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Thermodynamic and scattering properties of dense fluids of monodisperse isotropic particles: an information theory approach

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Abstract. — The purpose of this paper is to use (X-ray or neutron) scattering spectra to assess the degree of order — more precisely, translational entropy — in a fluid of monodisperse isotropic particles, avoiding to rely on microscopic models and on computer simulations. The mathematical approach, borrowed from information theory, is based upon an ideal stochastic process: a particle is cast in a box containing a known number of particles, with a probability density corresponding to the distribution of interparticle distances defined by the scattering experiment. If the a priori probability density (i.e. before the X-ray scattering experiment) is uniform, then the information associated with the pair of probability densities can be determined: its expression is a straightforward function of the radial distribution function of the interparticle distances, $g(r)$. The information, moreover, is proportional to the derivative, with respect to concentration, of the (translational) entropy in excess over the perfect gas. The correlation with the thermodynamic properties of the system is discussed. By way of illustration, the treatment is applied to neutron scattering experiments performed on Ar and Kr: the agreement of the entropy determined by the thermodynamic and the scattering procedures is quite satisfactory. The validity of the treatment, and more generally the very possibility of determining the function $g(r)$ from the scattering data is shown to require that the function $[g(r) - 1]$ have a finite support.

1. Introduction.

We discuss in this paper the scattering properties of dense fluids of discrete particles. The analysis, formulated in terms of X-ray scattering, can be easily extended to other radiations, in particular neutrons.

In the absence of additional information, scattering studies of fluids of this type can yield the values of isothermal compressibility and of the average electron density fluctuations, provided that the experiments be performed on an absolute scale. If, moreover, the concentration is variable and the partial specific volume is known, then the particle mass can also be determined (reviewed in [1] and [2]). Besides, if the particles (and their interactions) are isotropic, the ratio $S(s ; n)$ of the intensity scattered at particle density $n$ and that corresponding
to an isolated particle can be determined experimentally. When $S(s; n)$ is known from $s = 0$ to $\infty$, then the radial distribution function $g(r; n)$ can be determined (see Sect. 3 and Fig. 1).

![Graphs showing intensity curves and radial distribution functions.]

Fig. 1. — Schematic representation of some of the functions in real (right frames) and in reciprocal space (left frames). $i(s; n)$ and $i(s; 0)$ are the intensity curves recorded at particle density $n$ and at infinite dilution: $S(s; n)$ is the ratio $i(s; n)/i(s; 0)$ scaled to be equal to 1 at large $s$. The Fourier transform (FT) of $[S(s; n) - 1]/n$ is the function $h(r; n) = g(r; n) - 1$. $g(r; n)$ is the pair correlation function, namely $[N(N - 1)2\pi r^2 g(r; n)/V]$ $dr$ is the number of pairs of particles whose distance is in the range $r; (r + dr)$.

The main purpose of this paper is to approach the problem using a procedure borrowed from information theory and to seek an explicit expression of entropy in terms of the pair distribution function $g(r; n)$. We first define two stochastic models and the corresponding probability densities, one relevant to a state of ignorance (namely, before the scattering experiment), the other to a state of knowledge (acquired via the experiment). Once the two probability densities are known, the determination of the information associated with the experiment, and thus of entropy, is a matter of routine. More precisely, we put forward an explicit expression of the excess of translational entropy over an ideal gas (at the same values of $T$ and $n$), in terms of the function $g(r; n)$.

Our analysis hinges upon the hypothesis that the support of the function $[g(r; n) - 1]$ is finite, i.e. that $g(r; n)$ becomes identically equal to 1 as $r$ is larger than a length $D$ much smaller than the dimensions of the sample.
Entropy, on the other hand, can be determined by standard thermodynamic procedures, at least when the system obeys an equation of state \( f(P, v, T) = 0 \). The "thermodynamic" and the "scattering" values of entropy can thus be compared. This test was performed on Ar and Kr, two fluids extensively studied by neutron scattering and thermodynamic techniques.

2. Notation.

- \( \mathbf{r} \) and \( r \): vector specifying position in real space and its modulus (in Å);
- \( \mathbf{s} \) and \( s \): vector specifying position in reciprocal space and its modulus (in Å\(^{-1}\));
- \( s = 2 \sin \theta / \lambda \), where \( 2 \theta \) is the scattering angle, \( \lambda \) the wavelength;
- \( V \): volume of the sample;
- \( \langle f(t) \rangle \): average value of the function \( f(t) \) over the volume of the sample:

\[
\langle f(t) \rangle = \frac{\int_V f(t) \, dv}{V} \tag{1}
\]

\( \langle f(t) \rangle \) [\( = f(t) \)]: average value of the function \( f(t) \) over the spherical shell of radius \( t \);

- \( \rho(\mathbf{r}) \) and \( \langle \rho \rangle \): electron density at the point \( \mathbf{r} \) and its average:

\[
\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \langle \rho \rangle \tag{2}
\]

- \( p(\mathbf{r}) \): autocorrelation function of \( \Delta \rho(\mathbf{r}) \):

\[
p(\mathbf{r}) = \int_V \Delta \rho(\mathbf{r} - \mathbf{R}) \Delta \rho(\mathbf{R}) \, dv_R \tag{3}
\]

- \( i(s) \): intensity function:

\[
i(s) = \int p(\mathbf{r}) \exp(-2\pi i \mathbf{r} \mathbf{s}) \, dv_r \tag{4}
\]

- \( N \): number of particles in the sample;
- \( c \) and \( n = N/V \): concentration (gm.cm\(^{-3}\)) and particle density (cm\(^{-3}\));
- \( i(s; n) \): intensity scattered by a system of identical isotropic particles, at density \( n \);
- \( i(s; 0) \): form factor of the particles;
- \( S(s; n) \): structure factor of the sample, normalized by setting its asymptotic value equal to 1:

\[
S(s; n) = i(s; n)/i(s; 0) \quad S(s; n) \Rightarrow 1 \quad \text{as} \quad s \Rightarrow \infty \tag{5}
\]

- \( g(r; n) \): radial distribution function; \( [2\pi r^2 nN g(r; n) \, dr] \) is the number of pairs of particles whose distance is in the range \( r \) to \( r + dr \) (Fig. 1):

\[
g(r; n) = 1 + (2/r) \int_0^\infty (s/n) [S(s; n) - 1] \sin(2\pi rs) \, ds \tag{6}
\]

- \( k, A, R \): Boltzmann’s constant, Avogadro’s number, gas constant \( (R = kA) \);
- \( P, v, T \): pressure, volume, temperature;
- \( \pi \): osmotic pressure;
- \( \chi_T \): isothermal compressibility. For a gas or a liquid:

\[
\chi_T = - (1/v) (\partial v/\partial P)_T \tag{7a}
\]
For a solution:

\[ \chi_T = \left[ 1/(C_0 \pi /\partial C) \right]_T. \]  

(7b)

3. Scattering properties.

In the absence of *a priori* informations on the structure of the sample, X-ray scattering experiments yield the value of but a few parameters of straightforward physical significance. One is the integral intensity; when the experiments are performed on an absolute scale [1], this parameter takes the form:

\[ 4 \pi \int_0^\infty s^2 \rho_\text{normal}(s) \, ds = \langle [\Delta \rho(r)]^2 \rangle / \langle \rho \rangle. \]  

(8)

Another parameter is forward scattering:

\[ i_\text{normal}(0) = \left\langle \Delta \rho(r) \int_{v_\text{cor}(r)} \Delta \rho(r + R) \, dv_R \right\rangle / \langle \rho \rangle \]  

(9)

where \( v_\text{cor}(r) \) (if it exists, see below) is the volume beyond which the electron density correlations (as defined by (8)) fade away. As a corollary (see Eq. (3)), the function \( p(r) \) is identically nil at all values of \( r \) larger than the dimension \( D \) of the volume \( v_\text{cor}(r) \). \( p(r) \) is then said to have a finite support of length \( D \).

The notion of finite support plays a prominent rôle in the analysis of scattering experiments: the possibility of extrapolating and interpolating a function \( i(s) \) defined by a finite set of measurements \( \{i(s_j)\} \), and thus the very existence of its Fourier transform \( p(r) \), require the support of \( p(r) \) to be finite. This condition has important practical consequences, discussed in the appendix.

When the sample consists of identical particles, the forward scattering is proportional to isothermal compressibility \( \chi_T \) [3]:

\[ S(0 : n) = nkT \chi_T. \]  

(10)

The expressions of \( \chi_T \) relevant to fluids and solutions are given in (7). If, moreover, the particles are spherically symmetric, then the scattering experiment may lead to the determination of the function \( g(r : n) \) (6). For the sake of clarity, let us specify the notation used in this work (Fig. 1):

\[ h(r : n) = g(r : n) - 1 \]  

(11)

\[ H(s : n) = [S(s : n) - 1]/n. \]  

(12)

These two functions form a 3D Fourier pair:

\[ h(r : n) = \int H(s : n) \exp(-2\pi i r \cdot s) \, dv_s. \]  

(13)

As a consequence of spherical symmetry, the functions \( rh(r : n) \) and \( sH(s : n) \) also form a 1D Fourier pair:

\[ rh(r : n) = 2 \int_0^\infty sH(s : n) \sin(2\pi rs) \, ds. \]  

(14)
4. Information content.

Suppose \( N \) particles in the sample, centered at the points \( \{ r_j \} \). A new particle is now cast in \( V \), with the constraint that its distance \( (r - r_j) \) to each of the \( N \) previous particles obeys a probability law proportional to \( g(r - r_j; n) \). The conditional probability \( r(r ; Y) \, \text{d}v_r \) of finding the new particle in the volume \( \text{d}v_r \), centred at the point \( r \), given the positions \( Y = \{ r_j \} \) of the \( N \) previous particles, is:

\[
r(r ; Y) \, \text{d}v_r = \left\{ \prod_{j=1}^{N} g(r - r_j ; n) \right\} \, [A(Y)] \, \text{d}v_r \tag{15a}
\]

\[
A(Y) = \int \left\{ \prod_{j=1}^{N} g(r - r_j ; n) \right\} \, \text{d}v_r . \tag{15b}
\]

We call \( r(r ; Y) \) the \textit{a posteriori} probability of \( r \), when \( Y \) is known. The \textit{a priori} probability, in the absence of correlations with the previous particles, is:

\[
t(r) \, \text{d}v_r = (1/V) \, \text{d}v_r . \tag{16}
\]

The probability associated with the pair of probability densities \( \{ r(r ; Y); t(r) \} \) is [4]:

\[
P(Y) = 2^{-\mathcal{K}(Y)} \tag{17a}
\]

\[
\mathcal{K}(Y) = \int r(r ; Y) \log_2 [r(r ; Y)/t(r)] \, \text{d}v_r \quad \text{(in bits)} \tag{17b}
\]

\( \mathcal{K}(Y) \) is usually called the \textit{information}. Using the expressions of \( r(r) \) (15) and of \( t(r) \) (16), \( \mathcal{K}(Y) \) takes the form:

\[
\mathcal{K}(Y) = \log_2[V/A(Y)] + \left[ \sum_{j=1}^{N} B_j(Y) \right] / [A(Y)] \tag{18a}
\]

\[
B_j(Y) = \int g(r - r_j ; n) \log_2 [g(r - r_j ; n)] \prod_{k \neq j} g(r - r_k ; n) \, \text{d}v_r . \tag{18b}
\]

The terms \( A(Y) \) (15b) and \( B_j(Y) \) (18b) are functions of the positions \( \{ r_j \} \). Although it would be desirable to tie these positions down to the radial distribution function \( g(r ; n) \) observed experimentally, we restrict our treatment (and thus avoid awkward mathematical problems) to the case each of the vectors \( r_j \) is a random independent variable. We thus obtain the first-order approximation — at vanishing particle density — of the \( n \)-dependent expression of the information. The empirical results discussed in section 6 seem to indicate that the high-order correlations between the position of the new particle and those of two or more of the particles previously present in the system do not play a major role, even at the fairly high densities of some of the experiments discussed in section 6.

If \( Y_0 \) is a set of random uncorrelated positions \( \{ r_j \} \), then the terms \( A \) (15b) and \( B \) (18b) take the form:

\[
A(Y_0) = \int \left[ \prod_{j=1}^{N} g(r - r_j ; n) \right] \, \text{d}v_r \approx V \left[ \langle g(r ; n) \rangle \right]^N \tag{19}
\]

\[
B_j(Y_0) = \int g(r - r_j ; n) \log_2 [g(r - r_j ; n)] \prod_{k \neq j} g(r - r_k ; n) \, \text{d}v_r \approx [ \langle g(r ; n) \rangle ]^{N-1} \int g(r - r_j ; n) \log_2 [g(r - r_j ; n)] \, \text{d}v_r . \tag{20}
\]
Substituting (19) and (20) in (18) yields:

$$\mathcal{I}(Y_0) = \frac{N}{V} \left( \langle g(r; n) \rangle \log 2 \right)^{-1} \int_V g(r; n) \log [g(r; n)] \, dr - N (\log 2)^{-1} \log \left( \langle g(r; n) \rangle \right)$$

(21a)

(log stands for natural logarithm). Finally, replacing $\langle g(r; n) \rangle$ by $S(0; n)$ (11-13):

$$V \left[ \langle g(r; n) \rangle - 1 \right] = H(0; n) = [S(0; n) - 1] (V/N) \ll V$$

(21b)

and taking into account spherical symmetry, the expressions of $\mathcal{I}(Y_0)$ and of $S(0; n)$ take the form:

$$\mathcal{I}(Y_0) = \frac{\partial \mathcal{I}}{\partial n} = \frac{N}{V} \left( \log 2 \right)^{-1} 4 \pi \int_0^\infty r^2 \{g(r; n) \log [g(r; n)] - g(r; n) + 1\} \, dr$$

(21c)

$$S(0; n) = 4 \pi n \int_0^\infty r^2 \{g(r; n) - 1\} \, dr + 1.$$  

(21d)

The information associated with casting one additional particle in the volume $V$, where $N$ particles are already present, entails an increase $\Delta n = 1/V$ of the particle density. Therefore, $\mathcal{I}$ is the derivative of information with respect to density:

$$\frac{\partial \mathcal{I}}{\partial n} = \frac{N}{V} \log 2 \, \kappa_{\text{scat}}(n)$$

(22a)

$$\kappa_{\text{scat}}(n) = 4 \pi \int_0^\infty r^2 \{g(r; n) \log [g(r; n)] - g(r; n) + 1\} \, dr$$

(22b)

$\kappa_{\text{scat}}(n)$ refers to one particle; its units are $\text{Å}^3$.

5. Thermodynamic implications.

We suppose that the fluid obeys an equation of state $f(P, v, T) = 0$.

Since information is proportional to entropy [5]:

$$- S = k \log 2 \, \mathcal{I}$$

(23)

a correlation may be sought between the parameter $\kappa_{\text{scat}}$ (or $\kappa_{\text{scat}}$) determined by the scattering experiments (22) and the thermodynamic properties of the system. It is timely, for that purpose, to analyze the operations ideally involved in the determination of the information content:

a) all the operations are performed at constant temperature;

b) the reference stochastic process — namely the uniform a priori probability density $t(r)$ (16) — corresponds to a perfect gas. Therefore, (22) refers to the entropy in excess to a perfect gas (at temperature and volume equal to those of the sample). Let $S_0(T, v)$ be the entropy of the perfect gas;

c) the stochastic operations disregard the work involved in bringing the extra particle from a reference pressure to the pressure $P$ of the sample; the contribution of that work must be subtracted from the entropy of both the sample and the perfect gas. Let $S_a$ and $S_{a; 0}$ be those terms.
The balance takes the form:

\[-\kappa_{\text{therm}}(n) = (kN)^{-1} \left\{ \partial \left[ (\bar{s} - \bar{s}_w) - (\bar{s}_0 - \bar{s}_{w,0}) \right] / \partial n \right\}_T \]  \hspace{1cm} (24)

Changing variable:

\[ n = N^2/v \]

\[ \partial n = - (N^2/v^2) \partial v \]  \hspace{1cm} (25a)

\[ \partial n = -(N^2/v^2) \partial v \]  \hspace{1cm} (25b)

yields the following expression of \( \kappa_{\text{therm}} \):

\[ \kappa_{\text{therm}}(n) = (v^2/kN^2) \left\{ \partial \left[ (\bar{s} - \bar{s}_w) - (\bar{s}_0 - \bar{s}_{w,0}) \right] / \partial v \right\}_T \]  \hspace{1cm} (26)

The various terms of (26) can be determined when the equation of state \( f(P, v, T) = 0 \) of the system is known (see, for example, [6]):

\[ (\partial \bar{s} / \partial v)_T = (\partial P / \partial T)_v \]  \hspace{1cm} (27a)

\[ (\partial \bar{s}_w / \partial v)_T = P/T \]  \hspace{1cm} (27b)

\[ (\partial \bar{s}_0 / \partial v)_T = (\partial \bar{s}_{w,0} / \partial v)_T = R/v. \]  \hspace{1cm} (27c)

The final « thermodynamic » expressions of \( \kappa(n) \) thus takes the form:

\[ \kappa_{\text{therm}}(n) = (v^2/kN^2) \left\{ (\partial P / \partial T)_v - (P/T) \right\} . \]  \hspace{1cm} (28)

Note that the larger \( \kappa \), the larger is also the decrease of entropy associated with the addition of one particle to the system.

Equations (22b and 28) refer to simple fluids. The same equations can be extended to macromolecular solutions, osmotic pressure \( \Pi \) replacing pressure \( P \).

6. Examples and verifications.

Any system whose function \( S(s) \) has been determined by X-ray or neutron scattering experiments and whose thermodynamic parameters \( \{P, v, T, (\partial P / \partial T)_v, (\partial v / \partial P)_T \} \) are known yields a test of the results of sections 4 and 5. Argon and krypton fluids (and of other elements of the group of the inert gases) are ideal for that purpose: the molecules are monoatomic, the atoms and the interatomic correlations are spherically symmetric, neutron scattering experiments have been performed in a variety of thermodynamic states, the thermodynamic equations of state are carefully explored. Only in a few of those scattering studies, yet, are the functions \( g(r) \) available in the literature.

One such case is Ar. In an early neutron scattering study, Yarnell et al. [7] tabulated the function \( g(r) \). We applied equations (21d and 22b) to that function and computed the parameters \( S(0)_{\text{scatt}} \) and \( c_{\text{scatt}} \). The values of the thermodynamic parameters \( \{P, (\partial P / \partial T)_v, (\partial v / \partial P)_T \} \) are reported in [8]; we thus computed \( S(0)_{\text{therm}}(10) \) and \( \kappa_{\text{therm}}(28) \). The values of all these parameters are given in the table (experiment \# 8).

More recently, Fredrikze et al. [9] and Barocchi et al. [10] have performed an extended series of neutron scattering experiments on gaseous Ar (over an \( s \)-range of approximately 0.020 to 1.59 Å⁻¹) and on liquid Kr (approximately 0.057 < \( s < 2.58 \) Å⁻¹) and have determined the function \( g(r) \). Dr R. Magli kindly performed the computation of the parameters \( S(0)_{\text{scatt}} \) and \( c_{\text{scatt}} \) using equations (21d and 22b). The values of \( S(0)_{\text{therm}}(10) \) and of \( \kappa_{\text{therm}}(28) \) were determined using the thermodynamic data reported in [11, 12]. The values of all these parameters are presented in the table.
Table. — Thermodynamic and scattering parameters. The neutron scattering experiments $\# 1$ to $\# 7$ were performed by Fredikze et al. [9] and by Barocchi et al. [10]; the functions $g(r)$ and the parameters $S(0)_{\text{scatt}}$ and $\theta_k_{\text{scatt}}$ (Eqs. 21d, 22b) were computed by Dr. R. Magli. The thermodynamic parameters $n$, $(\partial P/\partial T)_n$, and $\kappa_{\text{thermod}}$ (Eq. 28) correspond to the equations of state reported in [12] for krypton and in [11] for argon. Experiment $\# 8$ is reported in [7]; the parameters $S(0)_{\text{scatt}}$ and $\theta_k_{\text{scatt}}$ were determined using the function $g(r)$ tabulated in that paper. The values of the thermodynamic parameters were taken from [8]. In none of the examples was the function $g(r)$ computed under the constraint $S(0)_{\text{scatt}} = S(0)_{\text{thermod}}$ (see Appendix); for this reason the differences between $S(0)_{\text{thermod}}$ and $S(0)_{\text{scatt}}$ are fairly large.

<table>
<thead>
<tr>
<th>Experiment system</th>
<th>$# 1$ Kr</th>
<th>$# 2$ Kr</th>
<th>$# 3$ Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (deg)</td>
<td>199.2</td>
<td>169.1</td>
<td>130.1</td>
</tr>
<tr>
<td>$P$ (10$^6$ dyne cm$^{-2}$)</td>
<td>66.20</td>
<td>55.27</td>
<td>16.33</td>
</tr>
<tr>
<td>$n$ (10$^{21}$ cm$^{-3}$)</td>
<td>11.86</td>
<td>14.57</td>
<td>16.83</td>
</tr>
<tr>
<td>$(\partial P/\partial T)_n$ (10$^6$ dyne (cm$^2$ deg)$^{-1}$)</td>
<td>4.81</td>
<td>8.80</td>
<td>15.03</td>
</tr>
<tr>
<td>$S(0)_{\text{thermod}}$</td>
<td>0.711</td>
<td>0.191</td>
<td>0.065</td>
</tr>
<tr>
<td>$S(0)_{\text{scatt}}$</td>
<td>0.619</td>
<td>0.200</td>
<td>0.159</td>
</tr>
<tr>
<td>$\kappa_{\text{thermod}}$ (10$^{-24}$ cm$^3$)</td>
<td>230.6</td>
<td>289.2</td>
<td>381.2</td>
</tr>
<tr>
<td>$\theta_k_{\text{thermod}}$ (10$^{-24}$ cm$^3$)</td>
<td>242.0</td>
<td>274.2</td>
<td>347.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment system</th>
<th>$# 4$ Ar</th>
<th>$# 5$ Ar</th>
<th>$# 6$ Ar</th>
<th>$# 7$ Ar</th>
<th>$# 8$ Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>140.0</td>
<td>140.0</td>
<td>140.0</td>
<td>140.0</td>
<td>85.0</td>
</tr>
<tr>
<td>$P$ (14.93)</td>
<td>21.23</td>
<td>26.21</td>
<td>29.99</td>
<td>7.89</td>
<td></td>
</tr>
<tr>
<td>$n$ (0.90)</td>
<td>1.40</td>
<td>1.90</td>
<td>2.40</td>
<td>21.24</td>
<td></td>
</tr>
<tr>
<td>$(\partial P/\partial T)_c$ (0.141)</td>
<td>0.234</td>
<td>0.339</td>
<td>0.455</td>
<td>21.08</td>
<td></td>
</tr>
<tr>
<td>$S(0)_{\text{thermod}}$ (1.384)</td>
<td>1.719</td>
<td>2.216</td>
<td>3.010</td>
<td>0.052</td>
<td></td>
</tr>
<tr>
<td>$S(0)_{\text{scatt}}$ (1.316)</td>
<td>1.564</td>
<td>1.856</td>
<td>2.204</td>
<td>-0.045</td>
<td></td>
</tr>
<tr>
<td>$\kappa_{\text{thermod}}$ (307.3)</td>
<td>304.4</td>
<td>304.5</td>
<td>302.6</td>
<td>336.9</td>
<td></td>
</tr>
<tr>
<td>$\theta_k_{\text{thermod}}$ (274.2)</td>
<td>275.9</td>
<td>278.5</td>
<td>282.1</td>
<td>324.3</td>
<td></td>
</tr>
</tbody>
</table>

As illustrated in figure 2, the asymptotic convergence of the functions \( \int_0^r r^2 \{g(r) \log [g(r)] - g(r) + 1\} \, dr \) is smooth and reasonably fast, much more so at any rate than that of the functions \( \int_0^r r^2 \{g(r) - 1\} \, dr + 1 \): consequently, the computation of $\theta_k_{\text{scatt}}$ is easier and more accurate than that of $S(0)_{\text{scatt}}$. More precisely (see Fig. 2), the value of $\theta_k_{\text{scatt}}$ is strongly dependent upon the sharp fluctuations of the function $g(r)$ at small $r$ which, in turn, are sensitive to the shape of the function $S(s)$ at $s$ large. On the other hand, the value of $S(0)_{\text{scatt}}$ is strongly dependent on the form of $g(r)$ at large $r$, and thus (and obviously) on the properties of $S(s)$ near $s = 0$. It must be stressed, in this respect, that the value of $S(0)_{\text{thermod}}$ was used to extrapolate the scattering data to $s = 0$.

The agreement between $\theta_k_{\text{scatt}}$ and $\kappa_{\text{thermod}}$ (see the Tab.) is quite good, although $\kappa_{\text{thermod}}$ seems to be systematically larger. Not surprisingly (see Fig. 2 and Appendix) the agreement between $S(0)_{\text{scatt}}$ and $S(0)_{\text{thermod}}$ is less satisfactory. It would be premature to attempt...
to interpret these small effects — and to tackle other problems as discussed in section 7 — in terms of the properties of the fluids, at least before the experimental and computational errors are properly taken into account.

7. Discussion.

The aim of this work is to assess the degree of order, not to determine the microscopic properties of the system. For this reason we avoided to involve microscopic models in our analysis and to use computer simulations. The main result is the derivation of an explicit expression of translational entropy in terms of the function \( g(r) \). A similar expression of entropy has been obtained by Morita and Hiroike [13] using quite a different approach: equation (4.25) in their work is equivalent to equation (22b) in ours, provided the \( n \)-dependence of the function \( g(r; n) \) is negligible (I am grateful to S. Cicciariello for calling this result to my attention).

On the other hand, entropy can be measured by thermodynamic experiments and thus the results of the analysis tested empirically. We used, for that purpose, the data relevant to Ar and Kr, particularly favourable for the purpose. The overall agreement between the parameters \( \kappa_{\text{scatt}} \) and \( \kappa_{\text{thermod}} \) provided a rewarding justification of the approach adopted in this work.
The limitation to monodisperse spherically-symmetric particles is common to most treatments of dense fluids. The approximation involved in the choice of the stochastic model defining the a posteriori probability law \( r(r) \) (see Sect. 4) could set a more serious drawback. The model takes into account only the first-order correlations between the new particle cast in the sample and each of the particles previously present, on the assumption that the higher-order correlations which stem from the non-random distribution of the particles already present in the system are negligible. In spite of the observation reported by Barocchi et al. [10] that in some of the experiments of the table the influence of the tree-body interactions are not negligible, the absence of systematic correlations between the difference \( g_{\text{scatt}} - \kappa_{\text{thermol}} \) and the density \( n \) suggests that the effects of those higher-order correlations on \( \kappa_{\text{scatt}} \) are not large. A formal analysis of the contributions of the higher-order correlation terms can also be found in [13].

We also emphasize in this work the role played by the length \( D \) of the support of the function \( [g(r : n) - 1] \), i.e. the dimensions of the correlation volume \( v_{\text{corr}}(r) \) (6). This parameter is a novelty in the field and its value is worthwhile to explore. Besides, the knowledge of \( D \) leads to the elegant data reduction procedure described in the appendix. Those algorithms, nevertheless, have not been applied to the data analysed in section 6.

The results of this work could be extended to systems containing planar lamellae or cylindrical rods — instead of spherical particles — provided that the lamellae (or the rods) be infinitely extended (or infinitely long), all identical and parallel to each other and that their structure be invariant with respect to concentration. In contrast, and at least in its present form, the treatment does not apply to systems formed by elements whose structure is concentration-dependent (for example association colloids).

By way of conclusion we can conjecture about potential applications. One suggestion is to take advantage of the two approaches — thermodynamic techniques sense the whole of entropy, scattering techniques only the translational component — to discriminate the translational from the non-translational (rotational, etc.) components.

Examples of practical interest can be found in biology. One class of these examples is the highly concentrated protein solution present in some specialized organelles of living organisms; haemoglobin in erythrocytes [14], lens proteins in the eye-lens [15]. It may be interesting to assess the two classes of entropy components in these systems and to seek correlations with other parameters of physiological interest. Another example is crystallogenesis of macromolecular solutes (say, proteins). Entropy, of all thermodynamic parameters, is likely to be particularly relevant to crystallization. The concentration-dependence of entropy in the mother-liquor may thus mirror the propensity of the macromolecular solute to crystallize. Moreover, the relative evolution of the translational and the non-translational components of entropy as a function of a variety of physical and chemical parameters (temperature, pH, solvent composition, etc.) may perhaps help to understand the nature of the interactions that control crystallization processes.

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Appendix. Practical consequences of the support being finite in direct space.

The determination of the length $D$ of the support and the role that $D$ plays in the analysis of the scattering experiments have been discussed elsewhere [16-18], within the framework of small-angle X-ray and neutron scattering studies of macromolecular systems in solution. We shall briefly summarize those results and discuss their application to the present problem.

As a consequence of Shannon’s theorem [19], the Fourier transform $si(s)$ of a function $rp(r)$ identically nil beyond $r = D$ is entirely defined by its values at the lattice points $s_{h} = h/2D$ (from $h = 0$ to $\infty$):

$$si(s) = \sum_{h = 1}^{\infty} (h/2D) i(h/2D) \Phi(s, h)$$  \hspace{1cm} (A.1a)

$$\Phi(s, h) = \sin \left( \pi(2Ds - h) \right) / \pi(2Ds + h) - \sin \left( \pi(2Ds + h) \right) / \pi(2Ds + h).$$  \hspace{1cm} (A.1b)

If a set of $J$ measurements $\{Y_{j}\}$ is available:

$$\{Y_{j}\} = \{s_{j} i(s_{j})\}$$  \hspace{1cm} (A.2)

and if beyond $s = s_{\min}$ the $si(s)$ can be expressed as a function of a small number $K$ of parameters $\{A_{k}\}$ [16, 20]:

$$si(s) = f(\{A_{k}\}, s) \text{ for } s > s_{\min}$$  \hspace{1cm} (A.3)

then the system of $J$ equations:

$$Y_{j} = \sum_{h = 1}^{2D_{\min}} \left\{ (h/2D) i(h/2D) \right\} \Phi(s_{j}, h) + \sum_{h = 2D_{\min} + 1}^{\infty} f(\{A_{k}\}, h/2D) \Phi(s_{j}, h)$$  \hspace{1cm} (A.4)

can be solved and the values of the degrees of freedom $\{(h/2D) i(h/2D), A_{k}\}$ determined, provided their number $(2D_{\min} + K)$ is equal to or smaller than the number of measurements $J$.

A few equations should be added to the system. One expresses the condition $p(D) = 0$ (see (15)):

$$rp(r) = (1/D) \sum_{h = 1}^{\infty} (h/2D) i(h/2D) \sin(\pi hr/D)$$  \hspace{1cm} (A.5a)

$$p(D) = [rp(r)]'_{r = D} = (2 \pi/D) \sum_{h = 1}^{\infty} (h/2D)^{2} i(h/2D) \cos(\pi h) = 0.$$  \hspace{1cm} (A.5b)

Another takes into account the fact that geometric constraints often define the value of $p(0)$ (for example, $h(0) = -1$, see Fig. 1):

$$p(0) = [rp(r)]'_{r = 0} = (2 \pi/D) \sum_{h = 1}^{\infty} (h/2D)^{2} i(h/2D).$$  \hspace{1cm} (A.6)

A third equation corresponds to $i(0)$, whose value often is determined experimentally by thermodynamic measurements (10). The expression of $i(0)$ is given by (A.1):

$$i(0) = [si(s)]'_{s = 0} = \sum_{h = 1}^{\infty} (h/2D) i(h/2D) \Phi'(0, h)$$
$$= -2 \sum_{h = 1}^{\infty} i(h/2D) \cos(\pi h).$$  \hspace{1cm} (A.7)
When, moreover, the measurements \( \{ W(s_m) \} \) are distorted by experimental aberrations [17]:

\[
W(s_m) = \int_0^{\sigma_0} C(s, s_m) si(s) \, ds
\]

(A.8)

\( C(s, s_m) \) is the operator defining the aberrations, equations (A.4) should be replaced by a system of equations expressing the raw measurements \( \{ W(s_m) \} \) as a function of the same unknowns \( \{ (\hbar/2 \, D \, i, (\hbar/2 \, D), A_i \} \).

The system of equations can be solved by standard mathematical procedures. The statistical weight of the measurements \( \{ W(s_m), i(0) \} \) must of course be properly assessed and taken into account. Equations (A.5b, A.6) should be considered as infinitely accurate.

The final problem is to estimate the value of \( D \). Taupin and Luzzati [17] advocate, for that purpose, the use of a \( \chi^2 \) test of the difference between the observed and the expected values of the \( \{ W(s_m) \} \). The procedure consists in solving the mathematical problem (i.e. in determining the values of the \( \{ (\hbar/2 \, D \, i, (\hbar/2 \, D), A_i \} \)) for a series of values \( D \), and in exploring the graph \( \chi^2(D) \) vs. \( D \) in a search for the onset of the region where \( \chi^2(D) \) becomes quasi-independent of \( D \) (see Fig. 2 in [18]). It must be stressed that \( D \), of all the degrees of freedom of the problem, is peculiar in at least two respects: only its lower limit, not its value, can be assessed experimentally; the estimate of the lower limit is more sensitive to the statistical weight of the measurements than to their most probable value.

References