

A Refined Ionic Model for Clusters Relevant to Molten Chloroaluminates

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A model of ionic interactions in neutral and ionized aluminium trichloride clusters, which accounts for ionic deformability through (i) effective valences and (ii) electrostatic and overlap polarizabilities, is evaluated for applications to classical simulation studies of the pure melt and of molten alkali chloroaluminates. The disposable parameters in the model are determined from the measured values of the bond length in the $(\text{AlCl}_4)^-$ molecular ion and of an Al-Cl bond length and a vibrational frequency in the Al_2Cl_6 molecular dimer. The model is tested against the remaining available data from experiment and from quantum chemical calculations on molecular bond lengths, bond angles and vibrational frequencies for Al_2Cl_6 , $(\text{AlCl}_4)^-$ and $(\text{Al}_2\text{Cl}_7)^-$ clusters. Structural and dynamical properties are also evaluated for the $(\text{Al}_2\text{Cl}_5)^+$, AlCl_3 and $(\text{AlCl}_2)^+$ clusters. The results for the energetics of dissociation, ion transfer and isomer excitation reactions are compared with as yet unpublished data obtained by P. Ballone in first-principles calculations by a density functional method. The overall quality of the tests supports the approximate validity and transferability of the model.

Key words: Ionic Clusters; Liquid Structure; Molten Salts.

1. Introduction

The melts of alkali chloroaluminates, represented by the formula $(\text{AlCl})_{1-x}(\text{AlCl}_3)_x$ where A is an alkali, have been studied extensively (for recent reviews see [1, 2]). They provide a striking example of a system in which the stability and coexistence of different complex anions depend strongly on composition. Evidence from Raman and infrared spectroscopy, thermodynamic measurements, X-ray and neutron diffraction and molecular dynamics calculations supports the view that, while the stoichiometric mixture at $x = 0.5$ can be regarded as a simple molten salt of alkali ions and tetrahedral $(\text{AlCl}_4)^-$ anions, the species $(\text{AlCl}_4)^-$, $(\text{Al}_2\text{Cl}_7)^-$, $(\text{Al}_3\text{Cl}_{10})^-$ and Al_2Cl_6 coexist in acidic melts ($0.5 \leq x \leq 1$) in proportions which vary with the overall composition. The larger complex anions consist of $(\text{AlCl}_4)^-$ tetrahedra sharing corners, while Al_2Cl_6 is formed by two tetrahedra sharing an edge.

At the end of the acidic composition range, pure AlCl_3 liquifies from a sixfold-coordinated crystalline

layer structure into a fourfold-coordinated melt [3, 4]. A cooperative rearrangement of the assembly of Al ions between octahedral and tetrahedral sites in the AlCl_3 crystal would drive a transition to the AlBr_3 type of structure, having dimeric Al_2Cl_6 units as basic constituents [5]. The view that melting of AlCl_3 yields a molecular liquid of correlated Al_2Cl_6 dimers was proposed a long time ago on the basis of X-ray data [6] and is consistent with the measured values of the thermodynamic melting parameters [7] and of transport coefficients of the melt [1], as well as with Raman scattering data and *ab initio* calculations of vibrational frequencies [8]. The Al-Al bond length in the melt should directly reflect the proportion of edge-sharing to corner-sharing $(\text{AlCl}_4)^-$ tetrahedra, but unfortunately the presently available neutron diffraction data are totally insensitive to the Al-Al interference [4].

In contrast, early simulation work by Rahman and coworkers [9 - 11] have shown extreme sensitivity of the predicted Al-Al bond length to the model adopted for the ionic interactions. For instance, Saboungi *et al.* [11] report that in their simulation model for liquid

NaAlCl_4 the mean Al-Al bond length drops from 4.6 Å to 2.5 Å on allowing for the induction of dipoles on the chlorines by the electric field. They also stress that within an ionic model the formation of the double-bridged Al_2Cl_6 species results from the stabilization of bent Al-Cl-Al triplets, relative to linear triplets and this is crucially dependent on halogen polarizability.

The above-mentioned results from studies of molten chloroaluminates have already motivated attempts at quantitative refinements of the ionic model used by Rahman and coworkers. These were aimed at accounting for the structure of the $(\text{AlCl}_4)^-$ molecular ion [12] and of the Al_2Cl_6 dimer [13] in the isolated state by inclusion of overlap deformations of chlorine ions. A suitable adaptation of the shell model developed in the sixties for the theory of lattice dynamics in ionic and semiconducting crystals [14] was used for this purpose. In essence, overlap polarizability accounts for changes in the state of overlap between the outer electronic shells of the halogens and of the metal ions, arising from relative displacements of the two ionic species. In the dipole approximation such short-range electronic distortions counterbalance the dipole induced on each halogen by the prevailing electric field. For alkali halides this approach has received a quantum mechanical justification from exchange perturbation theory [15, 16].

While the inclusion of overlap deformability in the ionic model yields excellent agreement with the available structural data for various halide clusters of Al and other trivalent metals, comparisons with their measured vibrational frequencies show a tendency to overestimate the stiffness of the bond-stretching modes [13, 17, 18]. A quantitative improvement of the usefulness of the model is the object of the present work. This is achieved through further simultaneous adjustments of the effective valence and of the core radius of the metal ion. Since bond lengths and bond angles are in essence determined by a balance between Coulombic and overlap repulsive forces, the high quality of the earlier structural predictions on clusters remains unaltered. However, in the new force balance the decreased net Coulomb attractions lead to softer overlap repulsions. The results are a softening of the bond-stretching modes and an improved account of the energetics of various reactions, in overall very good agreement with the available data from experiment and from first-principles calculations based on quantum chemical and density functional approaches.

2. Interionic Force Model

We write the potential energy $U(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\})$ of a cluster, as a function of the interionic bond vectors \mathbf{r}_{ij} and of the dipole moments \mathbf{p}_i carried by the halogens, as

$$U = \sum_{i \neq j} \left[\frac{z_i z_j e^2}{2r_{ij}} + \frac{1}{2} \Phi_{ij}(r_{ij}) - \frac{C_i C_j}{2r_{ij}^6} \right] + U_{\text{pol}}^{\text{cl}}(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\}) + U_{\text{shell}}(\{\mathbf{r}_{ij}\}, \{\mathbf{p}_i\}). \quad (1)$$

The successive terms are the Coulombic energy of the ionic point charges, the overlap repulsive and van der Waals energies, the classical polarization energy $U_{\text{pol}}^{\text{cl}}$ associated with the induced dipoles and the shell deformation energy U_{shell} . Overall charge compensation is assumed in the choice of the effective valences z_i .

The form of the van der Waals energy assumes that each ion has a transferable interaction strength, thus reducing the number of parameters needed for each family of compounds (in practice this term is of some importance only for the halogens). On similarly practical grounds the overlap potentials are written in the form proposed by Busing [19]

$$\Phi_{ij}(r) = f(\rho_i + \rho_j) \exp[(R_i + R_j - r)/(\rho_i + \rho_j)], \quad (2)$$

where R_i and ρ_i are characteristic radii and hardness parameters for the individual ions. Simple proportionality between R_i and ρ_i holds for polyvalent metal ions [12]. Finally, the classical polarization energy is

$$U_{\text{pol}}^{\text{cl}} = \sum_{i \neq j} \left[-z_i e \frac{\mathbf{p}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3} + \frac{1}{2} \frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}^3} - \frac{3}{2} \frac{(\mathbf{p}_i \cdot \mathbf{r}_{ij})(\mathbf{p}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] + \frac{1}{2\alpha_h} \sum_j p_j^2, \quad (3)$$

and the shell deformation energy is written as

$$U_{\text{shell}} = \frac{\alpha_s}{\alpha_h} \sum_{i,j} \mathbf{p}_j \cdot \hat{\mathbf{r}}_{ij} \left| \frac{d\Phi_{ij}(r_{ij})}{dr_{ij}} \right|. \quad (4)$$

In these equations α_h is the electrical polarizability of the halogen and α_s is a short-range polarizability. The sum in (4) is restricted to run over $i_j = \text{metal ions}$ which are first neighbours of the j -th halogen.

Table 1. Interionic force parameters (m denotes Al and h denotes Cl).

	f (e ² /Å ²)	z_m	z_h	R_m (Å)	ρ_m (Å)	R_h (Å)	ρ_h (Å)	C_h (eÅ ^{5/2})	α_h (Å ³)	α_s (Å ³ /e)
[13]	0.05	3	-1	1.055	0.049	1.71	0.238	5.5	2.05	0.46
This work	0.05	2.47 ₂	-0.82 ₄	0.948	0.044	1.71	0.238	5.5	2.05	0.46

Minimization of (1) with respect to the dipoles yields the dipole p_h on a halogen as

$$p_h = \alpha_h E_h(\{r_{ij}\}, \{p_i\}) + \alpha_s \sum_{ij} \hat{r}_{ih} \left| \frac{d\Phi_{ih}(r_{ih})}{dr_{ih}} \right|, \quad (5)$$

where E_h is the self-consistent electric field on the halogen. Each component of the shell-deformation dipole in (5) lies along a metal-halogen first-neighbour bond and points toward the metal ion: it is, therefore, opposite to the corresponding contribution to the electric-induction dipole, so that the net dipoles saturate as the ions deform in reaching their equilibrium positions.

The potential energy function of a cluster is then handled by a computer programme which is designed to perform two functions, namely (i) the optimization of a given configuration of the cluster by minimization of its energy towards states of static (stable or unstable) equilibrium and (ii) the study of static and dynamic deformations of the cluster for the evaluation of its vibrational frequencies and of its dynamical evolution at constant total energy. A description of the static and dynamic algorithms used in the programme can be found in [13].

The expressions (1) - (4) involve a number of parameters. As in our previous studies of the $(AlCl_4)^-$ and Al_2Cl_6 clusters, we assume transferability of the parameters between different compounds and adjust the radius of the Al ion and the electric polarizability of the Cl ion to Al-Cl bond lengths. We assume a value of 2.15 Å for the Al-Cl bond length in $(AlCl_4)^-$, its values in the literature [3] being in the ranges 2.11 - 2.16 Å from experiment and 2.15 - 2.17 Å from molecular orbital calculations. The value 2.065 Å has been determined for the bond length between Al and a terminal chlorine in Al_2Cl_6 by electron diffraction on the vapour [20]. In addition, we adjust the effective valence of Al to the frequency of the topmost stretching mode of the Al_2Cl_6 cluster, that is $\nu_3 = 625$ cm⁻¹ from spectroscopic data on the vapour [20]. The proposed values of all the model parameters are presented in Table 1.

Comparison with the parameters obtained in our earlier study [13], which are also reported in Table 1, shows that a decrease of the effective valence of the ions by about 17% and a parallel decrease of the ionic radius of Al by about 10% have been necessary to account quantitatively for the ν_3 mode of Al_2Cl_6 .

With regard to the effective valences that we have obtained, we wish to remark that they could be grossly compared with the results of first-principles calculations via the evaluation of the electric field in the outer regions of the dimer. On account of electronic screening, which is explicitly taken into account in our model through the halogen polarizabilities, and using a value of ≈ 2.5 for the high-frequency dielectric constant, we estimate that the effective ionic charges in such first-principles calculations should be of order $2.47/\sqrt{2.5} \approx 1.5$ for the Al ion.

3. Equilibrium Structure and Energetics of Al Chloride Clusters

3.1. The Al_2Cl_6 Dimer

Table 2 reports the calculated bond lengths and bond angles in the Al_2Cl_6 dimer at equilibrium and compares them with our earlier results [13] as well as with data from electron diffraction measurements in the vapour [20] and with results of quantum chemical calculations (QCC) [8]. The notations Cl^B and Cl^T have been used to denote a bridging chlorine and a terminal chlorine, respectively.

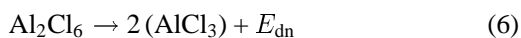
Evidently, the adjustment of model parameters that we have carried out to account for a reduced effective

Table 2. Equilibrium structure of Al_2Cl_6 (bond lengths in Å, bond angles in degrees). Underlined values have been fitted to the diffraction data on the Al_2Cl_6 vapour.

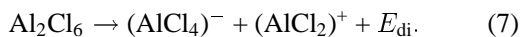
	Al-Cl ^B	Al-Cl ^T	Al-Al	Cl ^B -Cl ^B	Cl ^T -Cl ^T	$\angle Cl^B-Al-Cl^B$	$\angle Cl^T-Al-Cl^T$
[13]	2.268	<u>2.065</u>	3.22	3.19	3.60	89.5	121.3
This work	2.276	<u>2.065</u>	3.20	3.23	3.59	89.5	120.8
Expt. [20]	2.252	2.065	3.21	3.16	3.64	91.0	123.4
QCC [8]	2.289	2.083	3.26	3.21	3.64	89.1	121.8

ionic valence has brought about very little quantitative changes in all the calculated bond lengths and bond angles, thus preserving the excellent agreement with the data from experiment and from first-principles calculations. As already remarked in Sect. 1, this is a consequence of the force-balance condition imposed in the determination of the ionic radius of Al.

The absolute value of the binding energy of the dimer relative to isolated ions is not meaningful from our calculations, in view of the assumption of effective non-integral valences in the bound molecular state. However, it seems meaningful to compare the relative energies of different bound states. In particular, we turn here to our estimates for the binding energy of the isolated dimer in regard to the dissociation reactions



and



The results will be discussed in Sect. 3.4 below in comparison with first-principles calculations.

For what concerns the dissociation reaction in (6), the AlCl_3 molecule is reported from experiment [21] to be planar or nearly planar with D_{3h} symmetry and an Al-Cl bond length of 2.06 Å. Our model yields its equilibrium shape as an equilateral triangle with an Al-Cl bond length of 2.06 Å and leads to $E_{\text{dn}} = 0.85$ eV.

On the other hand, the $(\text{AlCl}_4)^-$ molecular ion has tetrahedral shape with a (fitted) Al-Cl bond length of 2.15 Å. We find that the $(\text{AlCl}_2)^+$ molecular ion is linear with an Al-Cl bond length of 1.97 Å and obtain the value 4.9 eV for the energy E_{di} in (7). As one should expect, the dissociation of Al_2Cl_6 into ionized species *in vacuo* is strongly unfavoured relative to dissociation into the neutral monomers.

3.2. The Complex $(\text{Al}_2\text{Cl}_7)^-$ ion

Our calculations on the equilibrium structure of the $(\text{Al}_2\text{Cl}_7)^-$ anion also serve the purpose of testing the transferability of the model by comparison with the results of *ab initio* [22] and semi-empirical [3] molecular orbital calculations. These have shown that the isolated $(\text{Al}_2\text{Cl}_7)^-$ anion is formed by two AlCl_4 tetrahedra sharing a chlorine in a bent configuration. The anion admits four such corner-bridged structures, which are close in energy and differ only for internal

Table 3. Theoretical results for the C_2 and C_s structures of $(\text{Al}_2\text{Cl}_7)^-$ (bond lengths in Å, bond angles in degrees). The two lower rows report results obtained by Curtiss [22] for the C_s structure from molecular orbital calculations with two different basis sets. The ranges of values shown for bond lengths and bond angles span those appropriate to inequivalent terminal chlorines.

	Al-Cl ^B	Al-Cl ^T	∠Al-Cl ^B -Al	∠Cl ^T -Al-Cl ^B
C_2 (this work)	2.35	2.10-2.12	111.	100.-108.
C_s (this work)	2.34	2.10-2.12	112.	98.-110.
C_s (STO-3G)	2.24	2.086-2.089	133.6	103.9-105.6
C_s (3-21G)	2.37	2.200-2.203	131.6	103.3-105.2

rotations giving different relative orientations to the two triplets of terminal chlorines.

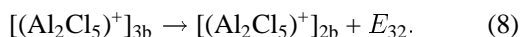
In an ionic model a bent corner-sharing configuration for $(\text{Al}_2\text{Cl}_7)^-$ is stabilized against a linear bridge by the specific inclusion of chlorine polarizability [13]. All the four corner-sharing configurations predicted by the quantum chemical calculations are obtained in our model as structures in static equilibrium, with the C_2 structure being mechanically stable and the C_s structure being almost degenerate with it. Excepting the C_2 structure, all structures are mechanically unstable and merely correspond to a multiplicity of saddle points separating several equivalent true minima in the energy-configuration landscape.

Our results for bond lengths and bond angles of $(\text{Al}_2\text{Cl}_7)^-$ in the C_2 and C_s structures are shown in Table 3, together with the Hartree-Fock results reported by Curtiss [22] for the anion in the C_s structure with two different basis sets denoted by STO-3G and 3-21G. His calculated bond lengths show strong sensitivity to the choice of the basis set. Semi-empirical molecular orbital calculations on the C_2 structure [3] yield a value of 2.30 Å for the Al-Cl^B bond length and values of 124.9° - 125.8° for the Al-Cl^B-Al bond angle. Evidently, our results for the Al-Cl bond lengths in $(\text{Al}_2\text{Cl}_7)^-$ are compatible with those available from quantum chemical calculations, but seem to underestimate the Al-Cl^B-Al bond angle.

3.3. The $(\text{Al}_2\text{Cl}_5)^+$ ion

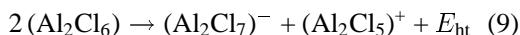
We reported in our earlier work [13, 17] that the $(\text{Al}_2\text{Cl}_5)^+$ ion admits two mechanically stable structures: (i) a symmetric triple-bridged ground state built from two AlCl_4 tetrahedra by face sharing, and (ii) an asymmetric double-bridged excited state which is obtained by direct stripping of a terminal chlorine from the Al_2Cl_6 dimer. The recalculated structural

parameters for these two configurations are almost unchanged relative to those reported earlier in the above-cited references. The equilibrium between the two structures is described by



Our calculations yield $E_{32} = 0.34$ eV.

From the results already discussed in this section we can also evaluate the energy required for the halogen transfer reaction



between isolated dimers *in vacuo*. We find $E_{ht} = 3.3$ eV within the present model. The relevance of such a transfer reaction as an initial step for ionic conduction in the dense liquid phase has been emphasized in [23].

3.4. Comparison with First-principles Calculations by a Density Functional Approach

The Al chloride ionic clusters of present interest have been evaluated by Ballone (unpublished) within a density functional theory (DFT) approach based on a local density approximation supplemented by gradient corrections. Although our main interest here is in a test of the energetics predicted for these clusters by the ionic model, we first briefly comment that the DFT results generally confirm those of the model on the structure of the clusters. In particular, the existence of two mechanically stable isomers for the $(\text{Al}_2\text{Cl}_5)^+$ ion is confirmed and there is close quantitative agreement in all the predicted bond angles. However, the DFT approach as realized by Ballone tends to overestimate the bond lengths by a few percents. The origins of this feature of the DFT results remain to be ascertained.

Table 4 reports a comparison between our calculated values of the reaction energies introduced earlier in this section and those obtained by Ballone in the DFT approach. The degree of agreement is clearly quite reasonable, especially if one bears in mind that

Table 4. Energies of cluster reactions (in eV) compared with DFT results by Ballone (unpublished).

	E_{dn}	E_{di}	E_{32}	E_{ht}
This work	0.85	4.9	0.34	3.3
DFT	1.1	—	0.39	1.66

Table 5. Frequencies of vibrational modes (in cm^{-1}). Values in parentheses are from experiment and from molecular orbital calculations as referenced in the main text. The underlined value has been fitted to the measured mode frequency in the Al_2Cl_6 vapour.

$(\text{AlCl}_4)^-$	$(\text{Al}_2\text{Cl}_7)^-/C_2$	Al_2Cl_6	$(\text{Al}_2\text{Cl}_5)^+_{73b}$	AlCl_3	$(\text{AlCl}_2)^+$
466 (490, 510)	548 (560, 583)	<u>625</u> (625, 647)	734	631($\times 2$)	891
	547 (550, 576)	616 (610, 636)	677		
	522 (540, 556)	529 (501, 537)			
	512 (526, 551)	484 (484, 497)			
355 (351, 353)	425 (429, 448)	428 (420, 430)	440($\times 2$)	424	496
	390 (383, 399)	349 (336, 351)	410		
	301 (336, 351)	309 (320, 329)	306		
	240 (310, 320)	235 (289, 267)			
170 (186, 192)	199 (226, 185)	226 (217, 232)	253	201	
	174 (—, 172)	167 (175, 191)	202($\times 2$)		
	161 (176, 164)	153 (166, 178)			
	151 (—, 149)	134 (144, 150)	193($\times 2$)		
	140 (—, 145)	124 (135, 138)			
	137 (152, 138)				
103 (121, 121)	103 (—, 109)	109 (—, 126)	118($\times 2$)	144($\times 2$)	127($\times 2$)
	83 (112, 88)	96 (116, 126)			
	75 (—, 81)	95 (99, 102)			
	67 (—, 79)	53 (—, 68)	71($\times 2$)		
	51 (—, 46)	18 (—, 23)			
	28 (—, 21)				
	21 (—, 7)				

each of the model results in Table 4 is obtained as the difference between energy values of order 100 eV.

4. Vibrational Frequencies

Our results for the vibrational frequencies of the ionic clusters that we have discussed above are reported in Table 5, in comparison with data from infrared and Raman spectroscopy and with results from molecular orbital calculations. The spectroscopic data are from work on molten chloroaluminates [24, 25] for $(\text{AlCl}_4)^-$, on solids [26] for $(\text{Al}_2\text{Cl}_7)^-$ and on the vapour [20] for Al_2Cl_6 . The quantum chemical results are from work at the Hartree-Fock level (basis set 6-31G*) by Curtiss and Nichols [27] for $(\text{AlCl}_4)^-$ and by Alvarenga *et al.* [8] for Al_2Cl_6 , while for $(\text{Al}_2\text{Cl}_7)^-$ in the C_2 structure they are from work carried out by Davis *et al.* [28] by a semi-empirical method. We do not consider fits of experimental data by the valence force field method.

The normal mode frequencies of the $(\text{AlCl}_4)^-$ tetrahedron provide a useful frame for a classification of the vibrational modes of the other clusters. $(\text{AlCl}_4)^-$ has four independent vibrational frequencies [29], corresponding to normal modes whose main character may be described as (i) stretching of an Al-Cl bond as a precursor to break-up into $\text{AlCl}_3 + \text{Cl}^-$ (a mode conventionally denoted by ν_3),

(ii) symmetric stretching of the four Al-Cl bonds (the ν_1 “breathing” mode), and (iii) deformation and torsion modes (denoted by ν_2 and ν_4). Table 5 follows the two main types of stretching modes and bending modes across the series of ionic clusters. The natural order of the modes then is that of decreasing frequency.

As discussed by Manteghetti and Potier [26], in $(\text{Al}_2\text{Cl}_7)^-$ the splitting of the ν_d vibration of a pyramidal AlCl_3 group by the loss of ternary symmetry and by the coupling of the two groups gives rise to four terminal asymmetric modes at frequencies higher than that of the ν_3 mode in $(\text{AlCl}_4)^-$. Four additional stretching modes in $(\text{Al}_2\text{Cl}_7)^-$ are related to the symmetric stretching motions of the terminal groups and of the Al-Cl^B-Al bridge. It is seen in Table 5 that the above two quadruplets of stretching modes in $(\text{Al}_2\text{Cl}_7)^-$ are correlated with the two stretching modes of $(\text{AlCl}_4)^-$ and with two quadruplets of modes in Al_2Cl_6 .

As again discussed by Manteghetti and Potier [26], the higher observed deformation modes in $(\text{Al}_2\text{Cl}_7)^-$ seem to be group vibration modes perturbed by the bridge bond and hence related to the ν_4 mode in $(\text{AlCl}_4)^-$. Table 5 suggests correlations between the two deformation modes of $(\text{AlCl}_4)^-$ and those of $(\text{Al}_2\text{Cl}_7)^-$ and Al_2Cl_6 .

It is seen from Table 5 that our results are in very reasonable agreement with all the available data on both the bond stretching and the bond deformation modes. This indicates that the model should describe rather accurately all the structural fluctuations taking place at equilibrium in molten chloroaluminates.

5. Concluding Remarks

We have in this work presented a refined classical model of ionic interactions in molten Al chloroaluminates, incorporating much of the quantitative information which is available on the structure and the vibrational dynamics of small clusters from experiment and from *ab initio* calculations. We have also seen that the model gives a reasonable account of the energetics of various reactions, in comparison with the results of first-principles calculations.

The reasonably accurate description of all the structural data and all the vibrational modes that we have achieved with the help of a minimal number of model parameters suggests that both the equilibrium liquid structures and the structural fluctuations around equilibrium should be well accounted for. It is hoped, therefore, that the model will find useful application in simulation work on these liquids.

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