The Soft Ion Model in Monte Carlo Simulation of Molten Salts

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This paper describes a method for a simple evaluation of the polarization energy in molten salt systems, by which it is possible to go, without heavy computational cost, from the rigid to the soft ion model. The method is based on the observation that, within the movements of single ions in the Monte Carlo chain, the deviation of the polarization energy is a linear function of the deviation of the Coulomb energy.

An extended numerical application has been carried out for molten LiI at 800, 1200 and 1453 (b.p.) K. The parameters that are mostly affected by the used model are put into evidence.

Key words: Interionic potential, Polarization, Monte Carlo, Simulation, Molten LiI.

Introduction

In Monte Carlo (MC) simulation of molten salts, the interionic pair potential is written, according to the Born-Huggins-Mayer form, as:

$$\varphi_{ij} = z_i z_j r^{-1} - c_{ij} r^{-6} - d_{ij} r^{-8} + a_{ij} \exp(-br), \quad (1)$$

where, r is the distance between ions i and j having charge z_i and z_j, c_{ij}, and d_{ij} are the van der Waals coefficients for the dipole-dipole and dipole-quadrupole interactions and a_{ij}, b are the parameters of the repulsive term. For these latter quantities, a set of values based on properties of solid alkali halides was given by Fumi-Tosi [1].

The pair potentials described by (1), classified as "rigid ion model" (RIM), proved to be partially inadequate [2, 3] to describe the basic thermodynamic properties of molten alkali halides, even though they are very useful because of their simplicity.

Among the various reasons given to explain the inadequacy of potentials type (1), it is to be noted in particular that, the ions being deformable, also the polarization energy of the system has to be considered, thus leading to a "soft ion model" (SIM). Nevertheless, the evaluation of the polarization energy within the MC chain implies unacceptable computation costs connected with the many-body interactions. Moreover it should be noted that also the shell model [4], proposed to account for the polarization of the system, implies heavy computational difficulties.

The aim of the present work is to take into account the polarization energy within a model that, using potentials of type (1), should be not only realistic but also sufficiently simple to be included in canonical MC simulations without unacceptable increase in computing time.

The Polarization Energy

For a system of ions with constant polarizability, α_i, it is convenient to neglect the contribution to the electric field, F_i, of the induced dipoles, $\alpha_i F_i$, and also to ignore quadrupoles and higher order multipoles. In this simplified scheme the polarization energy E^P is given by

$$E^P = -\frac{1}{2} \sum_i \alpha_i F_i^2 . \quad (2)$$

A preliminary study on the direct application of (2) in an MC cycle for a sample with 64 ions [5] showed that the system undergoes a "polarization catastrophe": after 10–20 kilosteps the molar volume of the sample is only 20–30% of the experimental one, and the E^P value becomes abnormally high while the ions tend to be surrounded by like ions.

In order to avoid this phenomenon, it was suggested to truncate or to modulate the polarization interactions for distances lower than a critical value;

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the same behaviour was found by Jaccucci et al. [6] in a molecular dynamics study and overcome by the introduction of a short range repulsion. However the direct utilization of (2) in normal size samples involves an unbearable increase in computing time.

At this point it seemed useful to analyze, at microscopical level within the MC chain, whether the deviations of the polarization energy, $\delta\varphi^P$, due to the movement of a single move ion in the sample could be estimated in a way different from (2), for example by a special two body interaction function. Thus we used the functions proposed by Rittner [7] and by Michielsen et al. [8] which are of the type

$$\varphi_{ij}^P \propto r^{-4}. \tag{3}$$

On a large set of random movements, the $\delta\varphi^P$ values computed with (2) were compared with those obtained with either one of the potentials of type (3). No correlation was found between these sets of data: this seems to preclude the possibility of using two-body potentials of type (3) for the evaluation of the polarization energy in molten salt systems.

On the other hand, we found that the $\delta\varphi^P$ values of single ions depend linearly (the observed correlation coefficients being in the range 0.95–0.98) on the corresponding deviations of the Coulomb energy, $\delta\varphi^c$, which are standard computed values of the MC steps:

$$\delta\varphi^P = A + B\,\delta\varphi^c. \tag{4}$$

Two typical examples of this correlation are shown in Figure 1. It should be noted that the use of (4) for the evaluation of each $\delta\varphi^P$ automatically prevents the polarization catastrophe.

From the operational stand-point, the soft-ion model can thus be introduced in MC simulations by systematically refining, during the equilibration of the system, the A and B coefficients of (4) every 100–200 kilosteps. Once equilibration is reached, their values remain practically constant. Within the MC chain it is then possible to evaluate the $\delta\varphi^P$ by (4) with almost no increase in computational time.

An idea on the physical significance of the B term in (4) can be obtained by analyzing the simple system of two isolated ions at distance r having constant polarizabilities α_+ and α_-, respectively. The Coulomb energy for this system is $-e^2/r$ while the polarization energy is $-0.5\,(\alpha_+ + \alpha_-)\,e^2/r^4$. Thus

$$\delta\varphi^P = \frac{2\,(\alpha_+ + \alpha_-)}{r^3}\,\delta\varphi^c. \tag{5}$$

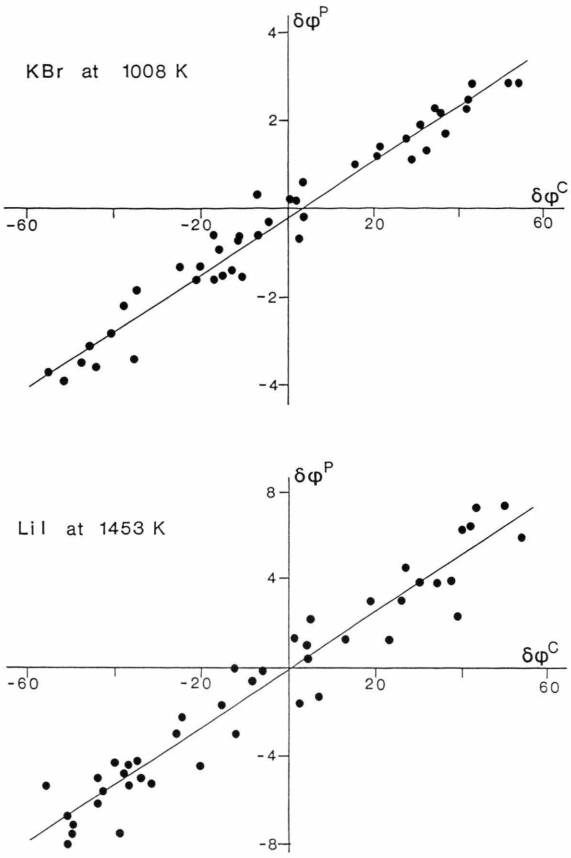

Fig. 1. The single ion deviation of the polarization energy due to the ion movement vs. the corresponding deviation of the Coulomb energy in molten KBr at the melting point, 1008 K, and in molten LiI at the boiling point, 1453 K. (all values are in 10^{-13} erg/cell). The least squares fitted equations are:

KBr: $\delta\varphi^P = -2.013\cdot10^{-14} + 0.064\,\delta\varphi^c$ with corr. coeff. 0.979.

LiI: $\delta\varphi^P = -1.032\cdot10^{-14} + 0.130\,\delta\varphi^c$ with corr. coeff. 0.967.

The Case of Molten LiI

The studies carried out on molten alkali halides by means of rigid-ion potentials of type (1) showed that

a) "the computed volumes are systematically greater than the experimental ones, the deviations being greater at higher temperatures..." and in the range 6–9% at the melting point [2];

b) the type of repulsive function assumed is very crucial. The exponential function is the one giving the

	800 K		1200 K		1453 K	
	SIM	RIM	SIM	RIM	SIM	RIM
V_m	43.7	44.6	46.9	50.3	48.6	53.8
U	−165.3	−164.9	−160.6	−160.2	−157.6	−157.3
E^C	−187.6	−185.8	−184.0	−180.6	−181.8	−178.1
E^R	27.8	25.5	27.6	23.8	26.9	22.8
E^W	−5.8	−5.6	−5.5	−4.8	−5.3	−4.4
E^P	−4.5	−3.8*	−5.9	−5.7*	−6.1	−6.3*

Table 1. Molar volumes and energies for molten LiI (in $cm^3\ mol^{-1}$ and kcal mol^{-1} respectively) obtained with the soft ion model (SIM) and the rigid ion model (RIM).

* Mean values computed on static configurations apart from the MC cycle.

best results, nevertheless it was found that "... the Fumi-Tosi potentials are generally too soft and the distances of closest approach of unlike ions at higher temperatures therefore too small." [3]

c) the value of the polarization energy, estimated on static configurations, shows that it contributes only by a small percent to the global energy value [3, 9]. On the contrary, the preliminary MC study on small samples suggested that it largely affects the molar volume of the system [5].

In the present paper, the MC method was used in the NPT version (at p = 1 atm.) which allows a direct comparison to be made with the experimental data for both the molar volume and the enthalpy [9].

Extended computations were carried out on molten LiI which among the alkali halides is the one having the smallest cationic polarizability (0.03) and the largest anionic polarizability (6.45) [10].

Simulations were carried out with both models RIM and SIM at three different temperatures: 800, 1200 and 1453 (b. p.) K. For RIM, (1) with the Fumi-Tosi parameters [11] was used. As regards SIM, the following relations of type (4) were obtained on the equilibrated system:

$$800\ \text{K}, \quad \delta\varphi^P = -3.182 \cdot 10^{-14} + 0.083\ \delta\varphi^c,$$
$$1200\ \text{K}, \quad \delta\varphi^P = -3.836 \cdot 10^{-14} + 0.130\ \delta\varphi^c,$$
$$1453\ \text{K}, \quad \delta\varphi^P = -1.032 \cdot 10^{-14} + 0.130\ \delta\varphi^c.$$

It should be noted that these relations were calculated by taking into account random ionic movements in the range 0–2% of the edge of the elementary cubic cell containing 216 ions, and that the energies are in erg/cell.

Table 1 reports the values obtained for the molar volumes and internal energies, U, of the melt according to the two models, along with the Coulomb, E^c, van der Waals, E^W, repulsive, E^R, and polarization, E^P components of the average configurational energy, E.

Table 2. Main features of the radial distribution functions for molten LiI at 800, 1200 and 1453 K (all distances in Å). The model including polarization was used.

		800 K	1200 K	1453 K
$Li^+ - Li^+$ pairs				
	d	2.7	2.6	2.6
	r^{max}	4.2	4.3	4.5
	r^{min}	6.1	6.2	6.2
	n	13.0	12.4	12.4
$Li^+ - I^-$ pairs				
	d	2.2	2.1	2.1
	r^{max}	2.7	2.7	2.7
	r^{min}	4.2	4.2	4.2
	n	4.8	4.5	4.5
$I^- - I^-$ pairs				
	d	3.1	3.0	2.9
	r^{max}	4.2	4.3	4.4
	r^{min}	6.2	6.2	6.2
	n	13.4	12.4	12.4
all ions				
	r^{max}	2.7	2.7	2.7
	r^{min}	3.4	3.4	3.4
	n	3.65*	3.5**	3.5**

* of which $Li^+ - I^- = 3.5$ and $Li^+ - Li^+ = 0.15$.
** of which $Li^+ - I^- = 3.3$ and $Li^+ - Li^+ = 0.2$.

Energies U and E are related by

$$U = E + 3RT. \tag{6}$$

For what concerns the experimental data, the literature reports density values that are reliable only for temperatures close to the melting point (742 K) since LiI tends to decompose with increasing temperature [12]. The value at 800 K is $V = 43.8\ cm^3\ mol^{-1}$, which is in agreement with that calculated by the SIM model. As regards the internal energy, the U values in Table 1 can be compared with those obtained on the basis of the crystal energy of the solid at 298 K along with the molar heat capacity and the fusion enthalpy. All these data are affected by some uncertainty: anyway by using Cubicciotti's U_{298} [13] and the thermal data reported by Blander [14], one obtains $U_{800} = -165$ kcal mol^{-1}, in good agreement with that of Table 1.

Finally, Table 2 reports the principal characteristics of the radial distribution functions (rdf) obtained with the SIM model, on the basis of the histograms of the ion pair distances, for fused LiI. In particular, the distance of minimum approach, d, the abscissa of the maximum of the main peak, r^{max}, and of the minimum following the main peak, r^{min}, are reported along with the apparent coordination number, n, at the three studied temperatures. For comparison, Fig. 2 reports the rdfs obtained at 1200 K by RIM and by SIM. As expected, in the dense liquid phase, the electronic polarizability effects that should be evident in higher order structural functions and in the dynamical and transport properties [15], emerge only to a minor extent in the spherically symmetrical radial distribution of ions.

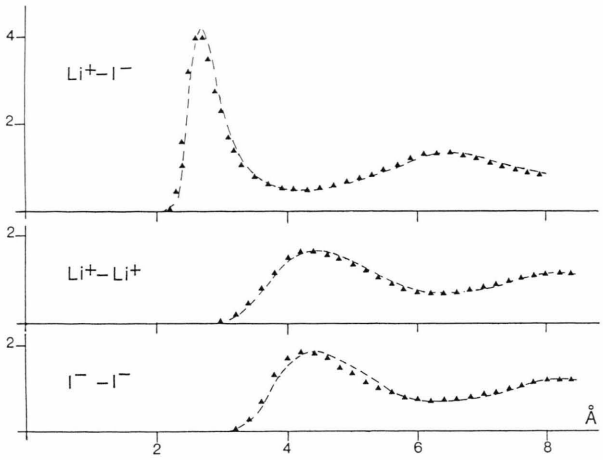

Fig. 2. Radial distribution functions of molten LiI at 1200 K according to RIM (dotted curves) and SIM (triangles).

We can thus conclude that the evaluation of the polarization energy by the proposed method can be included in MC simulations of molten salt systems with very little increments of comupting time and with a very rapid equilibration of the system. Among the results obtained, the significant molar volume reductions (which are larger at higher temperatures) are worth mentioning.

On the contrary, the global value of the internal energy shows small variations, since the observed increase in the absolute value of the Coulomb energy is compensated by a corresponding increase of the repulsive component.

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[1] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25,** 31 (1964).
[2] D. J. Adams and I. R. Mc Donald, J. Phys. C **7,** 2761 (1974).
[3] J. W. E. Lewis, K. Singer and L. W. Woodcock, J. Chem. Soc. Faraday Trans. II **71,** 308 (1975).
[4] See e.g.: M. J. L. Sangster and M. Dixon, Adv. Phys. **25,** 247 (1976); M. Dixon and M. J. Gillan, Phil. Mag. B **43,** 1099 (1981); M. Dixon, Phil. Mag. B **47,** 509 (1983).
[5] S. Romano and C. Margheritis, Physica **77,** 557 (1974).
[6] G. Jacucci, I. R. Mc Donald, and A. Rahman, Phys. Rev. A **13,** 1581 (1976).
[7] E. S. Rittner, J. Chem. Phys. **19,** 1030 (1951).
[8] J. Michielsen and L. V. Woodcock, in "Report of Workshop on Ionic Liquids" CECAM, 1974, page 96.
[9] See e.g.: C. Margheritis and C. Sinistri, Z. Naturforsch. **30a,** 83 (1975); C. Margheritis, Gazz. Chim. It. **106,** 309 (1976); C. Margheritis, C. Sinistri, and G. Flor, Z. Naturforsch. **31a,** 615 (1976).
[10] Mean vlaues among those reported by J. Deltour, Physica **51,** 292 (1971).
[11] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25,** 45 (1964).
[12] I. S. Yaffe and E. R. van Artsdalen, J. Phys. Chem. **60,** 1125 (1956).
[13] D. Cubicciotti, J. Chem. Phys. **34,** 2189 (1961).
[14] M. Blander, in "Molten Salt Chemistry", John Wiley, New York 1964, p. 141.
[15] M. Parrinello and M. P. Tosi, Riv. Nuovo Cim. **2,** 1 (1979).