Low-density properties of a hard-sphere fluid within a thermodynamically consistent theory

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We investigate the low-density limit of a theory for the structure of a fluid of hard spheres which is made fully consistent on the thermodynamic side [G. Giunta, C. Caccamo, and P. V. Giaquinta, Phys. Rev. A 31, 2477 (1985)]. The space behavior of the tail function is studied analytically up to second order in the packing fraction. The fourth virial coefficient predicted by the theory is also explicitly evaluated and found to slightly underestimate the exact result.

In a recent paper[1] a thoroughly self-contained and thermodynamically consistent approach was proposed for the study of the structure of a fluid of hard spheres. In that paper it was shown that, starting from a simple *ansatz* for the tail function $d(r)$, it is possible to derive the structural properties of the system within the Ornstein-Zernike (OZ) theoretical framework without resorting to any *a priori* availability of numerical simulation data. This goal was achieved by imposing a complete thermodynamic closure on the solution of the model, based on the existence of well-defined internal consistency constraints relating structural and thermodynamic properties of the fluid. The tail function of a liquid with interatomic potential $u(r)$, in a thermodynamic state specified by the temperature T and by the number density ρ, is defined in diagrammatic language as the sum of all distinct connected simple graphs with Mayer f bonds which are free from bridge points and lack direct bonds between the root points.[2] The relation of $d(r)$ to the more common pair-correlation function $h(r)$ and direct correlation function $c(r)$ which enter the OZ equation

$$h(r)=c(r)+\rho\int d\mathbf{r}'\,h(|\mathbf{r}-\mathbf{r}'|)c(r') \tag{1}$$

is given by[2,3]

$$c(r)=f(r)y(r)+d(r)\ , \tag{2}$$

where $f(r)=\exp[-\beta u(r)]-1$ is the Mayer function with $\beta=1/k_BT$, and $y(r)=[1+h(r)]\exp[\beta u(r)]$ is the cavity distribution function. The functional form adopted in Ref. 1 for the tail function of hard spheres was

$$d(r)=\begin{cases}\exp\left[\sum_{n=0}^{3}\alpha_n(r/\sigma-1)^n\right], & r<\sigma\\ \dfrac{K}{r/\sigma}\exp[-z(r/\sigma-1)], & r>\sigma\ ,\end{cases} \tag{3}$$

where σ is the hard-core diameter. In Ref. 1 the continuity of $d(r)$ at $r=\sigma$ is demanded up to its second derivative. These conditions leave undetermined three parameters—say K,z, and α_3—which are fixed, as a function of density, by solving a set of three differential equations arising from the invoked requirements of thermodynamic consistency. The problem can be considerably simplified if one resorts to the following change of variables:

$$z=z(y_0,a;\rho)\ , \tag{4a}$$

$$K=K(y_0,a;\rho)\ , \tag{4b}$$

where y_0 is the value of $y(r)$ at $r=\sigma$ and a is the inverse reduced compressibility. Such a change of representation was successfully exploited by Høye and Stell[4] in studying the structure of the OZ equation with a core condition and a direct correlation function of Yukawa form. In fact, the choice of the more direct physical quantities y_0 and a in place of K and z leads to a solution of the OZ equation which can be given in closed, analytical form. Such a simplification makes it possible to check explicitly the reliability of the scheme developed in Ref. 1 in the low-density limit through the calculation of the first four coefficients in the virial expansion whose value is known exactly.[3] After expanding y_0 and a in the form

$$y_0=\sum_{l=0}^{\infty}y_0^{(l)}\eta^l\ , \tag{5a}$$

$$a=\sum_{l=0}^{\infty}a^{(l)}\eta^l\ , \tag{5b}$$

where $\eta=(\pi/6)\rho\sigma^3$ is the packing fraction, we start by imposing consistency between the virial and fluctuation expressions for the equation of state (EOS). This condition leads to the following relations between the two sets of coefficients $y_0^{(l)}$ and $a^{(l)}$:

$$a^{(l+1)}=4(l+2)y_0^{(l)}\ , \tag{6}$$

with $l=0,1,\ldots$, and $y_0^{(0)}=a^{(0)}=1$. We truncate the expansion of y_0 after the term of second order in the packing fraction, which is equivalent to pushing the expansion of the EOS up to the fourth virial coefficient. The expanded form of a and of the remaining quantities which enter the present scheme can be obtained straightforwardly by making use of the formalism developed in Ref. 4. First of all, we focus on the low-density behavior of the original parameters K and z because of their relevance to the shape of the direct correlation function outside the core. We find that a necessary condition for the $\eta\rightarrow 0$ value of the inverse range parameter $z^{(0)}$ to be real is $y_0^{(1)}=\frac{5}{2}$, which yields the correct third virial coefficient. Once the value of $y_0^{(1)}$ is fixed, $z^{(0)}$ is found to depend on $y_0^{(2)}$ only. Its expression reads

$$z^{(0)}=\{3(y_0^{(2)}-4)+[3(y_0^{(2)}-4)(26-5y_0^{(2)})]^{1/2}\}\times(19-4y_0^{(2)})^{-1} . \tag{7}$$

In order to ensure that $c(r)$ asymptotically vanishes as $r\rightarrow\infty$ one also needs $z^{(0)}$ to be positive. This last requirement restricts the range of physically acceptable values for $y_0^{(2)}$ to

$$4\leq y_0^{(2)}<\tfrac{19}{4} . \tag{8}$$

We note that the lower and upper bounds in Eq. (8) correspond to the values which are obtained for $y_0^{(2)}$ in the Percus-Yevick (PY) approximation following the virial and fluctuation route, respectively, for the evaluation of the EOS. Furthermore, the known exact value of $y_0^{(2)}$ falls within the above range.[3] Figure 1 shows $z^{(0)}$ as a function of $y_0^{(2)}$. As a result of the virial-compressibility consistency requirement—which, so far, is the only constraint explicitly taken into account—the spatial range of the Yukawa tail in $c(r)$ monotonously increases from zero as $y_0^{(2)}$ is lowered from its upper bound value. On the other hand, the overall amplitude of the tail shrinks to zero as $y_0^{(2)}$ approaches its lower extreme. In fact, we find that K vanishes as η^2 in the limit of $\eta\rightarrow 0$

$$K=K^{(2)}\eta^2+\cdots , \tag{9}$$

with a coefficient $K^{(2)}=y_0^{(2)}-4$. Incidentally, we note that the low-density behavior exhibited by $c(r=\sigma^+)$ is consistent with the well-known result that the PY theory [where $c(r)=0$ outside the core] is exact up to first order in η at the level of pair correlation functions.[3] As a result of the expansion and of the continuity conditions imposed upon $d(r)$ at contact, it also follows that the tail function vanishes over the whole range of r up to first order in η. Hence, only the $\eta\rightarrow 0$ value of α_3 is needed in the expansion of $d(r)$ to order η^2. The quantities $y_0^{(2)}$, $z^{(0)}$, and $\alpha_3^{(0)}$ can be univocally determined by exploiting the residual conditions which arise from the $r\rightarrow 0$ behavior of $y(r)$. In fact, the value of the cavity distribution function and of its first spatial derivative at $r=0$ are related to the excess chemical potential and virial pressure, respectively. The ensuing consistency requirements lead to Eqs. (11) and (15) of Ref. 1 which, in the limit of $\eta\rightarrow 0$, reduce to

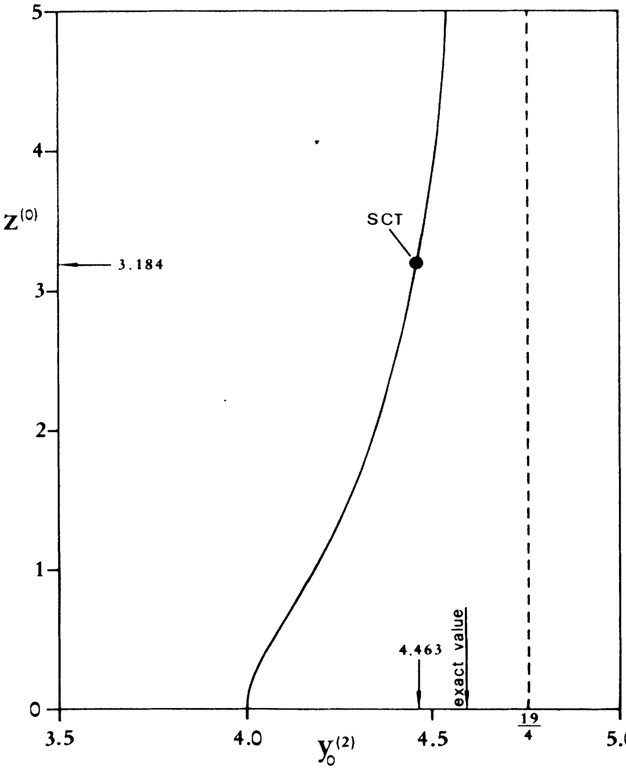

FIG. 1. Zero-density limit of the inverse range parameter z as a function of $y_0^{(2)}$. The point on the curve marked by a closed circle corresponds to the values for $y_0^{(2)}$ and $z^{(0)}$ which are predicted by the self-consistent theory (SCT).

$$y_0^{(2)}=4+17\exp\left[-\tfrac{2}{3}(z^{(0)}+\tfrac{151}{68})\right] , \tag{10}$$

$$\alpha_3^{(0)}=z^{(0)}/3+\tfrac{1}{51} . \tag{11}$$

By solving the coupled set of equations (7), (10), and (11) we find

$$y_0^{(2)}=4.463 ,$$

$$z^{(0)}=3.184 ,$$

$$\alpha_3^{(0)}=1.081 .$$

The above prediction for $y_0^{(2)}$ leads to a result for the fourth virial coefficient $B_4/\sigma^9=2.563$ which slightly underestimates the exact value (2.636).[3] Furthermore, the inverse range parameter z of the Yukawa tail in the direct correlation function is found to tend to a finite nonzero value as $\eta\rightarrow 0$.

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[1]G. Giunta, C. Caccamo, and P. V. Giaquinta, Phys. Rev. A **31**, 2477 (1985).
[2]G. Stell, in *The Equilibrium Theory of Classical Fluids,* edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), p. II-171.
[3]J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids,* (Academic, New York, 1976).
[4]J. S. Høye and G. Stell, Mol. Phys. **32**, 195 (1976).