On the Entropy of the Hard Sphere Fluid

András Baranyai* and Denis J. Evans

Research School of Chemistry, Australian National University, Canberra, Australia

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The expansion of the entropy into one-body, two-body, three-body, etc. contributions was applied to estimate the excess entropy of the hard sphere fluid. Configuration samples provided by computer simulation were used to determine the two-particle and three-particle correlation functions. The results show that even at intermediate densities a non-negligible part of the structural information is represented by four-body and higher order correlations.

Introduction

Recently we developed a direct method for calculating the entropy of simple classical fluids at equilibrium [1]. The method is based on a systematic expansion of the entropy in terms of the partial N-particle distribution functions given first by H. S. Green [2] for *the canonical* ensemble and subsequently by Nettleton and M. S. Green [3] and Raveché [4] for the *grand canonical* ensemble. Recently Green's expansion has been corrected for minor errors by Wallace [5]. However Wallace's paper itself contained some conceptual errors regarding the ensemble dependence of the entropy expansion. We [1] clarified these matters and proved, for the first time, that the form of the entropy expansion derived by Raveché for the *grand canonical* ensemble, is in fact a *local* expression and is thus an *ensemble invariant* form. The local, ensemble invariant, form derived by us is the key to the present method of computing the entropy. It can be written as

$$s = s_{pg} - \frac{1}{2} \varrho \int g^{(2)} \ln(g^{(2)}) \, d\mathbf{r} + \frac{1}{2} \varrho \int (g^{(2)} - 1) \, d\mathbf{r}$$

$$- \frac{1}{6} \varrho^2 \iint g^{(3)} \ln(\delta g^{(3)}) \, d\mathbf{r}^2$$

$$+ \frac{1}{6} \varrho^2 \iint (g^{(3)} - 3 g^{(2)} g^{(2)} + 3 g^{(2)} - 1) \, d\mathbf{r}^2 \ldots, \quad (1)$$

where $g^{(2)}$ and $g^{(3)}$ are the two- and three-particle correlation functions, respectively. We denote the total entropy by S, the entropy per particle, $S/N k_B$, by s, and the perfect gas contribution to the entropy per particle by s_{pg}. The contributions to the entropy can be identified with the highest order correlation functions present in the integral. Thus the two-body contribution, s2 is given by the first two integrals of (1) while the second two integrals of (1) is the three-body term, s3. The definition of $\delta g^{(3)}$ is,

$$\delta g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad (2)$$
$$= g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)/(g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \, g^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \, g^{(2)}(\mathbf{r}_2, \mathbf{r}_3)).$$

In [1] we performed numerical comparisons of (1) and a nonlocal alternative form which is valid *only* for the canonical ensemble. The comparisons were only carried out for the two-body contributions to the entropy.

To see the convergence of the expansion, we calculated and integrated the entire three-particle correlation function for the Lennard-Jones liquid at different state points in [6]. In order to avoid any kind of uncontrollable numerical uncertainties we discretised the three-particle correlation function. Thus, the integration could be replaced by summation in (1), starting from the origin and increasing the argument step by step for larger and larger upper limits. The resulting entropy expressions for the two-particle contribution, s2(R), and for the three-particle contribution, s3(R), as functions of the upper limit of the integration, R, are approaching an asymptotic region from where the further contributions to the entropy become negligible as it might be expected from the finite range of pair and triplet correlations in liquids.

We do not want to go into the technical details of the calculation in the present paper because a detailed account of this is given in [6]. To save some space and

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* Permanent address: Laboratory of Theoretical Chemistry, Eötvös University, Budapest, Múzeum krt 6–8, 1088 Hungary.
Reprint requests to Dr. A. Baranyai, Laboratory of Theoretical Chemistry, Eötvös University, Múzeum krt 6–8, Budapest-1088, Ungarn.

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Table 1.

ϱ	$-s2$	$-s3$	$-(s2+s3)$	$-s(ex)$	error(s2)	error(s3)	$-s2$ [8]	$-s3^*$	$-(s2+s3^*)$	s2%	$(s2+s3)\%$	$1/\Delta$
0.1	0.211	0.012	0.223	0.224	0.002	0.002	0.21	0.013	0.224	94.2	99.5	14
0.2	0.431	0.037	0.468	0.482	0.004	0.004	0.42	0.047	0.478	89.5	97.2	16
0.3	0.673	0.071	0.744	0.780	0.008	0.008	0.65	0.095	0.768	86.2	95.3	16
0.4	0.948	0.102	1.050	1.130	0.014	0.014	0.91	0.152	1.100	83.9	93.6	18
0.5	1.280	0.140	1.420	1.544	0.022	0.022	1.23	0.213	1.493	82.9	92.0	18
0.6	1.713	0.170	1.883	2.042	0.030	0.030	1.63	0.275	1.988	83.9	92.2	18
0.7	2.262	0.231	2.493	2.649	0.035	0.040	2.15	0.339	2.601	85.4	94.1	20
0.8	3.047	0.454	3.501	3.403	0.045	0.060	2.92	0.406	3.453	89.5	102.9	20
0.9	4.046	0.751	4.797	4.359	0.060	0.090	–	0.481	4.527	92.8	110.0	20

time we follow also the notation of this paper; therefore the reader should consult this reference when it is necessary.

The aim of the present paper is solely to provide the results obtained for the simplest model of fluids: for the system of hard spheres over its entire fluid density range.

Results and Discussion

The configuration samples were obtained from a standard Metropolis Monte Carlo simulation. The number of particles, N, in the periodic cube increased from 108 to 864 with the density in order to provide the system size neccessary for correlations to become negligible within a half of the boxlength. The maximum of random displacements was adjusted during the equilibrating part of the simulation so that about half of the trial moves was rejected. The reduced density, $\varrho = \sigma^3 N/V$, where V is the volume of the box and σ the diameter of spheres, $\sigma = 1$ for all cases.

We employed the same grid sizes for the calculations of the pair and triplet correlation functions for the sake of consistency. The grid size, Δ, decreased with the density in order to avoid the smoothing of the sharp first peaks of the correlation functions. In Table 1 we show the reciprocal values of Δ as used in our calculations for different densities.

The decline in the long range tail of $s3(R)$ has been extrapolated by a third order polynomial as function of $1/n$, where n is the number of configuration samples. This method differs from the one used in [6], where we applied only a linear extrapolation. This way we diminished considerably the slowly decaying feature of the extraplated curves for low and intermediate densities. For the high density cases, however, much longer runs are neccessary in order to reduce the uncertainty for the extrapolation scheme.

In Fig. 1 we display $s2(R)$, $s3(R)$ and $s2(R)+s3(R)$, for $\varrho = 0.7$ together with the pair-correlation function in order to compare the convergence of the 2 and 3 body components of the entropy to $g^{(2)}(R)$. They behave in a similar way to the corresponding curves for the Lennard-Jones liquid in [6].

Figure 2 shows the comparison of the two-particle entropy contributions, $s2(R)$, as running integrals for different densities. They have very similar characters: decreasing steeply in the hard core (excluded volume) region, then only a small contribution is given to them from the oscillations of the pair-correlation function. As a result of the high, sharp first peak and the less pronounced further oscillations of $g(R)$ for hard spheres (which is an obvious consequence of the hard sphere interaction) the $s2(R)$ function is much shorter ranged for this system than for a Lennard-Jones liquid at corresponding densities.
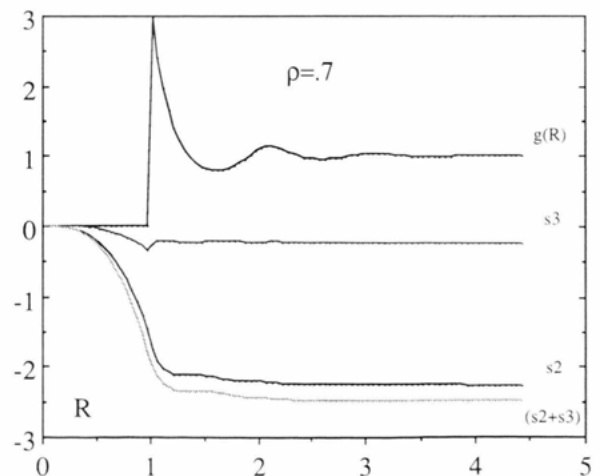

Fig. 1. The pair-correlation function, $g(R)$, the two-particle entropy, $s2(R)$, the three-particle entropy, $s3(R)$, and the sum of the latter two are shown as functions of distance, R, for $\varrho = 0.7$.
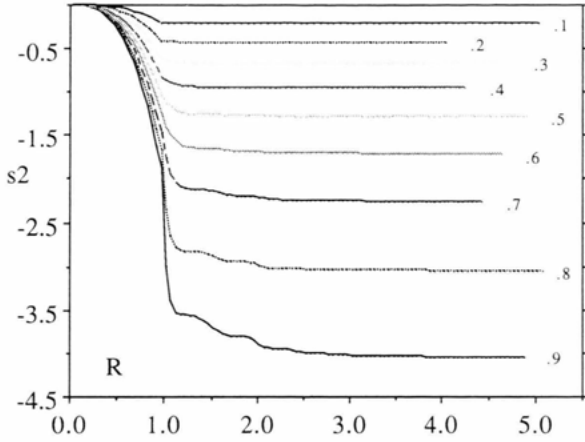
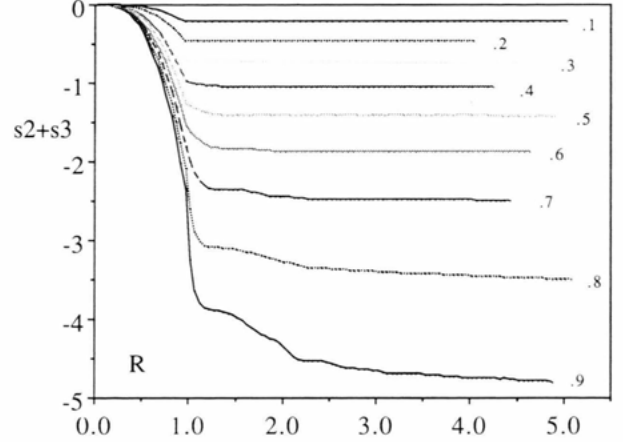Fig. 2. Two particle entropies, s2(R), for different densities as functions of distance, R.

Fig. 4. The sum of two-particle and three-particle entropies, $s2(R) + s3(R)$ for different densities as functions of distance, R.
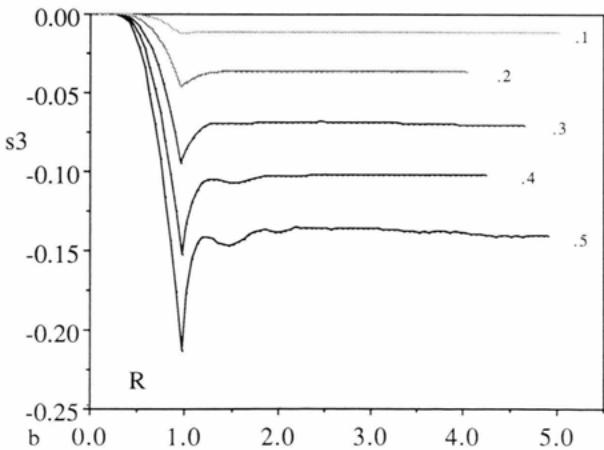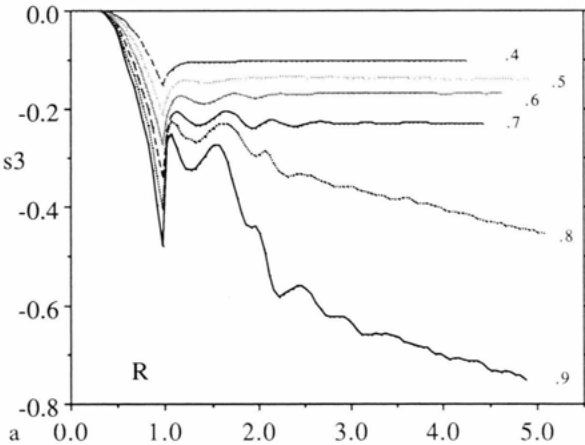

Fig. 3. Three-particle entropy contributions, s3(R), for different densities as functions of distance, R (a: high density cases; b: low density cases).

Figure 3 contains the three-particle entropy running integrals, s3(R), separately for higher (Fig. 3a) and lower (Fig. 3b) densities in order to show the fine structure of the low density cases as well. There is one obvious difference between the Lennard-Jones liquid and the hard sphere fluid three-particle entropy curves. In the former case we could distinguish three different regions of the s3(R) curves: at low densities the excluded volume term makes the major contribution but still some small part is given by the first peak region; at intermediate densities the excluded volume effect underestimates the final entropy while at high densities the converse is true. If we look at the low density s3(R) curves carefully, we can see that the hard core value of the functions at $R = 1$ is lower then the final asymptotic one. This means that the first, low density type of behaviour identified for the Lennard-Jones liquid is missing for hard spheres, clearly, as a result of the missing attraction part of their pair interaction.

Similarly to s2(R), the oscillations of the $s2(R) + s3(R)$ curves are also weaker for hard spheres then for the Lennard-Jones liquid at the corresponding densities. This can be seen from Figure 4.

In Table 1 we present all the interesting data concerning our calculations for hard spheres.

s2 and s3 are the two- and three-particle contribution, respectively, calculated by our method. s(ex) is the entropy of hard spheres calculated from the Carnahan-Starling equation of state [7]. We also show the entropy contributions (s2% and (s2+s3)%) as percentages of the total, s(ex), value. s2 [8] means the
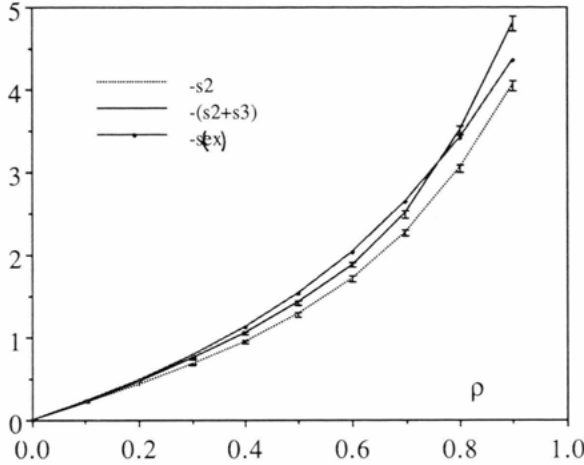
Fig. 5. Comparison of the entropy contributions s2 and s2 + s3, as function of density, ϱ, to the excess value, s(ex), calculated from [7].
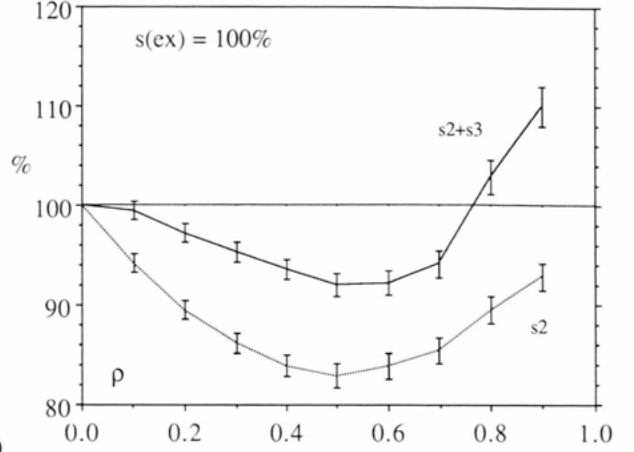

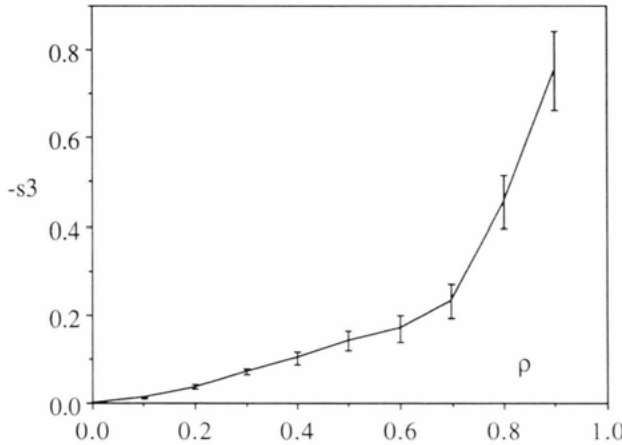Fig. 7. The percentage of the total configurational entropy given by s2 and s2 + s3.

Fig. 6. Calculated three-particle contributions, s3(R), with the errorbars originating from the imperfect extrapolation scheme for different densities as functions of distance, R.
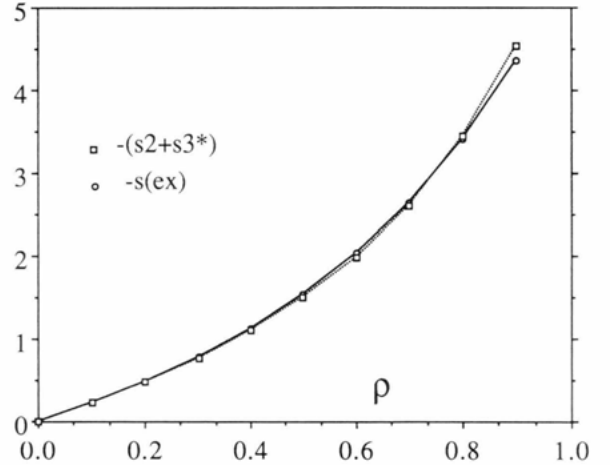

Fig. 8. Comparison of the excess entropy to s2 + s3* where s3* = s3(R = 1).

two-particle entropy values calculated by Mountain and Raveché [8] from the solution of the Percus-Yevick equation. The differences between our two-particle entropies and those of [8] probably come from the approximate nature of the Percus-Yevick form of $g(R)$. We marked the value of s3(R) at R = 1 as s3*. The reason why these values are shown explicitly lies in the fact that the sum of s2 + s3* is very close to the s(ex) values. In the low density cases the excess entropy is more negative then the sum of the first two configurational contributions. So the more negative

excess volume part added to s2 gives much better, as a matter of fact excellent, agreement with s(ex). In the high density region the reverse is true. The smaller s3* corrects the s2 + s3 values closer from below to s(ex). Nevertheless we do not think that this accidental agreement has any deep physical origin.

Figure 5 shows s2 and s2 + s3 from our calculation compared with s(ex). On Fig. 6 we depicted s3 alone to see the features of s3 and the errors of the determination more clearly on an enlarged figure. As we pointed out in [6], the large errors in the determina-

tion of the three-particle entropy are due exclusively to the imperfect extrapolation scheme used to obtain s3. The extrapolation is necessary to remove the unphysical entropy contribution coming from the more structured $g^{(3)}$ caused by the noise of the finite number of configurational samples. The error originating from the integration is smaller by two orders of magnitude.

Figure 7 shows the first two contributions to the total configurational entropy as percentages. The error in relative terms are much more uniform. At last, on Fig. 8 the remarkable agreement between s(ex) und s2 + s3* is shown.

Conclusions

The excess entropy of the hard sphere fluid is known very correctly since two decades. This provided a good opportunity to compare the two-body and three-body contributions of the entropy expansion to the total configurational entropy. It turned out that even at intermediate densities a small but unnegligible part of the total configurational entropy is provided by four-body and higher order correlations. Similarly to that what we experienced for the Lennard-Jones liquid near to the freezing density, the sum of the two- and three-particle contributions overestimates the excess entropy. This means that in the case of hard spheres too, the sum of the four-body and higher order terms must change sign at higher densities. In contrast to the Lennard-Jones liquid, the hard spheres entropy curves show only two and not three types of behaviour as functions of density. The difference in their low density behaviour can be attributed to the lack of an attractive wing in the hard sphere interaction potential.

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