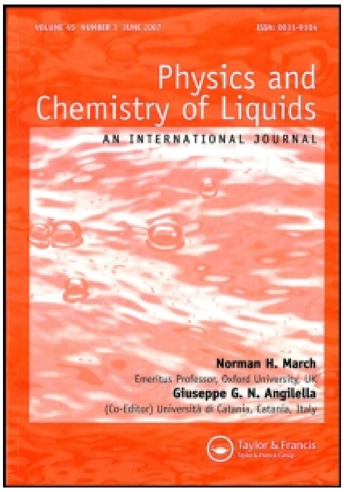

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

A Less Arbitrary Determination of Coordination Numbers in Disordered Systems

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To cite this Article McGreevy, R. L. , Baranyai, A. and Ruff, I.(1986) 'A Less Arbitrary Determination of Coordination Numbers in Disordered Systems', Physics and Chemistry of Liquids, 16: 1, 47 — 54
To link to this Article: DOI: 10.1080/00319108608078499
URL: http://dx.doi.org/10.1080/00319108608078499

Phys. Chem. Liq., 1986, Vol. 16, pp. 47–54
0031-9104/86/1601-0047$18.50/0

Printed in the United Kingdom

A Less Arbitrary Determination of Coordination Numbers in Disordered Systems

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(*Received January 20, 1986*)

The radial distribution functions, $4\pi r^2 g_{ij}(r)$, of molten alkali halides, obtained by Monte Carlo simulations, have been deconvoluted into contributions from the first, second, third, etc. neighbours. These individual distribution functions indicate that in alkali halide melts the first coordination sphere of the ions contains an integral or half integral number of unlike charged ions. The shapes of the individual distribution functions show characteristic changes from first coordination shell neighbours to second shell ones and this can be utilised to make the selection of the boundary of the coordination sphere less arbitrary. Such a deconvolution reveals more of the structure in the case of the like charged ion distributions as well.

1 INTRODUCTION

Coordination number is an important characteristic quantity of the structure of condensed phases, since it can usually be associated with one or a few possible geometrical arrangements of the particles surrounding the one taken as central. The major part of the interactions between the particle and its environment can then be estimated.

In the original concept a coordinated particle is an adjacent neighbour to the central one. The definition of the latter, however, is only unequivocal if the same kind of neighbours are at the same definite distance from the central one, i.e. in the cases of rather highly symmetric crystals of the elements or simple compounds. Then even the extension of the concept to next nearest neighbours, etc., leading to second, third, etc., coordination spheres, is still definite. The criteria of the definitions soon become arbitrary if either the order decreases or the chemical composition becomes more complicated. It is not our aim to discuss the latter case in which the existence of a chemical bond between neighbours is more important than their actual geometry. Instead we intend to compare purely geometrical definitions of coordination number with the physical significance usually expected of the concept. The comparisons are made on the Monte Carlo simulated configurations of 20 different alkali halide melts.[1]

2 RESULTS AND DISCUSSION

The most common methods of determining coordination number are based on the partial pair correlation functions. In an ideal and fluctuationless crystal the pair correlation functions would consist of a series of Dirac delta functions which can be considered to be Gaussian curves (or some similar function) degenerated from those constituting the pair correlation functions of real crystals at non-zero temperature. In simple cases at finite temperatures some of the first peaks are still well separated, thus the coordination number can be calculated by integrating the partial radial distribution function $G_{ij}(r) = 4\pi r^2 g_{ij}(r)$ (where $g_{ij}(r)$ is the usual partial pair correlation function) from $r = 0$ to the first minimum for the first coordination sphere, or from one minimum to the next for subsequent coordination spheres. If the minima are deep enough the overlap between coordination spheres is small and the coordination number obtained is rather accurate.

In highly disordered systems, however, the overlaps are considerable. Integration from minimum to minimum would still yield accurate values provided that the overlaps of the individual coordination spheres give rise to mutual compensations. Since this is incidental one can never be sure whether the coordination number so calculated indeed expresses what it is meant to, i.e. the number of adjacent neighbours. In addition the positions of the minima in the pair correlation functions are not usually well defined which brings about a statistical uncertainty.

This type of calculation has the advantage, in comparison to other methods discussed below, that it can be applied to experimental $g_{ij}(r)$ functions, while others are based on the complete set of spatial coordinates including angular correlations. There are, however, a number of variations on the method which within themselves produce different answers. They have been reviewed in relation to coordination in molten salts by Biggin and Enderby.[2] Integration of $G_{ij}(r)$ can be performed either to the first minimum in $g_{ij}(r)$ or in $G_{ij}(r)$. Because of the poor definition of these minima another approach is to assume that the first coordination shell contribution to $rg_{ij}(r)$ or $r^2g_{ij}(r)$ is symmetric about its peak, and hence to double the integral of $G_{ij}(r)$ to the peak in either of these functions.

The discrete geometrical concept of the Voronoi polyhedra provides another definition of coordination number.[3,4] A Voronoi polyhedron is the minimum volume polyhedron around a given particle whose faces are comprised of the perpendicular bisecting planes of the vectors pointing from the central particle to the others. Thus a strict geometrical definition of an adjacent neighbour might be based on the criterion that there is a face corresponding to it on the Voronoi polyhedron. There are, however, always some faces with very small surface area which correspond to particles obviously not in the given coordination sphere (e.g. the second neighbours in a simple cubic lattice do have corresponding faces on the Voronoi polyhedra). The coordination number thus derived is always, therefore, greater than that calculated by integration to a minimum.

In order to select only the relevant neighbours either some arbitrary criterion is set up on, say, the minimum surface area of a face, or an additional ad hoc geometrical criterion is added, e.g. a neighbour is considered "direct" when the vector pointing to the given particle from the central one pierces the corresponding face (otherwise the particle is mainly hidden behind a first neighbour).

An additional complication is introduced when the Voronoi polyhedra of unlike particles are to be determined. Although Fisher and Koch[5] have suggested an easily computable procedure to divide the space with respect to particle size yet preserving the properties of the Voronoi polyhedra of their filling the total space completely, there is some arbitrariness in choosing exact particle radii. It should also be considered that in a liquid there will be a significant number of particles that may be considered to be either "vacancies" or "interstitials". A method of identifying such "defects" is necessary before an appropriate definition of the relevant Voronoi polyhedra can be made.

In Figure 1 we show the partial pair distribution functions $g_{+-}(r)$ from Monte Carlo simulations of molten LiI and RbCl,[1] together with the first coordination sphere contributions from direct and indirect Voronoi polyhedra as defined above. The coordination numbers found by these methods and those found by integration of $G_{+-}(r)$ are summarised in Table I.

The method we suggest in this paper diminishes the arbitrariness of the determination of coordination numbers. It is based on a deconvolution of the radial distribution functions $G_{ij}(r)$, obtained from simulated configurations, into components corresponding to the radial distribution functions of first, second, third, etc. nearest neighbours. The results for LiI and RbCl are shown

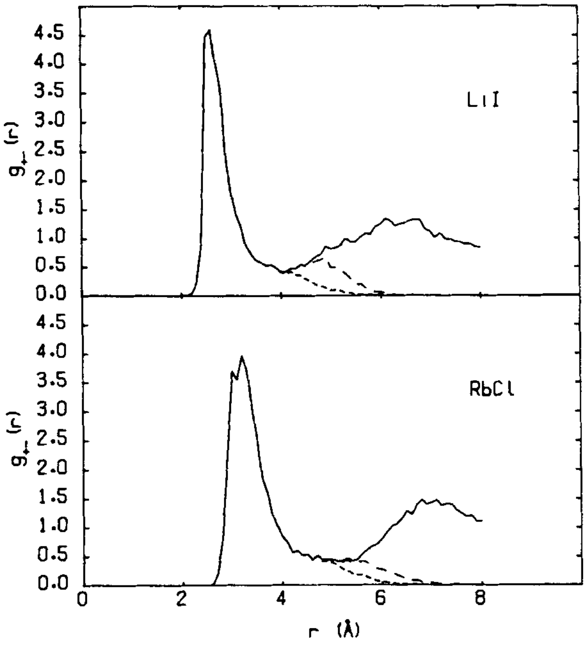

FIGURE 1 Simulated pair correlation function of unlike charged ions in molten LiI and RbCl (full curve) together with that of Voronoi polyhedra selected adjacent neighbours (long dashes) and direct neighbours (short dashes). For definitions see text.

TABLE I

Unlike neighbour coordination numbers derived by various methods.

Method	Coordination number	
	LiI	RbCl
1. Integration.		
(a) $g(r)$ minimum	4.2	5.7
(b) $r^2g(r)$ minimum	3.9	5.4
(c) $r^2g(r)$ symmetric	2.2	3.6
(d) $rg(r)$ symmetric	2.2	3.6
2. Voronoi.		
(a) Normal	7.3	8.2
(b) Direct	5.2	6.7
3. Deconvolution.	4	5.5

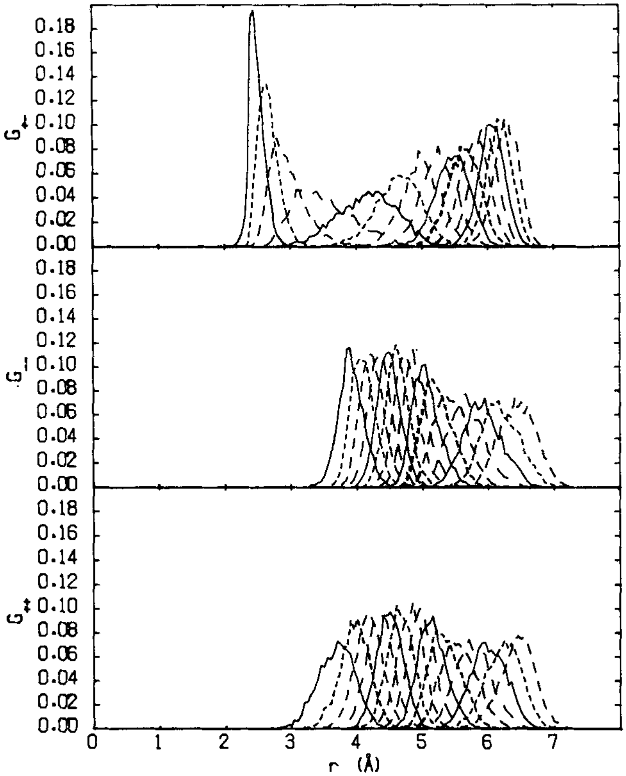

FIGURE 2 Deconvolution of the partial radial pair distribution functions ($4\pi r^2 g_{ij}(r)$) into components corresponding to the first, second, third, etc., nearest neighbours in molten LiI simulated by the Monte Carlo method.

in Figures 2 and 3. These are typical of those for all other molten alkali halides. It is clearly seen that the fourth and fifth unlike charged neighbours in the case of LiI are distributed in a characteristically different way, while for RbCl the distribution of the sixth unlike neighbour is intermediate between the characteristically different curves of the fifth and seventh neighbours. On the grounds of a qualitative impression one would conclude that the coordination number in LiI is 4, whereas that in RbCl is 5.5 in the sense that the sixth neighbour is shared equally between the first and second coordination spheres.

These distributions may be parameterised by their peak position, height, width at half-height, etc. Any of these parameters has been found to be useful for the determination of whether a given radial distribution curve is the last

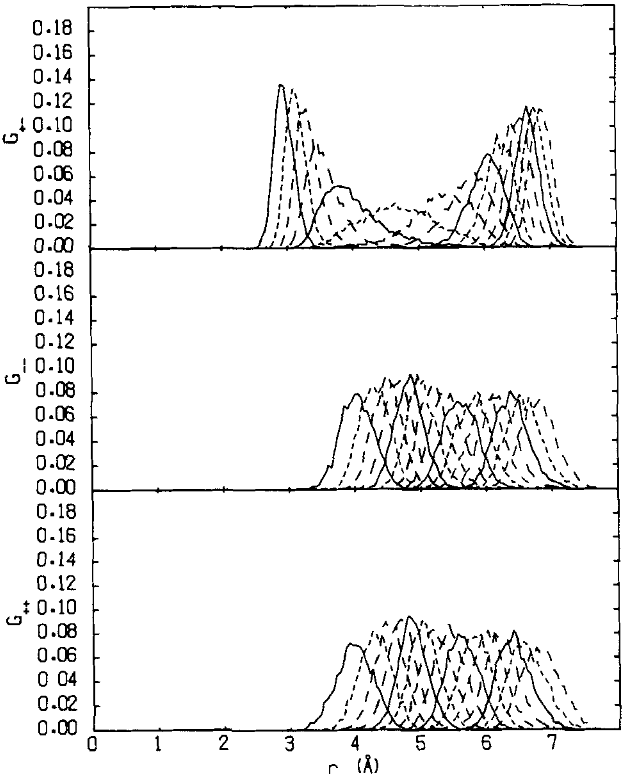

FIGURE 3 The same as Figure 2 for molten RbCl.

one of an inner coordination sphere, or an intermediate one, or the first one of an outer sphere. However the borderline between two coordination spheres is best determined by the distance where the ratio of the half-widths measured to either limit of the curves from the peak position is equal to unity. At the same time the average width at half-height is a maximum while the peak height is a minimum. This width ratio is shown in Figure 4 for molten LiI and RbCl.

In the case of like charged ions, where the differences between individual distribution functions are found to be smaller, statistical errors and the small size of the sample make such parameters more uniform and, thus, less useful. It can be found, however, that in LiI the like ion coordination is ≅ 10, while in RbCl it is ≅ 14 with a distinction between the first 8 and the remaining 6 ions. This distinction is visible as a shoulder in $g_{++}(r)$ and $g_{--}(r)$.

In Table I we compare the coordination numbers determined by this method with those obtained by the other methods described above. It can be

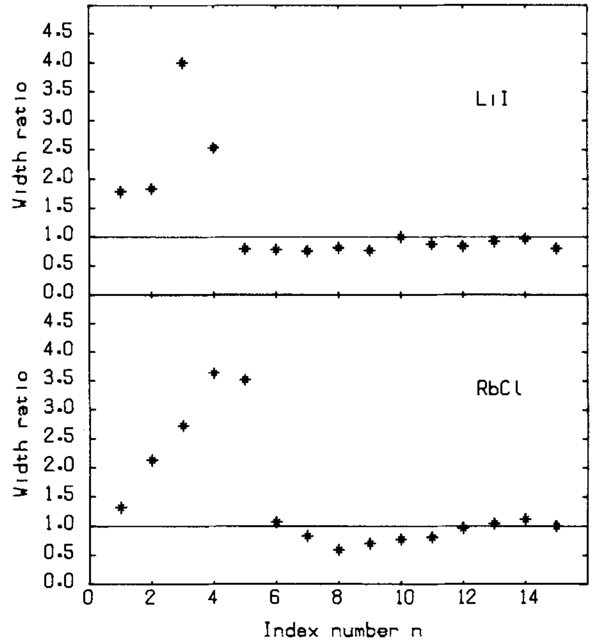

FIGURE 4 The ratio of the left-hand-side half width to the right-hand-side half width of the individual radial distribution curves (shown in Figures 2 and 3)as a function of their serial number.

concluded that the Voronoi procedures, as expected, overestimate the coordination, although they do provide direct geometrical information. Of the various integration procedures those assuming symmetry of either $rg_{+-}(r)$ or $r^2g_{+-}(r)$ about the peak underestimate the coordination because only the distribution of the first and second ions is anywhere near symmetric. The others are notably asymmetric. Integration to the first minimum in either $g_{+-}(r)$ or $G_{+-}(r)$ produces very similar coordination numbers (the difference depending on the depth of the minimum). From the individual ion distributions it can be seen that there is a considerable degree of mutual compensation of the contributions of first and second coordination sphere ions and that this is approximately symmetric about the minimum in $G_{+-}(r)$. Integration to the first minimum in $G_{+-}(r)$ produces, therefore, the closest estimate of the coordination to that found bv deconvolution. It is generallv an underestimate. The coordination number for experimental data may, therefore, be considered to be the closest integral or half-integral value above this estimate. The coordination numbers for the complete set of alkali halides are given in Table II.

TABLE II

Unlike neighbour coordination numbers found by deconvolution of $G_{+-}(r)$ for Monte Carlo simulations of molten alkali halides, (i), as compared to results of integration, always rounded up to the nearest integral or half-integral value, to the first minimum in $G_{+-}(r)$, (ii). Experimental values obtained by the latter method are given in brackets.

		F	Cl	Br	I
Li	(i)	4	4	4	4
	(ii)	4	4	3.5	4
Na	(i)	4.5	4.5	4.5	4.5
	(ii)	4.5	5 (5)[2]	5	4.5
K	(i)	5.5	5.5	5.5	5
	(ii)	5	5.5	5.5	5
Rb	(i)	5.5	5.5	5.5	5.5
	(ii)	6	5.5 (7)[6]	5.5	5.5
Cs	(i)	5.5	5.5	5.5	5.5
	(ii)	5.5	5.5 (5.5)[7]	6	5.5

The information on coordination derived by this deconvolution method suggests that there is a distinct geometrical aspect to the short range order in ionic melts. In RbCl the "sixth" ion appears to be an interstitial (presumably highly mobile). There may be a set of corresponding "vacancies". Such aspects of liquid structure deserve further consideration, particularly in relation to theories of melting.

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