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Density fluctuations and entropy

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A functional for the entropy that is asymptotically correct both in the high- and low-density limits is proposed. The new form is $S=S^{(id)}+S^{(ln)}+S^{(r)}+S^{(c)}$, where the term $S^{(c)}$ depends on the p-body density fluctuations α_p and has the form $S^{(c)}/k=\langle N\rangle\{\ln 2-1+\Sigma_{p=2}^{\infty}(\ln 2)^p/p!\,\alpha_p-[\exp(\alpha_2-1)-\alpha_2]\}+\hat{S}$. $\hat{S}$ renormalizes the ring approximation $S^{(r)}$. This result is obtained by analyzing the functional dependence of the most general expression of the entropy. Two main results for $S^{(c)}$ are proved: (i) In the thermodynamic limit it is only a functional of the one-body distribution function and (ii) by summing to infinite order the leading contributions in the density a numerical expression for the entropy [Eq. (33)] with a renormalized ring approximation is obtained. The relation of these results to the incompressible approximation for the entropy is discussed and preliminary numerical results on hard spheres are presented.

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I. INTRODUCTION

Entropy is one of the very important and challenging thermodynamic quantities in statistical mechanics because it depends on all the n-particle distribution functions. The problem is to obtain equations that are both accurate and manageable from a theoretical and numerical point of view. Among the exact expressions we cite the classical work of Nettleton and Green [1] and, more recently, the ones of one of us (J.A.H.), Pouskari, and Prestipino and Giaquinta [2–4]. Approximate expressions have also been derived [3,5–8]. In [5] we have shown how an infinite subset of terms (dependent exclusively on the one- and two-body distribution functions) can be analytically summed, giving rise to the so-called ring approximation (RA) and, through a minimization of the free energy functional, the well-known HNC approximation [9] is obtained as an optimized superposition approximation. Later on, Bush *et al.* [6] derived sets of integral equations by analyzing several levels of approximation to the grand potential function and, in a recent and very interesting article, Puoskari [3] extends the RA to three-particle functions, showing how the HNC2 equations either of the Wertheim [10] or Baxter [11] variety can be obtained. Baranyai and Evans [7] showed that, even though the derivations are done in the grand canonical ensemble, the entropy equations are, in fact, ensemble invariants if local expressions are used for the entropy. In this way, the comparison with canonical ensemble numerical simulations is justified. They also analyze the convergence range of some needed integrals showing how this range increases at high densities. Wallace [8] also worked with the same type of expression and, by analyzing the behavior of density fluctuations, proposed an incompressible approximation for the entropy of dense fluids (which, as Wallace himself states, is decidedly wrong in the low-density regime). He then concluded that the dilute gas and dense liquid regimes occupy different regions of the phase space. These conclusions have been criticized [7]. Laird and Haymet [12] have extended the RA to mixtures and applied it to electrolytes. They found that the correct Debye-Huckel expression for the entropy in the low-concentration limit is obtained when the RA is included. They have also discussed the incompressible approximation in dense fluids [13], and proposed an expression that differs from the one of Wallace, and applied it with good numerical results.

Summarizing, these works show that, at low densities, inclusion of the RA gives a very accurate entropy equation and the incompressible approximation is hopelessly wrong, while, at high densities, the ring term overestimates the entropy and the incompressible approximation is reasonably accurate. It has been suggested that more than two-body correlations must be incorporated in order to have an accurate expansion and, in this respect, Puoskari's work [3] is quite promising. It is the purpose of this article to elaborate on the compressibility-related contribution to entropy and improve the entropy expansion when truncated to the pair distribution level. In Sec. II we discuss the conceptual structure of the entropy when written as a functional of the n-body distribution function. In Sec. III it is shown by functional differentiation that the compressibility-related contribution only depends on the one-body distribution function as well as on thermodynamic parameters and, in Sec. IV, by summing three subsets of terms, we shed some light on the nature of the incompressible approximation, show how the correct low- and high-density limits can also be obtained, and present our entropy equation [Eq. (33)]. In Sec. V some numerical issues related to this equation are discussed, with hard spheres (HS) as the prototypical system, showing that the preliminary numerical results are promising but that more extensive studies are also needed. In Sec. VI we present our conclusions.

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II. ENTROPY STRUCTURE

We can think on two different criteria for the analysis of the entropy. The first one can be called the functional criterion; it is the one we take when interested in the entropy dependence on distribution functions, e.g., when a variational principle is formulated. The second point of view is the numerical one; i.e., the main goal is numerical accuracy. It is clear that it is not necessarily true that the same expression will fulfill satisfactorily both goals. In particular, the incompressible approximation [see Eq. (10)] is numerically correct at high densities, but has the wrong behavior at low densities and also lacks a sound theoretical foundation.

When the entropy dependence on all the n-body distribution functions is explicitly written, we obtain an approximate expression with the following distinct structure contributions [3,5].

(i) The ideal gas contribution

$$\frac{S^{(id)}}{k}=\langle N\rangle\left[\frac{5}{2}-\ln(\rho\lambda^3)\right], \tag{1}$$

where ρ is the number density and λ the thermal wavelength.

(ii) The ever present logarithmic contribution

$$\frac{S^{(\ln)}}{k}=-\sum_{p\geqslant 1}\frac{1}{p!}\int d\{\mathbf{p}\}n_p(\{\mathbf{p}\})\omega_p(\{\mathbf{p}\}), \tag{2}$$

where $n_p(\{\mathbf{p}\})$ is the p-particle distribution function and $\omega_p(\{\mathbf{p}\})$ the irreducible p-body contribution to the potential of average force. More specifically, the link with the more usual notation is

$$g_p(\{\mathbf{p}\})=\frac{n_p(\{\mathbf{p}\})}{\prod_i n_1(\mathbf{i})}, \tag{3}$$

$$e^{\omega_p(\{\mathbf{p}\})}=\frac{n_p\prod_{\{\mathbf{p-2}\}\subset\{p\}}n_{p-2}\prod_{\{\mathbf{p-4}\}\subset\{p}n_{p-4}\cdots}{\prod_{\{\mathbf{p-1}\}\subset\{p\}}n_{p-1}\prod_{\{\mathbf{p-3}\}\subset\{p}n_{p-3}\cdots}. \tag{4}$$

As usual, we have that $g_2=1+h_2$ and, through the use of the generalized superposition approximation (GSA) [14], we can write that, e.g.,

$$g_3(\{\mathbf{3}\})=[1+\Delta_3(\{\mathbf{3}\})]\prod_{\{\mathbf{2}\}\subset\{\mathbf{3}\}}g_2(\{\mathbf{2}\}),$$

$$\begin{aligned} g_4(\{\mathbf{4}\})&=[1+\Delta_4(\{\mathbf{4}\})]\frac{\prod_{\{\mathbf{3}\}\subset\{\mathbf{4}\}}g_3(\{\mathbf{3}\})}{\prod_{\{\mathbf{2}\}\subset\{\mathbf{4}\}}g_2(\{\mathbf{2}\})}\\ &=[1+\Delta_4(\{\mathbf{4}\})]\prod_{\{\mathbf{3}\}\subset\{\mathbf{4}\}}[1+\Delta_3(\{\mathbf{3}\})]\prod_{\{\mathbf{2}\}\subset\{\mathbf{4}\}}g_2(\{\mathbf{2}\}),\end{aligned} \tag{5}$$

which introduces the family of Δ_p functions which, when different from zero, correct for the difference with the GSA. They can also be written as

$$\Delta_p(\{\mathbf{p}\})=e^{\omega_p(\{\mathbf{p}\})}-1. \tag{6}$$

This $S^{(\ln)}$ contribution is the one that, when functionally differentiated, gives rise to the $\ln g$ contribution in the integral equations.

(iii) The ring term, which in its simplest, two-body version, is

$$\begin{aligned}\frac{S^{(r)}}{k}=\frac{1}{2}\sum_{p\geqslant 3}\frac{(-1)^{p-1}}{p}\int d\{\mathbf{p}\}\prod_{i=1}^{p}n_1(\mathbf{i})h_2(\mathbf{12})h_2(\mathbf{23})\cdots\\ \times h_2(\mathbf{p1}),\end{aligned} \tag{7}$$

and it can be summed in homogeneous systems [5] [see Eq. (35)]. This term is responsible for the contribution h_2-c_2 in the integral equations. The three-body version is derived in [3].

(iv) The compressibility related contribution

$$\frac{S^{(c)}}{k}=\sum_{p\geqslant 2}\frac{1}{p!}\int d\{\mathbf{p}\}\prod_{i=1}^{p}n_1(\mathbf{i})\Delta_p(\{\mathbf{p}\})\Gamma_p(\{n_p\}), \tag{8}$$

$$\Gamma_p(\{n_p\})=\frac{\prod_{\{\mathbf{p-1}\}\subset\{\mathbf{p}\}}g_{p-1}\prod_{\{\mathbf{p-3}\}\subset\{\mathbf{p}\}}g_{p-3}\cdots}{\prod_{\{\mathbf{p-2}\}\subset\{\mathbf{p}\}}g_{p-2}\prod_{\{\mathbf{p-4}\}\subset\{\mathbf{p}\}}g_{p-4}\cdots}. \tag{9}$$

Its first term is essentially the compressibility ($\Delta_2\equiv h_2$) and the sequence of products in Eq. (9) stops when reaching either g_3 or g_2. As far as we know there are no previous studies of the whole series given in Eq. (8); the compressibility approximation focuses on the first term of this series, which, for a one-component homogeneous system, is

$$\frac{S_2^{(c)}}{k}=\langle N\rangle\frac{\rho}{2}\int d\mathbf{r}h_2(r)=\frac{\langle N\rangle}{2}(-1+\alpha_2). \tag{10}$$

As in the dense liquid limit $\alpha_2\ll 1$, the incompressible approximation considers $\alpha_2=0$ in the whole ρ-T space.

III. FUNCTIONAL DEPENDENCE

In this section we prove that, in the thermodynamic limit, all the functional derivatives of the compressibility contribution with respect to the distribution functions can be summarized in the equation

$$\frac{\delta S^{(c)}/k}{\delta n_p(\{\mathbf{p}\})}=-\delta_{1p}+O(e^{-\langle N\rangle}). \tag{11}$$

Therefore,

$$\frac{S^{(c)}}{k}=-\int d\{\mathbf{1}\}n_1(\{\mathbf{1}\})+C(\rho,T)+O(e^{-\langle N\rangle}). \tag{12}$$

C is an integration constant as far as the functional integration refers but, in fact, it depends on ρ,T.

The derivation is straightforward. The origin of the compressibility term $S^{(c)}$ is quite clear and Eqs. (38)–(41) of Ref. [2] are the equations to look at. Equation (38) is our Eq. (10) and in Eqs. (39)–(41) we see that each one of them has, among other terms, the integral $\int\Pi n_1 g_p d\{\mathbf{p}\}$. When the GSA for g_p is used [Eq. (5)], the integral decomposes into a sum of two integrals $\int\Pi n_1\Gamma_p[1+\Delta_p]d\{\mathbf{p}\}$. The term without Δ_p contributes to the ring approximation plus neglected terms (such as those shown in Ref. [5]) and the term with Δ_p contributes to $S^{(c)}$.

As Γ_p can also be written as

$$\Gamma_p(\{n_p\})=\frac{\prod_{\{\mathbf{p-1}\}\subset\{\mathbf{p}\}} n_{p-1}\prod_{\{\mathbf{p-3}\}\subset\{\mathbf{p}\}} n_{p-3}\cdots}{\prod_{\{\mathbf{p-2}\}\subset\{\mathbf{p}\}} n_{p-2}\prod_{\{\mathbf{p-4}\}\subset\{\mathbf{p}\}} n_{p-4}\cdots},$$

using Eqs. (4) and (6) we conclude that

$$\frac{S^{(c)}}{k}=\sum_{p\geqslant 2}\frac{1}{p!}\int d\{\mathbf{p}\}\times\left[n_p-\frac{\prod_{\{\mathbf{p-1}\}\subset\{\mathbf{p}\}} n_{p-1}\prod_{\{\mathbf{p-3}\}\subset\{\mathbf{p}\}} n_{p-3}\cdots}{\prod_{\{\mathbf{p-2}\}\subset\{\mathbf{p}\}} n_{p-2}\prod_{\{\mathbf{p-4}\}\subset\{\mathbf{p}\}} n_{p-4}\cdots}\right]. \tag{13}$$

It is somewhat clear that each one of these integrals is related to p-body density fluctuations but a clearer explanation is to be found in the next section. This explains the origin of naming this contribution as compressibility related. Written in this way it is straightforward to show that the functional derivatives are

$$\frac{\delta S^{(c)}/k}{\delta n_1(\mathbf{x})}=\sum_{p\geqslant 1}(-1)^p\frac{\langle N\rangle^p}{p!}\left[1+O\left(\frac{1}{\langle N\rangle}\right)\right]=-1+O(e^{-\langle N\rangle}), \tag{14}$$

$$\frac{\delta S^{(c)}/k}{\delta n_s(\{\mathbf{x}_s\})}=\frac{1}{s!}\sum_{p\geqslant 0}(-1)^p\frac{\langle N\rangle^p}{p!}\left[1+O\left(\frac{1}{\langle N\rangle}\right)\right]=O(e^{-\langle N\rangle}), \tag{15}$$

and we arrive at Eq. (11).

This result shows that, in the thermodynamic limit, the compressibility term does not contribute to any set of equations we may derive by functional differentiation of a functional that includes the entropy; it only contributes to the constraint of fixed density. Therefore, while in the set of equations derived from variational principles we can safely ignore the compressibility term in front of all the other terms, when undertaking the numerical computation of the entropy we do not see sound reasons suggesting that we ignore it. Let us mention that it is possible that, due to partial cancellations, a simple dismissal of a whole series of terms can be, numerically speaking, more effective than a partial summation. The main inconvenience of this dismissal of terms is its uncontrollable nature; i.e., we can never be sure of its effectiveness.

IV. SERIES SUMMATION

For this reason we will cut the GSA [Eq. (4)] after the third-order terms; in this way g_p can be written in two equivalent forms

$$g_p(\{\mathbf{p}\})=\begin{cases}1+\sum_{\{\mathbf{2}\}\subseteq\{\mathbf{p}\}}h_2(\{\mathbf{2}\})+\sum_{\{\mathbf{3}\}\subseteq\{\mathbf{p}\}}h_3(\{\mathbf{3}\})+\cdots h_p(\{\mathbf{p}\}),\\ \prod_{\{\mathbf{3}\}\subseteq\{\mathbf{p}\}}[1+\Delta_3(\{\mathbf{3}\})]\prod_{\{\mathbf{2}\}\subseteq\{\mathbf{p}\}}[1+h_2(\{\mathbf{2}\})].\end{cases} \tag{16}$$

In Eq. (13) for the compressibility contribution we will sum to infinite order three subsets of terms. These subsets are clearly identified in the $p=3$ summand of Eq. (13), i.e.,

$$\begin{aligned}\frac{S_3^{(c)}}{k}&=\frac{1}{3!}\int d\{\mathbf{3}\}\prod_{i=1}^{3}n_1(\mathbf{i})\left[g_3(\{\mathbf{3}\})-\prod_{\{\mathbf{2}\}\subseteq\{\mathbf{3}\}}1+h_2(\{\mathbf{2}\})\right]\\ &=\frac{1}{3!}\int d\{\mathbf{3}\}\prod_{i=1}^{3}n_1(\mathbf{i})\left[h_3(\{\mathbf{3}\})-\sum_{i=1}^{3}\prod_{k\neq i}h_2(\mathbf{ik})\right.\\ &\quad\left.-h_2(\mathbf{12})h_2(\mathbf{13})h_2(\mathbf{23})\right].\end{aligned} \tag{17}$$

(A) The first subset includes the contribution of the integrals $\int h_p d\{\mathbf{p}\},p\geqslant 2$. The series is

$$\frac{S_a^{(c)}}{k}=\sum_{p=2}^{\infty}\frac{1}{p!}\int d\{\mathbf{p}\}\prod_{i=1}^{p}n_1(\mathbf{i})h_p(\{\mathbf{p}\})=\sum_{p=2}^{\infty}\frac{\langle C_p\rangle}{p!}. \tag{18}$$

The moment-cumulant relation [2] is

$$\begin{aligned}C_M(\{\mathbf{M}\})&=h_M(\{\mathbf{M}\})\prod_{i=1}^{M}n_1(\mathbf{i})\\ &=\sum_{k=1}^{M}\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}(-1)^{k-1}(k-1)!\prod_{i=1}^{k}n_{m_i}(\{\mathbf{m}_i\}).\end{aligned} \tag{19}$$

Here, the partition of the coordinate set $\{\mathbf{M}\}$ in k disjoint subsets $\{\mathbf{m}_i\}_{\mathbf{M}}$, $1\leqslant i\leqslant k$ is symbolized by $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}$ and therefore $\Sigma_{k=1}^{M}\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}$ indicates the sum over all the partitions in k subsets and for each k is $1\leqslant i\leqslant k$. In this way $\langle C_p\rangle$ is related to the integrals $\langle n_{p_i}\rangle=\int dp_i n_{p_i}$. On the other hand, $\langle n_{p_i}\rangle$ can be expanded in terms of $\langle N^k\rangle$ [15]:

$$\langle n_p\rangle=\langle N(N-1)\cdots(N-p+1)\rangle=\sum_{k=1}^{p}s(p,k)\langle N^k\rangle \tag{20}$$

for $p\geqslant 1$, where $s(p,k)$ are the Stirling numbers of first kind. One of its definitions is that $(-1)^{p-k}s(p,k)$ is the number of permutations of p elements which contain exactly k cycles. They satisfy the recurrence relation

$$s(p+1,k)=s(p,k-1)-ps(p,k),\quad 1\leqslant k\leqslant p,$$

with starting values

$$s(p,0)=s(0,k)=\delta_{0n}.$$

We also define the r-body density fluctuations α_r by

$$\alpha_r=\begin{cases} 1, & r=1, \\ \dfrac{\langle (N-\langle N\rangle)^r\rangle}{\langle N\rangle}, & r>1. \end{cases} \tag{21}$$

The first few $\langle C_p\rangle$ are then expressed in terms of the α_r and Stirling numbers as

$$\langle C_2\rangle=\langle N\rangle(-1+\alpha_2)=\langle N\rangle\sum_{i=1}^{2} s(2,i)\alpha_i, \tag{22}$$

$$\langle C_3\rangle=\langle N\rangle(2-3\alpha_2+\alpha_3)=\langle N\rangle\sum_{i=1}^{3} s(3,i)\alpha_i, \tag{23}$$

$$\begin{aligned}\langle C_4\rangle&=\langle N\rangle(-6+11\alpha_2-6\alpha_3+\alpha_4)+3\langle N\rangle^2\alpha_2^2\\ &=\langle N\rangle\sum_{i=1}^{4} s(4,i)\alpha_i+3\langle N\rangle^2\alpha_2^2.\end{aligned} \tag{24}$$

The $3\langle N\rangle^2\alpha_2^2$ term and similar ones from higher-order $\langle C_p\rangle$ will be included in the next partial sum. In order to sum to infinite order the contribution of each r-body density fluctuations we need the result [15]

$$\sum_{t=k}^{\infty}\frac{s(t,k)}{k!}x^k=\frac{[\ln(1+x)]^t}{t!}.$$

Therefore, the α_r contribution is

$$\Gamma_{\alpha_r}=\begin{cases}\ln 2-1, & r=1,\\ (\ln 2)^r/r!, & r\geqslant 2,\end{cases} \tag{25}$$

and our first partial sum, which includes contributions to infinite order of all the α_r, is

$$\frac{S_a^{(c)}}{k}=\sum_{p=2}^{\infty}\frac{\langle C_p\rangle}{p!}=\langle N\rangle\left\{\ln 2-1+\sum_{p=2}^{\infty}\frac{(\ln 2)^p}{p!}\alpha_p\right\}. \tag{26}$$

Let us remark on some characteristics of this result: (i) $\ln 2-1$ is the contribution in the absence of density fluctuations and it is also its high-density limit ($\alpha_p\leqslant 1$), (ii) as $\alpha_p \to 1$ when $\rho\to 0$, Eq. (26) vanishes in the low-density limit, and (iii) the series is rapidly convergent. Therefore, this sum goes in the right direction to improve on the incompressible approximation, both in its numerical results and in its theoretical foundation. This analysis makes also clear why this contribution is referred to as compressibility related. Last, the α_p are easily expressed as integrals of the correlation functions; the first ones are

$$\alpha_2=1+\frac{1}{\langle N\rangle}\int d\{\mathbf{2}\}\prod n_1(\mathbf{i})h_2(\{\mathbf{2}\}),$$

$$\alpha_3=-2+3\alpha_2+\frac{1}{\langle N\rangle}\int d\{\mathbf{3}\}\prod n_1(\mathbf{i})h_3(\{\mathbf{3}\}).$$

(B) When in the pth term of Eq. (13) the expansions given in Eqs. (16) are inserted, each $h_k, k<p$ expanded in terms of h_2,Δ_3 and terms like the $3\langle N\rangle^2\alpha_2^2$ which were left aside in the first partial series included, then all the unconnected (in the graph theory sense) terms cancel out and the first two sets of connected diagrams are those depicted in Eq. (17). We first evaluate the sum of ''star'' products of h_2 bonds:

$$\begin{aligned}\frac{S_b^{(c)}}{k}&=\sum_{p=3}^{\infty}\Psi_p\\ &=-\sum_{p=3}^{\infty}\frac{1}{p!}\sum_{i=1}^{p}\int d\mathbf{i}n_1(\mathbf{i})\prod_{k\neq i}\int d\mathbf{k}n_1(\mathbf{k})h_2(\mathbf{ik}).\end{aligned} \tag{27}$$

Each summand is easily evaluated as

$$\Psi_p=\frac{\langle N\rangle}{(p-1)!}(-1+\alpha_2)^{p-1},$$

and the second partial sum is

$$\frac{S_b^{(c)}}{k}=-\langle N\rangle[\exp(\alpha_2-1)-\alpha_2]. \tag{28}$$

Its low- and high-density limits are 0 and $-e^{-1}$, respectively.

(C) This series is a sum of rings very similar to Eq. (7), its first term is given in Eq. (17), and, as the symmetry number of p rings is $2p$, it can be written as

$$\frac{S_c^{(c)}}{k}=-\frac{1}{2}\sum_{p\geqslant 3}\frac{1}{p}\int d\{\mathbf{p}\}\prod_{i=1}^{p} n_1(\mathbf{i})h_2(\mathbf{12})h_2(\mathbf{23})\cdots h_2(\mathbf{p1}), \tag{29}$$

which can be summed for homogeneous systems in the same way as the original ring approximation was [5]:

$$\frac{S_c^{(c)}}{k}=-\frac{\langle N\rangle}{2\rho}\int d\mathbf{k}\left\{\ln[1-\rho\tilde{h}_2(k)]-\rho\tilde{h}_2(k)-\frac{[\rho\tilde{h}_2(k)]^2}{2}\right\}, \tag{30}$$

where $\tilde{h}_2(k)=\int d\mathbf{r}h(r)\exp(2\pi i\mathbf{k}\cdot\mathbf{r})$ is the Fourier transform of $h_2(r)$ and the integration is over $\mathbf{k}$ space. This contribution can be added to the original RA giving rise to a renormalized ring approximation (RRA) $\tilde{S}^{(r)}$, which is

$$\begin{aligned}\frac{\tilde{S}^{(r)}}{k}=-\frac{1}{2}\sum_{p\geqslant 2}\frac{1}{p}\int d\{\mathbf{2p}\}\prod_{i=1}^{2p} n_1(\mathbf{i})h_2(\mathbf{12})\\ \times h_2(\mathbf{23})\cdots h_2(\mathbf{2p1}),\end{aligned} \tag{31}$$

a sum over all even-order rings and, for homogeneous systems, the result is

$$\frac{\tilde{S}^{(r)}}{k}=\frac{\langle N\rangle}{2\rho}\int d\mathbf{k}(\ln\{1-[\rho\tilde{h}_2(k)]^2\}+[\rho\tilde{h}_2(k)]^2). \tag{32}$$

Collecting together the different results obtained, i.e., Eqs. (26), (28), and (32) with Eqs. (1) and (2), we arrive at an entropy equation which includes a partial summation of the compressibility related contribution, i.e.,

$$\begin{aligned}\frac{S}{k}&=\langle N\rangle\left[\frac{5}{2}-\ln(\rho\lambda^3)\right]-\sum_{p\geqslant 1}\frac{1}{p!}\int d\{\mathbf{p}\}n_p(\{\mathbf{p}\})\omega_p(\{\mathbf{p}\})\\&\quad+\frac{\langle N\rangle}{2\rho}\int d\mathbf{k}(\ln\{1-[\rho\tilde{h}_2(k)]^2\}+[\rho\tilde{h}_2(k)]^2)\\&\quad+\langle N\rangle\left\{\ln 2-1+\sum_{p=2}^{\infty}\frac{(\ln 2)^p}{p!}\alpha_p\right\}\\&\quad-\langle N\rangle[\exp(\alpha_2-1)-\alpha_2].\end{aligned}\tag{33}$$

It can be emphasized that this equation is, although an approximate one, a rather general one in the sense that does not depend on any kind of specific, system-related assumptions. In other words, it can be applied, e.g., to the associative Wertheim-Ornstein-Zernike equation [16,17] as well as to systems with directional forces [18].

V. HARD SPHERES

We will discuss some numerical aspects of our proposal by implementing it, in a preliminary way, in the paradigmatic system of liquid state theory, i.e., HS. Essentially, we propose two substitutions: (i) that the term $(\alpha_2-1)/2$ (or $-1/2$ in the incompressible approximation) be replaced by $(S_a^{(c)}+S_b^{(c)})/\langle N\rangle k$, i.e.,

$$\frac{\alpha_2-1}{2}\rightarrow\Gamma_1=\ln 2-1+\sum_{p=2}^{\infty}\frac{(\ln 2)^p}{p!}\alpha_p-\exp(\alpha_2-1)+\alpha_2,\tag{34}$$

and (ii) that the RA [a $-$ sign is missing in Eqs. (40) and (41) of Ref. [5]] be replaced by the RRA; i.e.,

$$\frac{S^{(r)}}{\langle N\rangle k}=\frac{1}{2\rho}\int d\mathbf{k}\left\{\ln[1+\rho\tilde{h}(k)]-\rho\tilde{h}(k)+\frac{[\rho\tilde{h}(k)]^2}{2}\right\}\tag{35}$$

is replaced by Eq. (32). Let us discuss them.

(A) The first difficulty is that the Γ_1 term depends on all the r-body density fluctuations α_r and so must be either approximated by a (guessed) functional of α_2 or its contribution from $p=3$ on neglected. As we think it is important to have the right limiting behavior, we choose to approximate $\Gamma_1'=\Sigma_{p\geqslant 3}$ by a functional of α_2 that obeys the known constraints, i.e., the high-density ($\Gamma_1'=0$) and low-density [$\Gamma_1'=1-\ln 2-(\ln 2)^2/2$] limits as well as its first term in a density expansion [$(\alpha_2-1)/2$]. We therefore propose for Γ_1' a quadratic expansion in α_2 and thus obtain, for Γ_1,

$$\begin{aligned}\Gamma_1&=\ln 2-1+\frac{\alpha_2}{2}[3-4\ln 2-\alpha_2(1-2\ln 2)]\\&\quad-\exp(\alpha_2-1)+\alpha_2,\end{aligned}\tag{36}$$

which has the correct limits at low and high densities as well as the correct limiting slope of 1/2. A more sophisticated approach, where α_3 is evaluated and a proposal for the remaining sum made, was discarded because, as the leading coefficient of Γ_1' is $(\ln 2)^3/3!\approx 0.055$, a highly accurate three-body function is needed for the improvement to make sense. In this way, Γ_1 envelopes the line $(\alpha_2-1)/2$. There is, in this context, another point worth mentioning. While the contribution

$$\Gamma_2=-\frac{\rho}{2}\int d\mathbf{r}[g(r)\ln g(r)-h(r)]\tag{37}$$

converges quite rapidly (as a function of the upper integration limit) [7], even in the high-density case, in our proposal we are forced to a separated evaluation of both integrals and each one of them has a oscillating and slowly decaying tail at high densities.

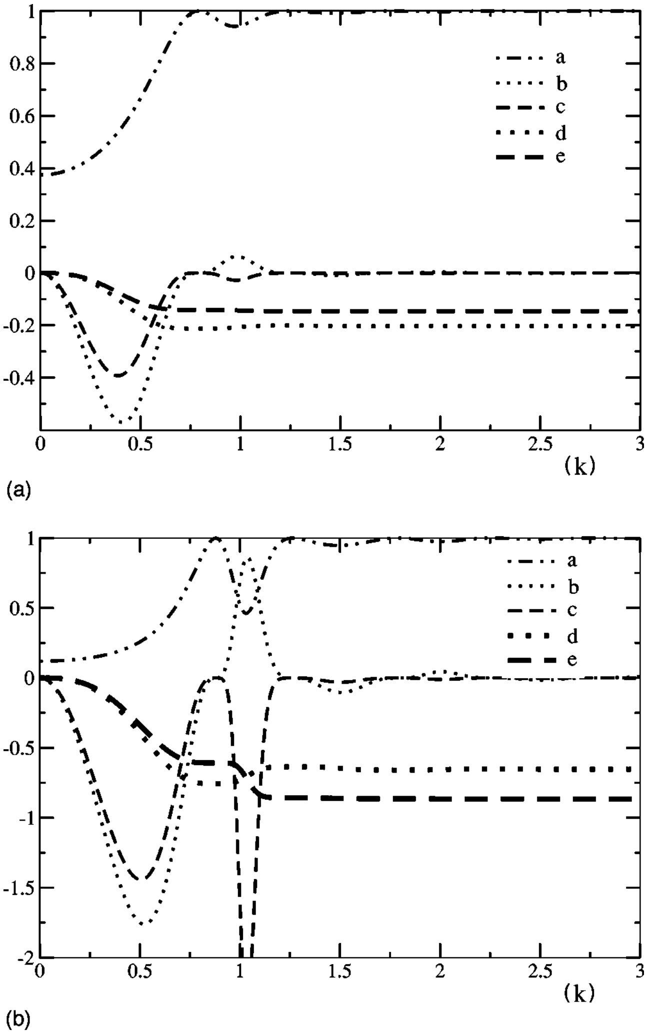

FIG. 1. (a) Results for $\eta=0.20$ are plotted. Curve a (dash–double-dotted line) shows the argument of the logarithm in the RRA, i.e., $\Lambda(k)=1-[\rho\tilde{h}(k)]^2$, the dotted curves b and d (heavier dots) show the integrand (including the factor $2\pi k^2/\rho$) and the integral, respectively, for the RA as a function of k, and the dashed curves c and e give the same information for the RRA. The units of k correspond to a HS diameter of 1 and the Fourier transform has been defined as $\tilde{h}(k)=\int d\mathbf{r}h(r)\exp(2\pi i\mathbf{k}\cdot\mathbf{r})$. (b) Results for $\eta=0.35$ are plotted and the meaning of the different curves is the same as in (a).

(B) Figures 1(a) and 1(b) show, for two different densities

TABLE I. Entropy results as a function of the density η, columns labeled S^{CS}, S^{Γ_2}, S^{RA}, and S^{RRA}, correspond to the (''exact'') Carnahan-Starling equation (37) [26] RA, and RRA, respectively.

η	S^{CS}	S^{Γ_2}	S^{RA}	S^{RRA}
0.1	-0.456	-0.412	-0.417	-0.453
0.15	-0.7374	-0.641	-0.763	-0.757
0.2	-1.063	-0.901	-1.103	-1.115
0.25	-1.444	-1.210	-1.532	-1.562
0.3	-1.898	-1.596	-2.070	-2.130

η $(=\pi\rho/6)$, medium-low ($\eta=0.2$) and medium-high ($\eta=0.35$), the behavior of the more relevant functions appearing both in the RA and the RRA. All of them were evaluated using the analytical solution of Wertheim and Thiele [22] of the Percus-Yevick (PY) approximation [23]. Depicted are (i) $\Lambda(k)=1-[\rho\tilde{h}_2(k)]^2$, the argument of the logarithm in the RRA, (ii) the integrands of both approximations, and (iii) their integrals. Important remarks are the following: (1) when the density increases $\Lambda(k)$ develops a deep well for $k\approx 1$, (2) due to this peak, the RRA outgrows the RA, and (3) the oscillations are longer ranged in the RA than in the RRA. The behavior of the RRA integrand underlines the importance of having an accurate description of the first peak in $h(r)$. In fact, for $\eta\gtrsim 0.4$, $\Lambda(k)$ becomes negative, pinpointing the breakdown of the PY approximation which, although remarkably accurate for low and medium densities, is well known to have essential failures at high densities, e.g., underestimates (by $\lesssim 10\%$ at $\eta=0.3$) the contact value of $h(r)$ (see, e.g., Ref. [24]).

Last, let us mention the importance of the neglected three- or more-particle contribution. Baranyai and Evans [25] have estimated the three-particle contribution to the entropy of HS and, although the expression they use should be modified for its inclusion in our formalism (there are compressibility contributions already included), their figures show, nevertheless, that the three-particle terms are already sizable for $\eta\gtrsim 0.2$.

For all these reasons we decided to test our entropy expression for hard spheres at η up to 0.3. As the PY approximation underestimates the contact $h(r)$ but lends itself to easy calculation of Fourier transforms and, on the other hand, the short-range behavior of $h(r)$ can be easily obtained from Monte Carlo (MC) simulations, while a reliable Fourier transform requires accurate knowledge of the long-range behavior of $h(r)$, we decided to use, on this density range, PY results for Fourier space and MC results for r space. More comprehensive results need not only MC extensive and reliable results, but also an estimation (at the very least) of the three-body term. This will be discussed in a future paper. Table I summarizes our numerical results and shows that there is an improvement at low densities. For larger densities a more complete study is needed, and will be left for future communications. It is also possible that the relation between the RA and RRA is similar to the one between the PY and HNC equations; i.e., although the HNC is a more complete (in the sense of including more diagrams in its expansion) theory than the PY, however, the PY equation yields better results for HS than the HNC equation, while the opposite is true for softer potentials. This is due to cancellations and, therefore, we will analyze our expression [Eq. (33)] for soft potentials in a forthcoming work.

VI. CONCLUSIONS

Through the discussion of the conceptual structure of the exact entropy expansion in terms of the distribution function we have proved two main results, summarized in Eqs. (12) and (33). We used two complementary points of view: the functional and the numerical one.

On the functional side, we have shown that, in the thermodynamic limit, the compressibility term only depends (as a functional) on the one-body distribution function [Eq. (12)]. Therefore, this functional dependence is such that it only enters in the constant density constraint and, in this way, the conceptual structure of the equation for the entropy is significantly simplified. As our results apply to the full entropy functional, they are valuable to any functional minimization, such as, e.g., those in [5,6]. It can also be mentioned that this theorem does not conflict with the work of Laird and Haymet [12]. They obtained the correct Debye-Huckel low-density expression for the entropy by including the $S^{(id)}$, $S^{(\ln)}$, and $S^{(r)}$ plus the compressibility related contribution of Eq. (10). As this term and, in fact, all the sums we did vanish when $\rho\rightarrow 0$ (including the one that renormalizes the RA), there is no contradiction between ours and theirs results. Last, as this result does not depend on the potential, it is also valid for the associative Wertheim-Ornstein-Zernike equation [16,17] as well as for systems with directional forces [18]. Turning now to Eq. (33) we see that, if, for just a moment, we neglect the renormalization in the RA, the contribution due to the r-body density fluctuations gives not only a theoretical understanding of the nature of the incompressible approximation, but also a description that is essentially correct in the low- and high-density limits (0 and $\ln 2-1-e^{-1}$, respectively). As the RA grows quite steeply when the density increases [12,13], one would expect that its renormalization has the right asymptotic behavior; however, this is not obvious at all and more careful (both in extension and potentials involved) numerical studies are needed. Let us also mention that these results extend trivially to mixtures (see, e.g., [13]) and, in this case, it is more convenient to work with the entropy per unite volume. This functional provides a robust and systematic way to develop fully analytical theories of liquids [19–21], which will be examined in future work.

From a numerical point of view, we have discussed the difficulties associated with the entropy equation and used, in a very rough and preliminary way, known results for HS to show, on the one hand, how an improvement at low densities is obtained and, on the other hand, to suggest that a more definite study should be done with greater care of the accuracy and internal consistency of the pair function used as an input. The numerical work presented in this paper is just a rough test that uses numerical simulations and PY results in a not altogether consistent way. In this context, it can be mentioned that the main difficulty is to obtain a good enough extrapolation of $h(r)$ [now both contributions to Eq. (37)

must be evaluated separately] in order to reliably evaluate both its integral and Fourier transform at high densities. This will be discussed in a paper now in preparation where an analytical description of the HS fluid is used. It has also been mentioned that work on a soft potential can help to elucidate the relative numerical accuracy of both the RA and the RRA.

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