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Entropy determination by scattering data

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Abstract. — It is shown that the entropy of simple fluids can be satisfactorily determined (i.e. with a 6 % relative error) from presently known structure factors by considering the Morita and Hiroike cluster expansion through the $O(\rho^4)$ contributions.

1. Introduction.

Scattering experiments can yield reliable estimates of the translational entropy of homogeneous systems, without any assumption on the (effective or McMillan-Mayer) particle interaction. This point has been emphasized by Luzzati [1] who obtained an approximation of the density derivative of the excess-entropy by an original method based on the information theory definition of the entropy. Actually, Luzzati's approximation coincides with the density derivative of the leading approximation of the entropy worked out by Green [2] in the canonical ensemble and by Nettleton and Green [3] in the grand-canonical ensemble. A few years later, the fundamental paper by Morita and Hiroike [4] showed how the virial series, relevant to the main thermodynamical potentials, can be partially resummed and expressed in terms of a « renormalized » cluster series [5]. Also this series can be written in terms of graphs which, however, obey stronger topological constraints and consist of new bond and vertex functions. In fact, the graphs can only be ring graphs (involving at least three bonds) or two-particle irreducible graphs (i.e. graphs which do not disconnect once one arbitrary bond has been taken away), while the vertex functions and the bonds respectively are the one-particle density-function ($\rho(r)$) and the two-particle total correlation function ($h(r_1, r_2)$). The practical importance of these results is evident, particularly for homogeneous systems where the one-particle density-function becomes a constant equal to the particle number density of the system and $h(r_1, r_2) = h([r_1 - r_2])$ can be obtained by Fourier inversion of the structure function measured by X-ray or neutron scattering experiments. Since the interparticle potential is not present in the cluster expansion of the entropy (see Eq. (1)), it is evident that the knowledge of the bond, of the vertex-function and of the graphs, at least in principle, allows one to determine the entropy of the system accurately by scattering data.

The aim of this paper is to report the results obtained by the aforesaid procedure for some typical liquid and gaseous states of argon and krypton.
Ravechè [6] explicitly worked out the first corrections to Nettleton and Green's approximation, in terms of the three and four-body correlation functions. These functions, however, are not easy to be determined. Nonetheless, Mountain and Ravechè [7] estimated the threeparticle correlation function contribution (3pcfc) to the entropy by using either the superposition approximation or a general relation which essentially expresses the contribution in terms of the density derivative of the isothermal compressibility. In this way, by the first method, the authors *approximately* determined the entropy through the 3pcfc only from the scattering data. The second method, *exact* through the 3pcfc, is a mixed one, since the required value of the isothermal compressibility derivative was obtained from the equation of state, so that its determination partly has a thermodynamical nature.

More recently, Baranyai and Evans [8] explicitly evaluated the three-body correlation function for a Lennard-Jones fluid by the Monte-Carlo method and obtained the first entropy determination relevant to the Lennard-Jones fluid, exact through the 3pcfc and based only on the two and three-point correlation functions.

Finally, Wallace [9] considered an approximation of the entropy which differs from Nettleton and Green's approximation because it contains the « canonical » factor 3/2 instead of the « grand-canonical » factor 5/2 (see Eq. (2)) and it neglects the contribution $- h(r)$ in the integrand of contribution $S_3$ (see Eq. (1)). Wallace's justification of this approximation was criticized by Baranyai and Evans [8], though from a numerical point of view the resulting entropy values for the considered liquid-metal cases turn out to be rather accurate.

The advantages of the Morita and Hiroike expression appear evident: from the renormalized cluster graphs the integral expression of the higher order contributions are known, since their bonds are the two-point correlation function, which can be determined from scattering experiments, whatever the interaction between the particles (provided these can be considered point-like).

2. Entropy theoretical expression.

Our analysis will focus on the case of one component simple fluids, as argon, where highly accurate experimental results are available. Owing to the facts that the samples are homogeneous and consist of one species of spherical particles, the renormalized cluster expansion of the entropy (see Ref. [4], Eq (4.25)) is

\[
\frac{S}{k_B} = \{V S_{\text{idl}}\} + \left\{ - V (\rho^{3/2}) \int_{R^3} \: dv \left[ \left[ 1 + h(r) \right] \ln \left( 1 + h(r) \right) - h(r) \right] \right\} \\
+ \{ \triangle - \square + \bigcirc - \bigcirc + \ldots \} \\
+ \{ \square \} \\
+ \{ \text{sum of all the diagrams, formed of } h\text{-bonds and (more than 4)} \rho\text{-vertices, which are more than doubly connected.} \} \\
= V \left[ S_{\text{idl}} + S_1 + S_4 + S_5 + S_6 \right].
\]  

(1)

In equation (1), $V$ denotes the volume of the system, $S_{\text{idl}}$ is the grand-canonical ideal-gas entropy per unit volume, i.e.

\[
S_{\text{idl}} = (5/2) \rho - \rho \ln (\lambda_T^3 \rho)
\]  

(2)

where $\lambda_T = (\hbar^2/2 \pi m k_B T)^{1/2}$ is the de Broglie thermal wavelength, $h$ is the Planck constant, $k_B$ is the Boltzmann constant, $T$ the absolute temperature and $m$ the particle mass.
The sum of the ring diagrams shown in equation (1) is denoted by $S, V$. It can be easily evaluated in terms of $\tilde{h}(q)$, the Fourier transform of $h(r)$,

$$\tilde{h}(q) = \frac{4\pi}{q} \int_0^\infty \sin(qr) r h(r) \, dr.$$  \hspace{1cm} (3)

Since $1/(2n)$ is the symmetry number [4] of the $n$-th order ring graph, $S, V$ becomes [10]

$$S, V = - \sum_{n=3}^\infty \frac{(-1)^n \rho^n V}{2n(2\pi)^3} \int \tilde{h}^2(q) \, dq \bigg[ \ln(1 + \rho \tilde{h}(q)) - \rho \tilde{h}(q) + \frac{\rho^2 \tilde{h}^2(q)}{2} \bigg]$$

$$= \frac{V}{4\pi^2} \int_0^{\infty} q^2 \, dq \left[ \ln \left( 1 + \rho \tilde{h}(q) \right) - \rho \tilde{h}(q) + \frac{\rho^2 \tilde{h}^2(q)}{2} \right].$$ \hspace{1cm} (4)

(The presence of the factor $V/(2\pi)^3$ in the first line above is due to the use of the formal identity $\delta(O) = \left( \frac{L}{2\pi} \right)^3$.) Finally, the integral expression of $S_4$, the two-particle irreducible graph with four vertices shown in equation (1), is

$$V S_4 = \frac{V \rho^4}{16} \int \cdot \tilde{h}(r_1) \tilde{h}(r_2) \tilde{h}(r_3) \tilde{h}(r_4) \prod_{1 \leq i < j \leq 4} (dv_i),$$  \hspace{1cm} (5a)

where $(1/16)$ is the symmetry number of the graph. By the same conventions adopted in handling Feynman graphs in momentum space, the previous contribution can be written as

$$S_4 = \frac{\rho^4}{16(2\pi)^9} \int \cdot \tilde{h}(q_1) \tilde{h}(q_2) \tilde{h}(q_3) \tilde{h}(q_4) \prod_{1 \leq i < j \leq 4} (dv_i).$$  \hspace{1cm} (5b)

This expression is more convenient from a computational point of view, since $\tilde{h}(q)$ is a quantity more directly related to the observed scattered intensity. In fact, $I(\theta)$, the intensity recorded at the scattering angle $\theta$, can generally be written as [11]

$$I(\theta) = N a^2(\theta) S(q)$$  \hspace{1cm} (6)

where

$$S(q) = 1 + \rho \tilde{h}(q).$$  \hspace{1cm} (7)

In equation (6) : $N$ is the number of the scattering particles while $a^2(\theta)$ is a known function which describes the elastic scattering of a particle of the neutron or photon beam by a particle (atom) of the sample and $q = (4\pi/\lambda) \sin(\theta/2)$ where $\lambda$ denotes the wavelength of the beam particle.

*Summarizing* : after having measured the scattered intensity, the so-called structure factor of the system ($\equiv S(q)$) turns out to be determined by equation (6) and, in turn, $\tilde{h}(q)$ is obtained from equation (7). Thus, by inversion of equation (3), $h(r)$ is determined by

$$h(r) = \frac{1}{2 \pi^2 r \rho} \int_0^\infty q [S(q) - 1] \sin(qr) \, dq.$$  \hspace{1cm} (8)

At this point, all the quantities present in equation (1) are known, at least in principle, and the entropy can be determined from the scattering data only. Of course, the precision of the
resulting values depends on the precision of the experimental $S(q)$’s, on that of the $h(r)$ obtained by equation (8) and on the number of terms accounted for in equation (1) as well as on the convergence rapidity of the renormalized cluster series. Being unable to answer these questions rigorously, we shall try to investigate them from an empirical point of view. In fact, we shall only evaluate contributions: $S_3$, $S_4$, $S_2$ and $S_1$. It is reminded that $S_{3\text{dl}}$ is given by equation (2); $S_1$ is Nettleton and Green’s contribution reported in equation (1). In terms of the radial distribution function $g(r) = 1 + h(r)$ it reads

$$S_1 = -2\pi\rho^2 \int_0^\infty r^2 \{g(r) \ln g(r) - g(r) + 1\}\,dr.$$  

(9)

$S_r$ is the sum of the ring contributions. By equations (4) and (7) it can be written as

$$S_r = \frac{1}{4\pi} \int_0^\infty q^2 \left\{ \ln S(q) + \frac{S^2(q) - 4 S(q) + 3}{2} \right\}\,dq.$$  

(10)

Finally, $S_4$ is contribution (5), which refers to the simplest more than doubly connected graph drawn in equation (1). By converting to polar coordinates, equation (5b) can be written as

$$S_4 = \frac{\pi^2 \rho^4}{(2\pi)^9} \int_0^\infty \tilde{h}(q_3)\,dq_3 \int_0^\infty \tilde{h}(q_1)\,dq_1 \int_0^\infty \tilde{h}(q_2)\,dq_2$$

$$\int_{|q_1 - q_2|}^{q_1 + q_2} \tilde{h}(t_1)\,t_1\,dt_1 \int_{|q_2 - q_1|}^{q_2 + q_1} \tilde{h}(t_2)\,t_2\,dt_2 \int_0^\pi \tilde{h}(X(\phi))\,d\phi$$  

(11a)

where

$$X(\phi) \equiv \sqrt{q_1^2 + q_2^2 - 2q_1q_2\cos(\theta_1)\cos(\theta_2) + \sin(\theta_1)\sin(\theta_2)\cos(\phi)}$$  

(11b)

and

$$\cos(\theta_i) \equiv \frac{q_i^2 + q_3^2 - t_i^2}{2q_iq_3}, \quad i = 1, 2.$$  

(11c)

In this way, our « best » approximation of the entropy will be

$$\frac{S}{k_B V} = S_\text{sc}^{(4)} = S_{3\text{dl}} + S_1 + S_r + S_4.$$  

(12a)

Subscript sc and superscript 4 respectively remind us that we are using quantities directly related to scattering data and that we are considering the first four contributions. By the same convention, we shall put

$$S_\text{sc}^{(2)} = S_{3\text{dl}} + S_1 \quad \text{and} \quad S_\text{sc}^{(3)} = S_{3\text{dl}} + S_1 + S_r.$$  

(12b, c)

For a given fluid, the accuracy of the $S_\text{sc}^{(n)}$ values ($n = 2, 3, 4$) will be estimated by comparing them with the thermodynamical entropy values, i.e. with the values obtained either by thermodynamical measurements or by using the fluid equation of state. For the comparison to be meaningful, owing to the uncertainties on the experimental $S(q)$’s, we must determine the resulting uncertainties on the $S_1$, $S_r$ and $S_4$ values. This will be done in the next section for the first two quantities. As expected, the accuracy of the different approximations will depend on the physical state of the fluid, i.e. on the region of the state parameters ($\rho, T$) where the fluid is. On general theoretical grounds, contribution $S_2$ as well as those related to the graphs
contributing to \( S_c \) are expected to be small at low densities, owing to factors \( \rho^n \) (with \( n \geq 4 \)) in front of their integral expressions and to the fact that the large number of \( \tilde{h}(q) \)'s, present in the integrands, considerably reduces the \( q \)-space region where the integrand is appreciably different from zero. This argument and the large computer time required in order to evaluate these contributions lead us to consider only the contribution \( S_\Gamma \) which, moreover, will be explicitly evaluated in one case only. Thus, as matter of fact, we shall mainly analyze approximation \( S^{(3)}_\text{nc} \) which appears to be the lowest order entropy approximation physically consistent throughout the fluid region. In fact, it is easy to show that approximation \( S^{(2)}_\text{nc} \) fails at the critical point. This interesting feature does not appear to have been noticed before, though its proof is very simple. At the critical point \( (\rho_c, T_c) \) in fact, the leading contribution of the total correlation function \( h(r) \), at very large \( r \)'s, is \( C/r^{(1-\eta)} \), where \( \eta = 0.06 \) is one of the critical indices \([12]\) and \( C \) is a suitable constant. Expanding the integrand of \( S_1 \) (see Eq. (1)) one finds

\[
- \frac{V \rho^2}{2} \left( \frac{h^2(r)}{r^2} - \frac{h^3(r)}{6} + \cdots \right) \approx - \frac{V \rho^2}{2} \left( \frac{C^2}{2 r^{2(1+\eta)}} - \frac{C^3}{6 r^{3(1+\eta)}} + \cdots \right)
\]

and the integral cannot converge owing to the slow decrease of the first contribution on the right hand side. By contrast, \( S^{(3)}_\text{nc} \) is satisfactory because \( S \) has a divergent behaviour which exactly cancels the divergence noted above. In order to make the point clear, it is first noted that the aforesaid asymptotic behaviour of \( h(r) \) implies that \( \tilde{h}(q) \approx \tilde{C}/q^{2-\eta} \) as \( q \to 0 \) (\( \tilde{C} \) is a suitable constant). Consequently, while the first two terms, present in the integrand of equation (4), have a singular but integrable behaviour as \( q \to 0 \), the remaining term \( h^2(q) \approx \tilde{C}^2/q^{4-2\eta} \) is not integrable. However, the Parseval equality implies that

\[
(1/(2 \pi)^3) \int \tilde{h}^2(q) \, dq = \int h^2(r) \, dr.
\]

Thus, the sum \( S_1 + S_\Gamma \) makes sense at the critical point. One concludes that \( S^{(3)}_\text{nc} \) is an entropy approximation that also works at the critical point, while \( S^{(2)}_\text{nc} \) does not. In passing, it is noted that this flaw is also present in Wallace's approximation which, in our notation, reads:

\[
S_{\text{wall}} = \rho + S_1 - (\rho^2/2) \int h(r) \, dr.
\]

Moreover, the subtraction of the last contribution makes the behaviour of this approximation, at the critical point, much worse than that of \( S^{(2)}_\text{nc} \).


From the analytical expressions (9) and (10) some general conclusions can be drawn both on the signs of contributions \( S_1 \) and \( S_\Gamma \) and on the \( r \)- and \( q \)-ranges which mostly contribute to the integrals. In fact, setting \( y = g(r) \), the integrand of \( S_1 \) will involve the function \( s_1(y) = y \ln y - y + 1 \). The plot of \( s_1 \) is shown by the continuous line of figure 1. It is always positive and presents a minimum (equal to zero) at \( y = g(r) = 1 \). This ensures that \( S_1 \) is always negative and that most of the contribution to \( S_1 \) comes up from the regions where \( g(r) = 0 \) and where \( g(r) \) shows pronounced peaks and dips. Thus one expects that \( S_1 \) turns out to be accurately determined once integral (9) has been numerically evaluated in the \( r \)-range which includes the first two peaks of \( g(r) \). In any case, since \( s_1(y) \approx 0 \), the numerically unavoidable truncation of the integral overestimates the exact value of
Fig. 1. — The continuous and the broken lines respectively plot the functions: $s_1(y) = y \ln y - y + 1$ (with $y = g(r)$) and $s_2(y) = \ln y + (y^2 - 4y + 3)/2$ (with $y = S(q)$) which, in turn, contribute to defining the integrands of (9) and (10), respectively.

$S_1$. Provided the fluid is not very close to the critical point this error will never be large because $h(r)$ has an exponentially decreasing behaviour.

We now consider contribution $S_1$ and set $y = S(q)$. The integrand of (10) involves the function $s_1(y) = \ln y + (y^2 - 4y + 3)/2$ whose plot is given by the broken line of figure 1. One sees that $s_1(y)$ monotonically increases from $-\infty$ to $+\infty$ as $y$ ranges in $[0, \infty)$. Thus the $q$-regions where $y = S(q)$ is smaller than one contributes to make $S_1$ negative, whilst the opposite takes place in the $q$-regions where $y = S(q) > 1$. Since $s_1(y)$ has an inflection and is zero at $y = 1$, one can reasonably expect that the most important contribution to $S_1$ is accounted for once integral (10) has been numerically evaluated in the $q$-range which extends up to the second/third peak of $S(q)$. In fact, the contributions arising from the small ripples at large $q$ average to zero, because $S(q) \approx 1$ and a further cancellation has to be expected on the basis of the integrand’s alternating sign. From these remarks one concludes that the sign of $S_1(q)$ as well as that of the error resulting from the truncation of integral (10) cannot be easily estimated in advance. However, the oscillatory behaviour, generally showed by $S(q)$ around the value $S(q) = 1$ [13], and the related alternating sign of the integrand $s_1(y)$ allow one to expect that $S_1$ is much smaller than $S_1$ [14].

The former discussion has implicitly assumed that $g(r)$ or, equivalently, $h(r)$ are accurately known. Actually $h(r)$ must be numerically determined by integral (8). An accurate evaluation of the latter requires that the experimental determination of $S(q)$ is carried through on a rather fine grid of values belonging to the explored interval $[q_{\text{min}}, q_{\text{max}}]$ and, moreover, that $q_{\text{min}}$ and $q_{\text{max}}$ respectively are sufficiently small and sufficiently large for the behaviour of $h(r)$ both at large $r$ s and at small $r$ s to be accurately determined.
experimental results, those of Yarnell et al. [15] are the ones which more closely meet these conditions. Therefore, the following discussion explicitly refers to the \( S(q) \) data of Yarnell et al. data obtained from neutron scattering experiments on liquid \(^{36}\)Ar at \( T = 85 \) K and \( \rho = 21.25 \) nm\(^{-3} \). Substituting these data in (8), the resulting \( h(r) \) turns out to be smaller than \(-1\) and shows some unphysical oscillations near the origin. Moreover, discarding some of the experimental \( S(q) \) values relevant either to the highest or the smallest \( q \) values observed, noticeable changes in the resulting \( h(r) \) take place near the origin, while no appreciable changes occur in the remaining \( r \)-range. This difficulty in obtaining the total correlation function from the observed structure function is well-known. In practice, it requires that \( h(r) \) is determined by \("hand\) at very small \( r \) s. Owing to the noted property that the region of small \( r \) s, where \( g(r) \approx 0 \), can largely contribute to \( S_1 \), it is important to estimate the uncertainty on the \( S_1 \) value resulting from the arbitrariness in the determination of \( h(r) \) near the origin. This has been done according to the following procedure. We have assumed that \( h(r) \) is given by integral (8), evaluated by the trapezoidal rule, in the range \( r = r_1 \), with \( r_1 \) to be defined later, and by the analytical expression

\[
h(r) = -1 + \alpha \left[ \exp(\beta r) - 1 \right] \quad \text{when} \quad 0 \leq r \leq r_1.
\]

Parameters \( \alpha \) and \( \beta \) were determined by requiring that expression (13) smoothly matches the value obtained by equation (8) at \( r = r_1 \). (More explicitly, denoting the values obtained from equation (8) by \( h_{\exp}(r) \), it was required that \( \hat{h}(r_1) = h_{\exp}(r_1) \) and that \( h'(r_1) = [h_{\exp}(r_1 + \delta/2) - h_{\exp}(r_1 - \delta/2)]/\delta \) with \( \delta = 0.025 \) Å.) Concerning the choice of \( r_1 \), this must lay outside and close to the upper bound of the noisy region. Of course this criterion is not sufficient to determine \( r_1 \) uniquely. To this aim, denoting by \( r_0 \) the largest \( r \) value where \( h(r_0) \approx -1 \) and \( h(r) \) starts to raise towards its main peak, we have considered the following \( r_1 \) values: \( r_{1,i} = r_0 + 0.1 \times k, \; k = 0, 1, 2, \ldots \). For each of these values, \( h(r) \) was determined by equation (13) in the range \( 0 \leq r \leq r_{1,i} \) and then, by equation (9), the value \( S_{1,i} \) was obtained for \( S_1 \). The set of the \( S_{1,i} \) values shows a neat minimum at a particular \( k \) value denoted by \( \bar{k} \). (In most of the cases \( \bar{k} = 2 \).) Thus the \( h(r) \) determination relevant to \( r_{1,i} = r_{1,\bar{k}} \) was taken as the most reliable one and \( S_1 \) was identified with \( S_{1,\bar{k}} \). Comparing this value with its nearest next ones, i.e. \( S_{1,\bar{k}+1} \) and \( S_{1,\bar{k}-1} \), we found a relative error of 3%. Although this value depends on the fact that the \( r_{1,i} \)'s have been taken spaced by 0.1 Å, it appears reasonable that the aforesaid error yields a first estimate of the error on \( S_1 \), related to the ambiguity in the \( h(r) \) determination at small \( r \) s. This ambiguity is related to the fact that the observed \( q \)-range is finite, to inaccuracies in the numerical evaluation of (8) and to the uncertainties on the \( S(q) \) values. It is advisable to consider the estimated error mainly due to the last two effects and to obtain an estimate of the errors resulting from a different choice of \( q_{\text{min}} \) and \( q_{\text{max}} \). This can be obtained by looking at the \( S_1 \) variations induced by a variation of the explored \( q \)-ranges. To this aim, in equation (8) we have neglected the \( S(q) \) values with \( q \ll 0.1175 \) Å\(^{-1} \) and we have applied the procedure illustrated above. The relative error in the resulting \( S_1 \) turned out to be equal to 1%. Quite similarly, neglecting all the \( S(q) \) values with \( q \gg 8.986 \) Å\(^{-1} \) (it is recalled that the \( q \)-range explored in the experiment of Yarnell et al. is \([0.0294 - 11.7474] \) Å\(^{-1} \) with a \( q \) spacing equal to \( \Delta q = 0.02937 \) Å\(^{-1} \)), the resulting relative error was 3%, so that the total error is \( \sim 4 \% \). In this way, adding the three errors, we conclude that the uncertainty on \( S_1 \) should not exceed 10%, at least for these experimental data. From equation (10), the uncertainty on \( S_1 \) arises only from the integral truncation. (It is recalled that the error on the \( S(q) \) is around 0.01 [15] and thus it can be neglected.) Proceeding as above, the small-\( q \) truncation yields an error of 20% while the high-\( q \) truncation error is 0.01%. One sees that the very small-angle scattering region is quite important in order to determine \( S_1 \) accurately and that the \( S_1 \) accuracy, using the accurate data of Yarnell et al., is roughly 20%. 
4. Results and conclusion.

The entropy values obtained by equations (8-10) and, in one case, by equation (11) (see the following discussion) and normalized in units kcal kg⁻¹ K⁻¹ are collected in the table I. They refer to argon and krypton fluids in some typical thermodynamical states, as specified in in columns one, two and three. The next three columns report the $\tilde{S}_{\text{ad}}$, the $\tilde{S}_1$ and the $\tilde{S}_r$ contributions to the entropy, where $\tilde{S}_{\text{ad}} = k_B S_{\text{ad}}/(\rho m_w)$ with $m_w$ the mass of a fluid molecule. (The definition of the remaining quantities with a bar is quite similar.) Column seven gives the sum of the evaluated contributions and, in parentheses, the number of the contributions accounted for. The thermodynamical values of the entropy [16, 17] are reported in column eight. In this way, the comparison of the values of the last two columns allows us to estimate the accuracy achieved in determining the entropy from scattering experiments.

| $^36\text{Ar}$ | 85 | 21.25 | 0.542 | −0.187 | −0.047 | 0.306(a) (3) | $S_{\text{thd}}$ |
| $^40\text{Ar}$ | 85 | 21.25 | 0.495 | −0.168 | −0.042 | 0.309(a) (4) | 0.322(d) |
| $^40\text{Ar}$ | 148 | 4.21 | 0.617 | −0.023 | −0.002 | 0.593(b) (3) | 0.585(d) |
| $^40\text{Ar}$ | 148 | 11.70 | 0.566 | −0.052 | −0.003 | 0.512(b) (3) | 0.485(d) |
| $^{84}\text{Kr}$ | 220 | 4.89 | 0.331 | −0.015 | −0.002 | 0.314(c) (3) | 0.315(c) |
| $^{84}\text{Kr}$ | 220 | 8.26 | 0.318 | −0.021 | −0.003 | 0.294(c) (3) | 0.293(c) |
| $^{84}\text{Kr}$ | 200 | 12.06 | 0.306 | −0.033 | −0.003 | 0.271(c) (3) | 0.267(c) |

The results of the first two rows have been obtained by the quoted Yarnell et al. results on $^{36}\text{Ar}$. Since common argon is mainly composed of $^{40}\text{Ar}$ (the latter mole fraction in fact is 99.6 %), owing to the entropy units used in reference [14], the values of the first row convert into those of the second. By direct computations, one immediately finds that $\tilde{S}_{\text{sc}}^{(2)} = 0.327$ while $\tilde{S}_{\text{sc}}^{(3)} = 0.285$ kcal kg⁻¹ K⁻¹. Recalling that the numerical uncertainty for both these values is $\sim 0.020$ kcal kg⁻¹ K⁻¹, the comparison with the thermodynamical entropy value shows that the first approximation is satisfactory, while the second is definitely unsatisfactory though it also accounts for contribution $\tilde{S}_r$. This result shows that the convergence of the renormalized cluster series is not quite uniform, in the sense that accounting for more contributions does not generally ensure more accurate results. Since $\tilde{S}_{\text{sc}}^{(2)}$ is more accurate than $\tilde{S}_{\text{sc}}^{(3)}$ close to the triple point, we addressed ourselves the question whether $\tilde{S}_{\text{sc}}^{(4)}$ were sufficient to yield an entropy approximation as accurate as the thermodynamical one. For this reason, we numerically evaluated contribution $\tilde{S}_d$ by equation (11). We found
\( \tilde{S}_4 = 0.025 \pm 0.005 \text{ kcal kg}^{-1} \text{ K}^{-1} \) [18]. The result reported in column seven shows that now the scattering and the thermodynamical values agree within the reported uncertainties.

The next two rows report the scattering entropy values obtained from the X-ray experimental data of Mikolaj and Pings [19]. The argon states are isothermal states close to the liquid and gaseous branches of the coexistence curve, while the temperature is not far from the critical one (\( \approx 150.86 \text{ K} \)). The relative discrepancies between the scattering and the thermodynamical entropies are \( \approx 2\% \) and \( 6\% \) for the gaseous and the liquid states, respectively. If one assumes that the previous error estimates on \( \tilde{S}_1 \) and \( \tilde{S}_4 \) also apply to these data, as in the former case the discrepancies appear to be too large and one would conclude that \( \tilde{S}_c \) cannot be neglected. However, owing to the fact that Mikolaj and Pings experiments are not as accurate as those of Yarnell \emph{et al.}, the errors on \( \tilde{S}_1 \) and \( \tilde{S}_4 \) are likely to be much larger, so that approximation (12b) or (12c) can be considered satisfactory in this parameter range.

Finally, the results of the last three rows have been obtained from the accurate neutron scattering data of Fredrikze [20] on krypton. The agreement with the thermodynamical values, obtained by interpolating the results reported in reference [17], appears quite satisfactory.

In general, from the results reported in the table one can conclude that, having accurate scattering results available, the simple approximation \( S_{\text{id}} \) is able to determine the entropies of the homogeneous systems composed of spherical particles with an accuracy better than \( 6\% \). The accounting for the \( S_{\tilde{S}} \) contribution generally does not yield better results except close to the critical point. Far from the latter, when \( S_{\tilde{S}} \) turns out to be large, the contribution of highly connected graphs cannot be neglected. Our analysis indicates that further evaluation of contribution \( S_{\tilde{S}} \) is sufficient to obtain an accurate result.

The aforesaid procedure can also be applied to multicomponent systems once all the relevant structure factors have been determined. Moreover, it could be usefully applied to monodisperse solutions of spherical micelles. The resulting entropy values in fact, would measure the degree of translation order of the micelles in the solution and are obtained independently on any assumption on the micelle effective interaction.

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References

[3] Nettleton R. E. and Green H. S., \emph{J Chem Phys.} 29 (1958) 1365. (By Nettleton and Green's approximation we mean Eq. (22) of this paper minus the triple integral contribution, which corresponds to the triangle graph shown in our Eq. (1). Anticipating the discussion carried through at the end of Sect. 2, one should note that also the full approximation considered by Nettleton and Green is satisfactory at the critical point.)
[5] A simpler derivation of these results was later reported by: Lebowitz J. L. and Percus J. K., \emph{J Math Phys.} 4 (1963) 116, 248 and 1495.
[14] Only close to the critical point, where $S(q)$ becomes large as $q \to 0$, $S$ can be expected to be positive and rather large.
[18] The evaluation was carried through both with the trapezoidal rule and with the Monte Carlo method. In the first case, the integration step was taken equal to $8 \Delta q$ in order to save computer time. The result was $\bar{S}_4 = 0.0198$ kcal kg$^{-1}$ K$^{-1}$ and the CPU time, on a 3 100-VAX station, was 102 h. The Monte Carlo method yielded $\bar{S}_4 = 0.0298$ kcal kg$^{-1}$ K$^{-1}$ with a CPU time of 2 h. The reported $\bar{S}_4$ value simply is the average of the previous values.