2yF(y)], \\ \text{Im}\chi_0(\vec{k}, \omega) &= -\rho\beta\sqrt{\pi}y \exp(-y^2), \end{aligned} \quad (2)$$

where  $y = (m\beta/2)^{1/2}\omega/k$ ,  $\beta = 1/k_B T$ , and  $F(y)$  is the Dawson integral.

Within the STLS theory, the effective potential can be related to the pair correlation function  $g(r)$  by the following expression:

$$\Psi(r) = - \int_r^\infty dr g(r) \frac{dV}{dr}, \quad (3)$$

where  $V(r)$  is the bare potential. In the present study, we consider the bare potential as

$$V(r) = \begin{cases} V_0, & r \leq \sigma \\ 0, & r > \sigma, \end{cases} \quad (4)$$

where  $\sigma$  is the hard-core diameter and  $V_0$  is the strength

of the potential at the diameter (a positive number). In the hard-core limit  $V_0$  must be taken as infinite.

On the other hand, through the fluctuation-dissipation theorem and the Kramers-Krönig relation, we can express the static density-density response function  $\chi(k)$  in terms of the static structure factor  $S(k)$  as

$$\chi(k) = -\rho\beta S(k). \quad (5)$$

By combining Eqs. (1) and (5), and using from Eq. (2) the result  $\chi_0(k) = -\rho\beta$  for the ideal system, we arrive at

$$S(k) = \frac{1}{1 + \rho\beta\Psi(k)}, \quad (6)$$

where now  $\Psi(k)$  is obtained by substituting Eq. (4) into Eq. (3) and taking the Fourier transform of  $\Psi(r)$ . The result for the hard-sphere system is [8]

$$\Psi(k) = 4\pi V_0\sigma^2 g(\sigma) \frac{j_1(k\sigma)}{k}, \quad (7)$$

where  $j_1(x)$  is the first-order spherical Bessel function and  $g(\sigma)$  is the radial correlation function at  $r = \sigma$ . The radial correlation function and the static structure factor are related through a Fourier transform:

$$g(r) = 1 + \frac{1}{(2\pi)^3\rho} \int [S(q) - 1] \exp(i\vec{q} \cdot \vec{r}) d^3q. \quad (8)$$

By introducing the dimensionless variable  $k = q\sigma$ , defining the packing fraction  $\eta$ , which is the expansion parameter in the virial series, by  $\eta = \pi\rho\sigma^3/6$ , and substituting Eq. (7) into Eq. (6) we obtain the following expression of the structure factor:

$$S(k) = \frac{k}{k + 24\eta f(\eta)j_1(k)}, \quad (9)$$

where  $f(\eta) = V_0\beta g(\sigma)$ . In the usual STLS scheme, Eq. (8) with  $r = \sigma$ , and Eq. (9) are solved in a self-consistent way in order to determine  $g(\sigma)$ . We expect that in the limit  $V_0 \rightarrow \infty$  (hard-core limit)  $g(\sigma^-)$  goes to zero [8]. However, for classical hard-core fluids such an interactive procedure leads to computational difficulties and furthermore to wrong results even in the regime of low densities ( $\eta \ll 1$ ) because of the highly repulsive nature of the hard-core region. One can also use  $g(\sigma)$  as an adjustable parameter taken from experiments [6]. In this work we choose an alternative way by taking the equation of state of a hard-sphere fluid which is given as [1]

$$\frac{\beta P}{\rho} = 1 + 4\eta f(\eta) \quad (10)$$

and the expression of Carnahan and Starling [14]

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (11)$$

in order to obtain the value of the function  $f(\eta)$ . It is worth emphasizing that the original Carnahan-Starling formula has an extraordinary accuracy as compared with molecular-dynamics results over the whole fluid range. It was used to construct a similarly accurate expression for

the radial distribution function [15]. It was argued that Eq. (12) can be derived from an unusual kind of mean-field theory, where the motions of a particle in different directions are uncorrelated [16]. Using Eqs. (10) and (11) into Eq. (9), the structure factor for the hard-sphere liquid assumes a simple analytical expression

$$S(k, \eta) = \frac{k}{k + [12\eta(2 - \eta)/(1 - \eta)^3] j_1(k)}, \quad (12)$$

and the direct correlation function, which are related to the effective potential through

$$c(k) = -\beta\Psi(k) \quad (13)$$

can be written as

$$\rho c(k, \eta) = -\frac{12\eta(2 - \eta)}{(1 - \eta)^3} \frac{j_1(k)}{k}. \quad (14)$$

Equations (12) and (14) are the main results of this paper. We must note that the PY integral equation, which is the most successful of the first-order integral equations as pointed out before, at least for short-ranged potentials, gives  $c(r, \eta)$  [17] while the STLS approach gives directly  $S(k, \eta)$  or  $c(k, \eta)$ .

### III. NUMERICAL RESULTS

In Fig. 1, we present the comparison of our analytical expression of  $S(k)$  for two values of the packing fraction  $\eta$  with the results, represented by points, from molecular-dynamic simulations [18]. We see the well-defined structure of the peaks at higher density, which agrees reasonably well with the “exact” computer simulations results. Figure 2 shows the direct correlation function of the hard-sphere system, given by Eq. (14) for some values of  $\eta$ . We have observed that even Eq. (12) is valid for all values of  $\eta$ , within the STLS scheme, the results come to present considerable differences from the numerical simulations for values of  $\eta$  above 0.3.

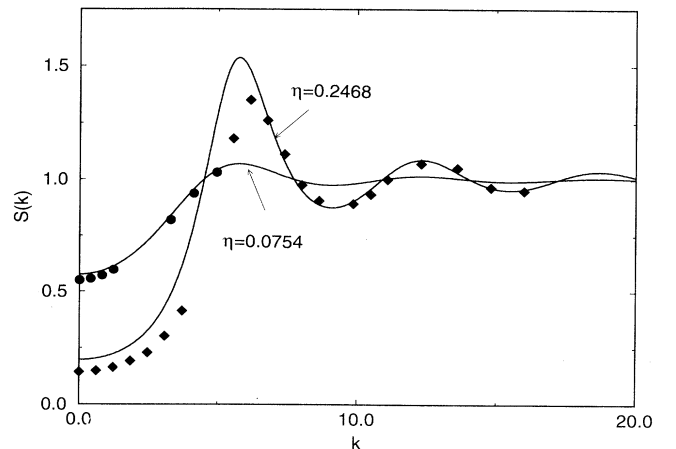


FIG. 1. Structure factor in the effective-field approximation, given by Eq. (12), for two values of the parameter  $\eta$ . The wave number  $k$  is in units of  $\sigma^{-1}$ . The points are results taken from dynamic molecular simulations (Ref. [18]).

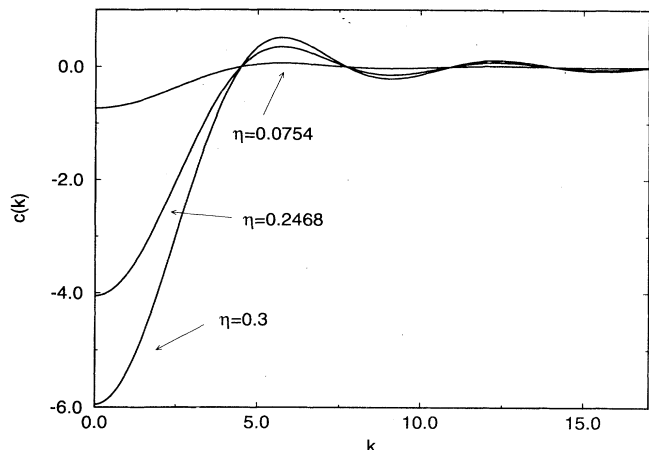


FIG. 2. Fourier transform of the direct correlation function, given by Eq. (14), for three values of  $\eta$ . The wave number  $k$  is in units of  $\sigma^{-1}$ .

The radial correlation function  $g(r, \eta)$ , where  $r$  is in units of  $\sigma$ , given by Eq. (8), can be rewritten in terms of the structure factor  $S(k, \eta)$  as

$$g(r, \eta) = 1 + \frac{1}{12\pi\eta r} \int_0^\infty k dk [S(k, \eta) - 1] \sin(kr), \quad (15)$$

The PY equation for  $g(r)$  was first solved by Wertheim [19] and Thiele [20]. Even though there are explicit analytical expressions for  $g(r)$  in the PY approximation in the literature, they are given, for instance, in terms of expressions involving complex variables and can be reproduced only by actual numerical calculations [21]. In Fig. 3,  $g(r)$  in the effective-field approximation is depicted for three values of  $\eta$  and compared with the results of Monte Carlo calculations by Barker and Henderson [22]. Although the STLS scheme predicts values of  $g(r)$  near the core, which are smaller than the MC values, it gives the correct period of the oscillations of  $g(r)$ . At higher  $\eta$ , the

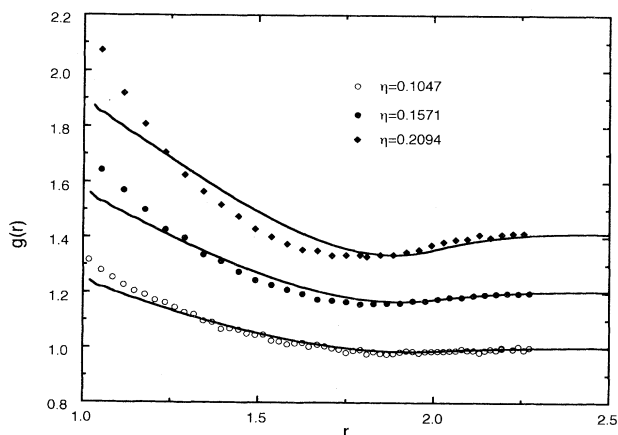


FIG. 3. Pair distribution function for the some values of  $\eta$ . The distance  $r$  is in units of  $\sigma$ . The points are the results of Monte Carlo calculations in Ref. [22]. Successive plots are displaced by 0.2.

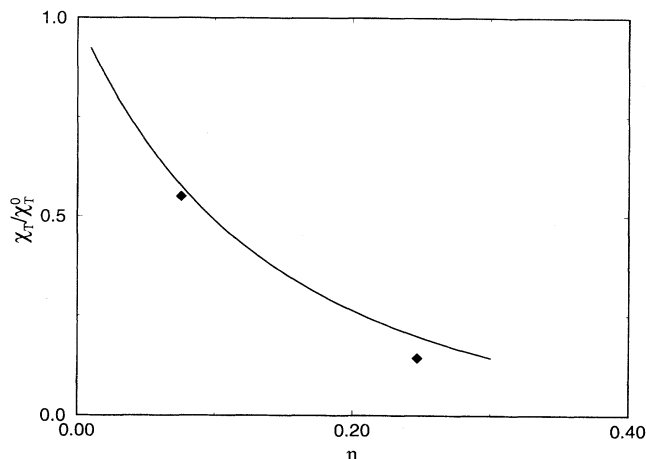


FIG. 4. Ratio of the isothermal compressibility for the hard-sphere fluid as a function of  $\eta$ . The points are results taken from Ref. [18].

pair correlation function (not shown in Fig. 3) exhibits clearly the oscillatory behavior, but the values are far away from these data.

The direct correlation function  $c(r, \eta)$  can also be obtained analytically. The Fourier transform of Eq. (14) gives straightforwardly the result  $c(r, \eta) = -3\eta(2 - \eta) / \pi(1 - \eta)^3$  independent of the distance. This result is in contrast to the PY solution in which  $c(r, \eta)$  has a polynomial expression. So, we conclude that the STLS theory reproduces the simple empty-core model for the direct correlation function, which consists in approximating  $c(r, \eta)$  by a rectangular empty-core function of a constant depth. This simple model shows the main thermodynamic features due to the insensitivity of  $c(k, \eta)$  to the short-range form of the direct correlation function [23].

The knowledge of  $S(k, \eta)$ , given by Eq. (12), allows us to determine the compressibility of the system since the compressibility equation relates the value of  $S(0)$  to the

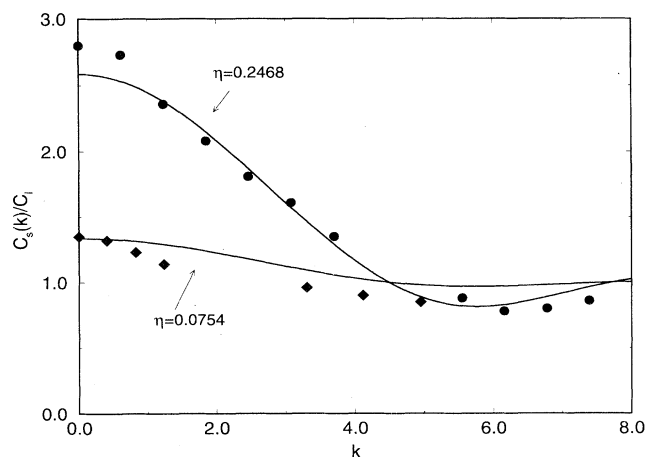


FIG. 5. Generalized adiabatic sound velocity as a function of  $k$  in units of  $\sigma^{-1}$  for two values of  $\eta$ . The points are results taken from dynamic molecular simulations (Ref. [18]).

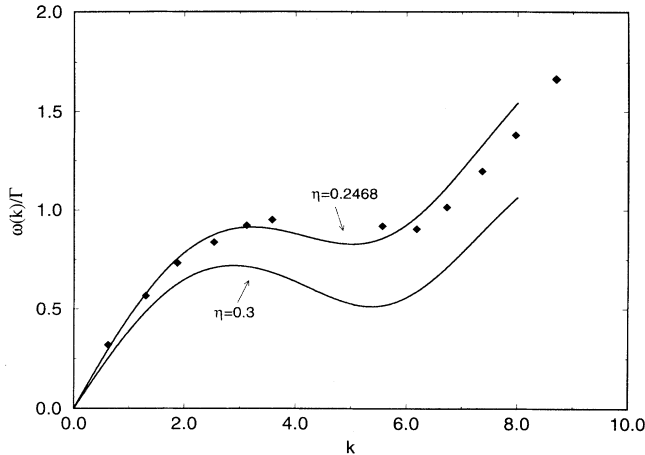


FIG. 6. Dispersion relation of the collective modes for two values of  $\eta$ . The wave number  $k$  is in units of  $\sigma^{-1}$ . The points are results taken from dynamic molecular simulations (Ref. [18]).

compressibility  $\chi_T$  through

$$\frac{\chi_T}{\chi_T^0} = S(0, \eta), \quad (16)$$

where  $\chi_T^0 = 1/\beta\rho$  is the compressibility of the ideal system. In Fig. 4 the ratio of compressibilities for the hard-sphere system is plotted as a function of  $\eta$  and compared with the two values available from the numerical simulations [18].

As the theory is dynamic in nature, we can also determine from the poles of the response density-density function  $\chi(\vec{k}, \omega)$ , given by Eq. (1), the long-wavelength collective modes of the system, which are sound waves [24]. However, we prefer to introduce the simple analytical expression of  $S(k)$  in the hydrodynamic approach

given in Ref. [18] to calculate the generalized adiabatic sound speed and compare with the results arising from computer experiments. We write the hard-core sound dispersion as

$$\omega(k) = C_s(k) k, \quad (17)$$

where  $C_s(k)$  defines the generalized adiabatic sound velocity. Following the derivation in Ref. [18] in the limit of short-time limit, whose behavior is correctly described by the kinetic theory, we obtain

$$\frac{C_s^2(k)}{C_I^2} = \frac{3}{5} \left\{ \frac{1}{S(k)} + \frac{2}{3} \left[ 1 + 12\eta f(\eta) \frac{j_1(k)}{k} \right]^2 \right\}, \quad (18)$$

where  $C_I^2 = 5/3\beta m$ . Figure 5 shows our results for the generalized sound velocity, which are compared with those from numerical simulations. Again the agreement is reasonably good. We also show in Fig. 6 the sound dispersion relation  $\omega(k)/\Gamma$  as a function of  $k$ , where  $\Gamma = 6y\sqrt{1/\pi\beta m\sigma^2}$  is the collision rate with  $y = \beta P/\rho - 1$ . As pointed out in Ref. [18], we note the striking resemblance of the curves with the phonon dispersion curves in liquid helium.

In summary, we have calculated some thermodynamical and transport properties of the hard-sphere system from an effective-field potential that provides a very simple analytical expression for the structure factor. Our results are in good agreement with numerical results from computer simulations for  $\eta$  below 0.3.

#### ACKNOWLEDGMENTS

This work was partially sponsored by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP). We are grateful to J. P. Rino and L. A. Cury for stimulating discussions on this subject.

- 
- [1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).
- [2] F. Lado, *J. Chem. Phys.* **47**, 4828 (1967); D. Henderson and E. W. Grundke, *ibid.* **63**, 601 (1975).
- [3] L. Verlet, *Mol. Phys.* **41**, 183 (1980).
- [4] M. Baus and J.-L. Colot, *J. Phys. C* **19**, L643 (1986).
- [5] K. S. Singwi, M. P. Tosi, R. P. Land, and A. Sjölander, *Phys. Rev.* **176**, 589 (1968); K. S. Singwi and M. P. Tosi, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1981), Vol. 36, p. 177, and references therein.
- [6] R. Lobo, *Phys. Rev. B* **12**, 2640 (1975); O. Hipólito and R. Lobo, *ibid.* **14**, 3892 (1976); A. A. Caparica and O. Hipólito, *Phys. Rev. A* **26**, 2832 (1982).
- [7] U. de Freitas and N. Studart, *Phys. Rev. B* **36**, 6677 (1987); U. de Freitas, L. Ioriatti, Jr., and N. Studart, *J. Phys. C* **20**, 5983 (1987).
- [8] T. K. Ng and K. S. Singwi, *Phys. Rev. Lett.* **57**, 226 (1986); *Phys. Rev. B* **35**, 1708 (1987).
- [9] H. V. da Silveira, M. H. Degani, and K. S. Singwi, *Phys. Rev. B* **46**, 2995 (1992).
- [10] K. S. Singwi, K. Sköld, and M. P. Tosi, *Phys. Rev. A* **1**, 454 (1970); K. N. Pathak and R. Bansal, *J. Phys. C* **6**, 1989 (1973); R. Bansal and N. K. Ailawadi, *Phys. Rev. A* **16**, 1228 (1977).
- [11] J. P. Rino and O. Hipólito, *Phys. Rev. E* **48**, 1375 (1993).
- [12] S. Ichimaru, *Basic Principles of Plasma Physics* (Benjamin/Cumming, Reading, 1973).
- [13] N. Studart and O. Hipólito, *Phys. Rev. A* **19**, 1970 (1979).
- [14] N. F. Carnahan and K. E. J. Starling, *J. Chem. Phys.* **51**, 635 (1969).
- [15] L. Verlet and J.-J. Weis, *Phys. Rev. A* **5**, 939 (1972).
- [16] Y. Song, E. A. Mason, and R. M. Stratt, *J. Chem. Phys.* **93**, 6916 (1989).
- [17] J.-L. Colot, M. Baus, and H. Xu, *Mol. Phys.* **57**, 809 (1986).
- [18] W. E. Alley and B. J. Alder, *Phys. Rev. A* **27**, 3158 (1983); W. E. Alley, B. J. Alder, and S. Yip, *ibid.* **27**, 3174 (1983).

- [19] M. S. Wertheim, *Phys. Rev. Lett.* **10**, 321 (1963).  
[20] E. Thiele, *J. Chem. Phys.* **39**, 474 (1963).  
[21] W. R. Smith and D. Henderson, *Mol. Phys.* **19**, 411 (1970).  
[22] J. A. Barker and D. Henderson, *Mol. Phys.* **21**, 187 (1971).  
[23] C. Croxton, *Introduction to Liquid State Physics* (John Wiley, London, 1975).  
[24] A. A. Kugler, *J. Stat. Phys.* **8**, 107 (1973).