Pair and Triplet Distribution Functions of Molten KCl from an MD-Simulation

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Z. Naturforsch. **34a**, 993–996 (1979); received May 31, 1979

Pair and triplet distribution functions of the NaCl-type lattice and MD-simulated molten KCl are compared. Some similarities in the arrangement of the nearest neighbours are observed.

Hosemann and coworkers [1], [2] have deduced from our earlier molecular dynamics simulation of molten potassium chloride at the melting point [3] that this melt has a distorted NaCl-type structure. In the present paper we report on pair and triplet distribution functions extracted from the same simulation run and compare them with corresponding crystal functions [3a].

General

Radial or pair distribution functions (RDF's) $g_{AB}(r)$ of large multiparticle systems describe the frequency of particle pairs formed by particles of types A and B in its dependence on one variable, the interparticle distance r.

The frequency of particle triplets ABC depends on three variables, namely the three quantities needed to define a triangle. The corresponding functions are called triangular or triplet distribution functions (TDF's). As variables we choose the distances r and l of A and B from C and the angle ϑ at C. For the corresponding TDF's we write $H_{ABC}(r, l, \vartheta)$. If the distances r and l are equal, we drop the l in the brackets. In the case of a pure salt we use the subscripts + and − instead of the subscripts A, B and C.

Since an angle does not occur in the RDF's, the most interesting feature of the TDF's is their dependence on the angle ϑ at constant r and l. One has

$$H(\vartheta) = N^{-1}\, dn/d\vartheta \tag{1}$$

with

$$\int_0^\pi H(\vartheta)\, d\vartheta = 1\,, \tag{2}$$

where n/N is the running relative frequency.

As an alternative, the functions $h(\cos\vartheta)$ may be used:

$$h(\cos\vartheta) = -N^{-1}\, dn/d\cos\vartheta \tag{3}$$

with

$$\int_{-1}^{1} h(\cos\vartheta)\, d\cos\vartheta = 1\,. \tag{4}$$

It is easily seen that

$$h(\cos\vartheta) = H(\vartheta)/\sin\vartheta\,. \tag{5}$$

The long distance behaviour of the TDF's of any substance is

$$\lim_{r \text{ or } l \to \infty} H_{ABC}(r, l, \vartheta) = \tfrac{1}{2}\sin\vartheta\,, \tag{6}$$

$$\lim_{r \text{ or } l \to \infty} h_{ABC}(r, l, \cos\vartheta) = \tfrac{1}{2}\,. \tag{7}$$

The specific structure of a substance is only apparent at small values of r and l.

Pair and Triplet Distribution Functions of Crystals

For later comparison with molten salts we state same relations which are valid for ideal NaCl- and CsCl-type lattices:

1) The functions $g_{++}(r)$, $H_{--+}(r, l, \vartheta)$, $H_{+++}(r, l, \vartheta)$ and $H_{-++}(r, l, \vartheta)$ are invariant against simultaneous exchange of the subscripts + and −. This reduces the variety of the RDF's and TDF's and enables their specification by one subscript less. Thus we can write $g_u(r)$, $g_l(r)$, $H_{uu}(r, l, \vartheta)$, $H_{ll}(r, l, \vartheta)$ and $H_{ul}(r, l, \vartheta)$, where the subscripts u and l mean "unlike" and "like". In the TDF's the subscripts u and l indicate if the ions at the distances r and l are unlike or like the ion at the vertex of the angle ϑ.

2) In the NaCl-type lattice

$$r_l^{I}/r_u^{I} = \sqrt{2} = 1.414\,, \tag{8a}$$

$$r_u^{II}/r_u^{I} = \sqrt{3} = 1.732\,, \tag{8b}$$

$$r_l^{II}/r_l^{I} = 1.414\,, \tag{8c}$$

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0340-4811 / 79 / 0800-0993 $ 01.00/0

and in the CsCl-type lattice

$$r_l^{\mathrm{I}}/r_u^{\mathrm{I}} = \sqrt{4/3} = 1.155\,, \tag{9a}$$

$$r_u^{\mathrm{II}}/r_u^{\mathrm{I}} = \sqrt{11/3} = 1.915\,, \tag{9b}$$

$$r_l^{\mathrm{II}}/r_l^{\mathrm{I}} = 1.414\,, \tag{9c}$$

where the superscripts I and II refer to nearest and next nearest neighbours.

3) In the NaCl-type lattice

$$H_{\mathrm{uu}}(r^{\mathrm{I}}, \vartheta) = \frac{4}{5}\,\delta(\vartheta - 90°) + \frac{1}{5}\,\delta(\vartheta - 180°)\,, \tag{10}$$

$$H_{\mathrm{ll}}(r^{\mathrm{I}}, \vartheta) = \frac{4}{11}\,\delta(\vartheta - 60°) + \frac{2}{11}\,\delta(\vartheta - 90°) + \frac{4}{11}\,\delta(\vartheta - 120°) + \frac{1}{11}\,\delta(\vartheta - 180°)\,, \tag{11}$$

$$H_{\mathrm{ul}}(r^{\mathrm{I}}, l^{\mathrm{I}}, \vartheta) = \frac{1}{3}\,\delta(\vartheta - 45°) + \frac{1}{3}\,\delta(\vartheta - 90°) + \frac{1}{3}\,\delta(\vartheta - 135°)\,, \tag{12}$$

and in the CsCl-type lattice

$$H_{\mathrm{uu}}(r^{\mathrm{I}}, \vartheta) = \frac{3}{7}\,\delta(\vartheta - 70°) + \frac{3}{7}\,\delta(\vartheta - 110°) + \frac{1}{7}\,\delta(\vartheta - 180°)\,, \tag{13}$$

$$H_{\mathrm{ll}}(r^{\mathrm{I}}, \vartheta) = \frac{4}{5}\,\delta(\vartheta - 90°) + \frac{1}{5}\,\delta(\vartheta - 180°)\,, \tag{14}$$

$$H_{\mathrm{ul}}(r^{\mathrm{I}}, l^{\mathrm{I}}, \vartheta) = \frac{1}{2}\,\delta(\vartheta - 55°) + \frac{1}{2}\,\delta(\vartheta - 125°)\,, \tag{15}$$

where $\delta(\vartheta - \vartheta_0)$ is a δ-function of ϑ and the superscript I refers again to nearest neighbours.

The angles and frequencies occurring as parameters in these TDF's of crystals can be compared with the angles and heights of the maxima occurring in the TDF's of melts for the r and l values of the first maxima of the respective RDF's of the melts.

The distortion of the structure of a melt will cause the infinitely narrow peaks of the TDF's of the ideal crystal to be broadened and shifted. In the $H(\vartheta)$-plot a peak at $\vartheta = 180°$ will be transformed into a hump with zero elevation at $\vartheta = 180°$. If the displacement of an ion in the melt is on average spherically symmetric with respect to the position of the ion in the crystal, the shift of the maximum towards $\vartheta = 90°$ will become smaller as the corresponding peak in the TDF of the crystal approaches $\vartheta = 90°$. A peak at 90° will be broadened but will not be shifted.

Another reason for broadenings and shifts arises in the exploitation of computer simulations because certain ranges of r and l must be included in ϑ-histogramming in order to obtain sufficiently well documented TDF's. These shifts are towards smaller values of ϑ, especially for crystal peaks at small ϑ values. For very large r- (and/or l-)ranges the ϑ-dependences given by (6) and (7) are approached.

Distribution Functions from the MD-Simulation

The information used for the evaluation of the pair and triplet distribution functions of molten KCl was extracted from an extension of the MD simulation run II described in [3]. The extension was from 3.6 ps in [3] to 12 ps in the present work. 480 subsequent configurations, 0.025 ps apart, were analyzed, while Steffen et al. [1] used only 6 subsequent configurations, 1.2 ps apart. The root mean square displacement $\sqrt{6Dt}$ of the ions is approximately 2 Å for $t = 12$ ps and 1.4 Å for $t = 6$ ps.

For the evaluation of TDF's from every configuration, each of the 216 ions of the periodic cube was taken as the reference ion and the angles ϑ of all the triangles formed by the reference ion and two other ions in chosen concentric shells around the reference ion were stored. The angles have been histogrammed with an increment of 1 degree and the histograms were then normalized according to (2).

Results and Discussion

Within the limits of the quality of our averaging the pair and triplet distribution functions obtained

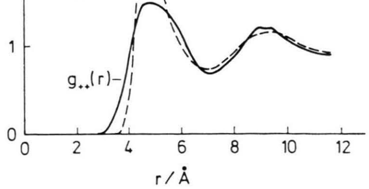

Fig. 1. Pair distribution functions of molten NaI from Ref. [4] for the rigid ion model, which is the model also used in our simulation.

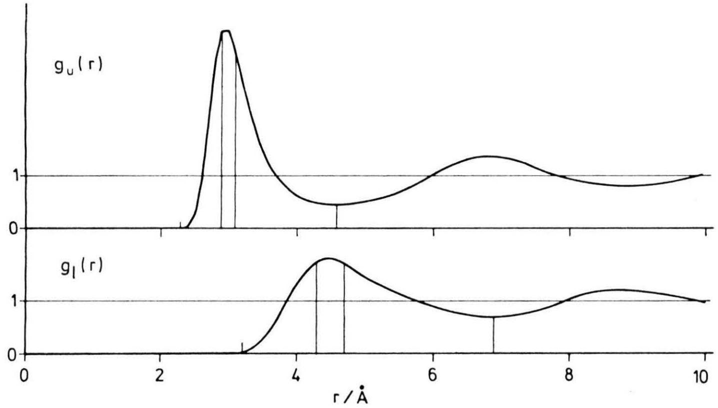

Fig. 2. Pair distribution functions of molten KCl obtained from 480 configurations, 0.025 ps apart. The chosen thicknesses of the r- and l-shells are indicated by vertical lines. For RDF's obtained from neutron diffraction and another MD-simulation, cf. Ref. [5] and Ref. [6], respectively.

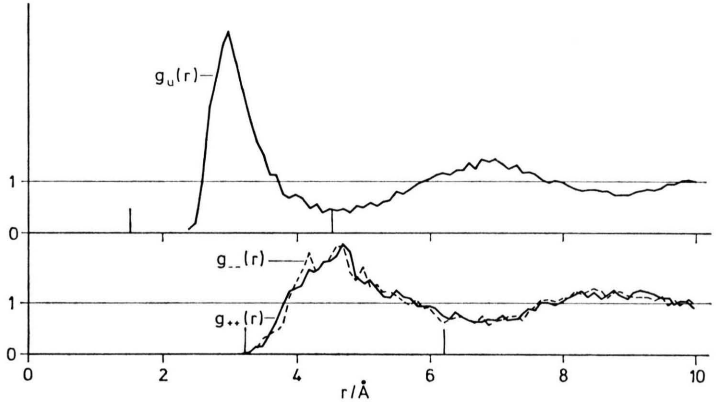

Fig. 3. Pair distribution functions of molten KCl obtained from 6 configurations, 1.2 ps apart, as underlying [1]. The chosen diameters of the LOVE spheres are indicated by vertical lines.

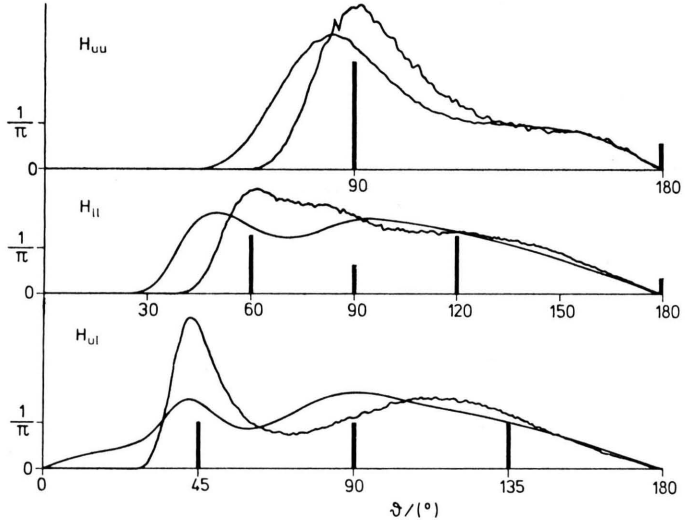

Fig. 4. Triplet distribution functions $H(\vartheta)$ of molten KCl. Rough curves: H_{uu} $(3.0 \pm 0.1, \vartheta)$, H_{ll} $(4.5 \pm 0.2, \vartheta)$ and H_{ul} $(3.0 \pm 0.1, 4.5 \pm 0.2, \vartheta)$. — Smooth curves: Huu $(3.45 \pm 1.15, \vartheta)$ H_{ll} $(5.05 \pm 1.85, \vartheta)$ and H_{ul} $(3.45 \pm 1.15, 5.05 \pm 1.85, \vartheta)$. The vertical bars indicate the positions and hights of the peaks of the nearest neighbours TDF's of the ideal NaCl-type lattice. The width of the bars is the increment of the histograms, i.e. 1°, and the hights are reduced by a factor 0.01.

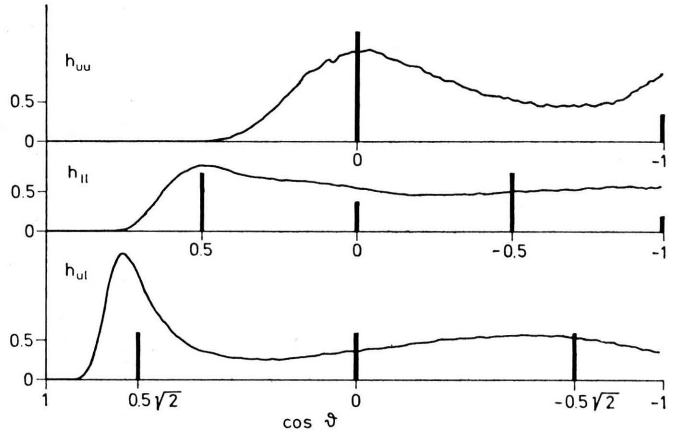

Fig. 5. The narrow shell TDF's h $(\cos \vartheta)$ of molten KCl. The vertical bars show again the peaks for the NaCl-type lattice. The width of the bars is the increment of the histograms, i.e. 1/90, and the hights are reduced by a factor 0.01.

are invariant against simultaneous exchange of the subscripts + and −. This is due to the similarity of the K^+- and Cl^--ions, except for the sign of their charges. If this is not the case, e.g. for molten NaI, the functions $g_{++}(r)$ and $g_{--}(r)$ are different [4], as illustrated in Figure 1. Because of this invariance we have accumulated our information to find g_u, g_l, H_{uu}, H_{ll} and H_{ul}.

The obtained functions $g_u(r)$ and $g_l(r)$ are shown in Figure 2. From these, the following ratios of distances of first (M_1) and second (M_2) maxima result:

$$r_l(M_1)/r_u(M_1) = 1.5, \quad r_u(M_2)/r_u(M_1) = 2.3\,,$$
$$r_l(M_2)/r_l(M_1) = 1.9\,.$$

The ratio 1.5 agrees quite well with the ratio $r_l^I/r_u^I = 1.4$ for the NaCl-type lattice, while the ratios involving next nearest neighbours (2.3 and 1.9) are much larger than the corresponding ratios for the NaCl-type lattice (1.7 and 1.4, respectively).

RDF's obtained from the less detailed information used in Ref. [1] are shown in Figure 3.

In the evaluation of the TDF's, the r- and l-values have been chosen to correspond to the first maxima of the RDF's. As examples for thin r- and l-shells the functions $H_{uu}(3.0 \pm 0.1, \vartheta)$, $H_{ll}(4.5 \pm 0.2, \vartheta)$ and $H_{ul}(3.0 \pm 0.1, 4.5 \pm 0.2, \vartheta)$ were evaluated, where the lengths are given in Å units; as examples for thick r- and l-shells the functions $H_{uu}(3.45 \pm 1.115, \vartheta)$, $H_{ll}(5.05 \pm 1.85, \vartheta)$ and $H_{ul}(3.45 \pm 1.15, 5.05 \pm 1.85, \vartheta)$ were calculated. The latter shells reach from the first appearance of the RDF's to their first minimum. The thicknesses of the shells are indicated in Fig. 2, and the TDF's $H(\vartheta)$ are shown in Figure 4.

In Fig. 4 it is seen that the first maxima of the thin shell TDF's lie close to the first peaks of the NaCl-type lattice, i.e. at 90°, 60° and 45°, respectively, and do not coincide with the first peaks of the CsCl-type lattice (70°, 90° and 55°, respectively). Little or no correspondence is seen between further humps of the TDF's and the other peaks of the crystal lattice functions. The curves for the thick shell TDF's are flattened and shifted towards smaller values of ϑ, as expected.

In Fig. 5 the thin shell TDF's $h(\cos\vartheta)$ are plotted to demonstrate the deviations from a homogeneous particle distribution within the shells, which would result in a horizontal line. In this plott we note an elevation of the h_{uu}-curve towards $\cos\vartheta = -1$, a phenomenon which corresponds to the peak at 180° of the NaCl-type lattice TDF. The elevation starts at $\cos\vartheta = -0.78$, which corresponds to a broad hump starting at $\vartheta = 141°$. As for the h_{ll} and h_{lu} functions, no correspondences with the crystal lattice other than those already seen in Fig. 4 can be detected in Figure 5.

Conclusion

In the present work, structural similarities between the melt and the NaCl-type lattice have been found

a) for the ratio of the radii of the nearest like and unlike neighbours shells,

b) as regards the smallest angles ϑ under which two ions in nearest neighbours shells are seen from the central ion, and

c) for the distribution of the ions within the nearest unlike neighbours shell.

A crystal like distribution of the ions in the nearest *like* neighbours shell, as was claimed in Ref. [1], is hardly evidenced by our h_{ll}-curve. The reason for this phenomenon may be sought in the limited statistics (cf. our Fig. 3) and the summary method of evaluation of the multiparticle DF's given in Ref. [1] or in the less structure sensitive nature of the TDF's as compared to the multiparticle DF's.

Our h_{ul}-curve as well does not reflect the NaCl-type structure except for the hump at $\vartheta \approx 45°$.

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