Monte Carlo Calculations on Molten Silver Bromide

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Using crystal data in the range 20–300 °C, the AgBr interionic pair potentials were calculated. By means of these potentials the melt was computer simulated with the Monte Carlo method at three different temperatures (694, 1000 and 1778 K). The system thus obtained is relaxed and it behaves as if an important cohesive force, like the homopolar one, would be lacking.

It was empirically proved that if the interionic repulsive potentials are reduced by about 40% the experimental values of the density and of the internal energy are reproduced.

The various computer simulations reported in recent years on ionic melts, mainly molten alkali halides [1, 2], proved the applicability of interionic potentials deduced from crystal data to a satisfactory simulation of the melt. No study has been made on ionic systems with presumably partial homopolar binding.

The present paper reports extensive calculations on molten AgBr carried out by the Monte Carlo (MC) method as used in previous works [2].

For this salt in the solid state, literature data seem to be not conclusive as regards the presence of homopolar binding. In particular Mayer [3] states "... that the homopolar contribution to the lattice energies of ..AgBr.. is practically insignificant..."; Sharma [4] finds that for AgBr the Rydberg's potential energy function for ionic crystals "...satisfactorily explains the lattice properties"; Ladd [5] reports for solid AgBr a difference of about 14 kcal mol^{-1} between the calculated cohesive energy and the thermodynamic value and thus "... no model yet proposed for ionic crystals gives satisfactory cohesive energy for the silver halides".

As regards the molten state of ionic salts with probable homopolar character the most conclusive results were reported by Hafner and Nachtrieb [6]: for thallium salts NMR measurements showed the presence of covalent binding in the melt.

It was thought that a simulation study on fused AgBr could give further information on the presence of homopolar energy. The MC method seems particularly suitable because it allows direct comparison with the system density and energies.

AgBr interionic potentials from crystal data

The interionic pair potentials of AgBr were obtained by a procedure which assumes for purely ionic systems only coulombic, van der Waals and repulsive contributions [7]. The thermal volume expansion coefficients used in the range 20–300 °C were those reported in Ref. [8]; the compressibilities in the same temperature range were those by Tannhauser [9]. Concerning the van der Waals coefficients, literature reports two sets of data as given in Table 1.

Table 1. Van der Waals coefficients for dipole-dipole (c_{ij} in 10^{-60} erg cm^6) and dipole-quadrupole (d_{ij} in 10^{-76} erg cm^8) interactions in AgBr.

Author	c_{+-}	c_{--}	c_{++}	d_{+-}	d_{--}	d_{++}
Mayer [3]	109	208	67	199	475	91
Ladd [5]	100	200	90	270	1020	110

The repulsive pair potential between ions i and j at distance r was assumed as:

$$^{\mathrm{R}}\varphi_{ij} = a_{ij} \exp(-b\,r)\,, \tag{1}$$

where a_{ij} and b are characteristic constants.

By fixing suitable values of b, the pairs of constants a_{u} $(=a_{+-})$ and a_1 $(=a_{++}+a_{--})$ were calculated with the aid of the Hildebrand's equation of state at different temperatures: the tern (b, a_{u}, a_1) that gives the best fitting was thus chosen. Further details can be found in Ref. [7].

Figure 1 shows the a_{u} and a_1 values vs. b as obtained using Mayer's van der Waals coefficients (see Table 1). The chosen values, indicated by the arrows, are:

$$\begin{aligned} b &= 3.31\ \text{Å}^{-1}\,, \\ a_{\mathrm{u}} &= 0.341 \cdot 10^{-8} \quad \text{and} \\ a_1 &= 0.977 \cdot 10^{-7}\ \text{erg molecule}^{-1}. \end{aligned} \tag{2}$$

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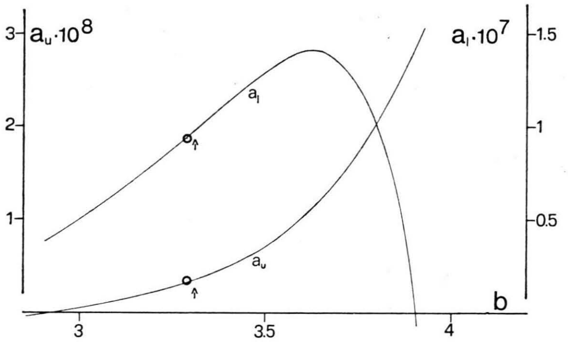

Fig. 1. Values of a_1 and a_u vs. b as obtained using Mayer's van der Waals constants. The arrows show the data corresponding to the best fitting. The circles indicate the best fitting obtained using Ladd's van der Waals constants (a in erg molecule^{-1}; b in Å^{-1}).

Using Ladd's van der Waals constants one obtains the following values:

$$\begin{aligned} b &= 3.29\ \text{Å}^{-1}, \\ a_u &= 0.339 \cdot 10^{-8} \quad \text{and} \\ a_l &= 0.934 \cdot 10^{-7}\ \text{erg molecule}^{-1}. \end{aligned} \tag{3}$$

which are in very good agreement with the previous ones.

In 1933 Mayer [3] proposed for the AgBr interionic repulsive potentials the following functions:

$$\begin{aligned} {}^{\mathrm{R}}\varphi_{+-} &= 0.180 \cdot 10^{-7} \exp(-3.85\, r), \\ {}^{\mathrm{R}}\varphi_{--} &= 0.832 \cdot 10^{-8} \exp(-2.90\, r), \\ {}^{\mathrm{R}}\varphi_{++} &= 0.391 \cdot 10^{-7} \exp(-5.71\, r). \end{aligned} \tag{4}$$

As regards the method used to obtain Eqs. (4) it is sufficient here to point out that for Mayer "... the repulsion between Ag$^+$ pairs is probably negligible and is neglected, that between Br$^-$ pairs is assumed to be the same function of r as in the alkali halides, and that between Ag$^+$ —Br$^-$ is calculated from the constants of the crystal".

The Mayer's repulsive functions in comparison with the present ones (2) show that, for distances in the range pertinent to the calculations, the ${}^{\mathrm{R}}\varphi_{+-}$ agree rather well; that Mayer's ${}^{\mathrm{R}}\varphi_{++}$ is extremely small and Mayer's ${}^{\mathrm{R}}\varphi_{--}$ is always smaller than the present ${}^{\mathrm{R}}\varphi_1$. For what concerns ${}^{\mathrm{R}}\varphi_{--}$ it is believed that single fitting of crystal data is preferable to a general repulsive potential valid for the alkali bromide family. Furthermore, as shown by the MC calculations reported in the following section, Mayer's assumption on ${}^{\mathrm{R}}\varphi_{++}$ seems not valid.

Monte Carlo calculations

a) With classical pair potentials

Firstly, MC calculations on molten AgBr have been carried out using the classical interionic pair potential:

$$\varphi_{ij}(r) = z_i z_j r^{-1} - c_{ij} r^{-6} - d_{ij} r^{-8} + {}^{\mathrm{R}}\varphi_{ij}(r) \tag{5}$$

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 and ${}^{\mathrm{R}}\varphi_{ij}(r)$ is the repulsive function (1) as obtained by crystal data.

When using data (2) and (3) the ratio a_{--}/a_{++} was assumed equal to 10. This value was obtained on the basis of the Huggins model [10] with the Br$^-$ basic radius of this reference and the Ag$^+$ radius as intermediate between those of Na$^+$ and K$^+$.

The computing procedure was the one fully described in previous papers [2]. The results obtained at the AgBr boiling temperature [11] (1778 K), at 1000 K and at the melting temperature [12] (694 K) using the parameters (2) along with Mayer's values for the van der Waals constants, are summarized in Table 2. The experimental molar volumes are those reported by Janz et al. [13]: the value at the boiling point was estimated by extrapolation of the results in the 720—930 K range. The U_{exp} were calculated using the 298 K thermodynamic value reported by Ladd [5], along with the C_P and the heat of fusion taken from standard tables [14].

Table 2. Thermodynamic properties of AgBr obtained using the parameters (2) along with Mayer's values for the van der Waals constants in the MC calculations.

Temperature	V		U		${}^{\mathrm{C}}E$	${}^{\mathrm{W}}E$	${}^{\mathrm{R}}E$
	calc	exp	calc	exp			
1778 (b. p.)	61.1	(42.0)	−163.8	−189.1	−188.4	−23.7	37.8
1000	43.8	35.6	−177.1	−201.7	−198.2	−28.2	43.3
694 (m. p.)	41.7	33.7	−181.8	−206.5	−201.6	−29.6	45.2

Temperatures in K; volumes in ml mol^{-1}; energies in kcal mol^{-1}.

Table 2 shows that the system thus obtained is relaxed: therefore the repulsive potential from crystal data does not yield an acceptable simulation of the melt. The system behaves as if an important cohesive force were lacking: it seems reasonable to identify it with the homopolar one.

The results obtained using the repulsive potentials (3) in connection with the van der Waals constants as given by Ladd [5] are practically identical.

With the repulsive potentials (4) proposed by Mayer is was not possible to reach the equilibration of the system because, owing to the smallness of ${}^{\mathrm{R}}\varphi_{++}$, some pairs of Ag^+ ions reach too low distances of closest approach. Mayer's potentials cannot be used as such in MC calculations.

Finally, the polarization energy of the system was calculated using the procedure previously outlined [2] and the following values for the ionic polarizabilities: $\alpha_{Ag^+} = 2.06$ (Ref. [15]); $\alpha_{Br^-} = 4.25$ Å^3 (Ref. [16]). The values of the polarization energy thus obtained were -9.5; -5.5 and -4.2 kcal mol^{-1} at 1778, 1000 and 694 K respectively.

b) Semiempirical pair potentials

Attempts were made to obtain a better simulation of molten AgBr by means of semiempirical pair potentials. The simplest possibility seemed to be the modulation of the repulsive term by an appropriate factor f: this is equivalent to the assumption that the homopolar interaction potential is not a directional one and is of the same exponential form as (1). The function $f\,{}^{\mathrm{R}}\varphi$ accounts for whatever in the system is neither coulombic nor van der Waals energy. Factor f should mainly reflect the homopolar contribution to the system total energy: in purely ionic systems $f = 1$.

Two different factors were tested: f_{tot} which modulates in the same way both ${}^{\mathrm{R}}\varphi_{\mathrm{u}}$ and ${}^{\mathrm{R}}\varphi_{\mathrm{l}}$, and f_{u} which modulates only ${}^{\mathrm{R}}\varphi_{\mathrm{u}}$. The f factors were optimized with respect to the experimental values of the molar volumes and of the internal energies by studying the functions $V_{\mathrm{calc}}(f)$ and $U_{\mathrm{calc}}(f)$. Figure 2 reports the detailed results at 1000 K: the experimental values V_{exp} and U_{exp} can be obtained using f_{tot} equal to 0.61 and 0.62, respectively; or f_{u} equal to 0.52 and 0.54. The optimized values $f_{\mathrm{tot}} = .615$ and $f_{\mathrm{u}} = .53$ can thus be estimated.

As the temperature increases the optimized f's also increase: f_{tot} ranges between 0.56–0.69 and f_{u} between 0.47–0.60 when the temperature rises from 694 to 1778 K.

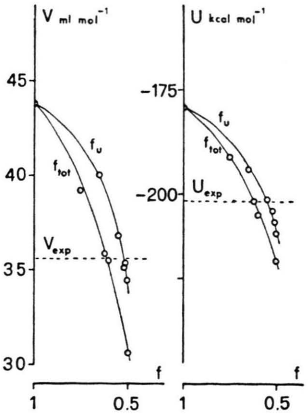

Fig. 2. Values of the calculated V and U at 1000 K as a function of factors f_{tot} and f_{u}.

Final remarks

The results obtained by MC calculations on molten silver bromide indicate that:

a) the pair potentials obtained by crystal data do not give an acceptable simulation of the thermodynamic properties of the melt;

b) the melt evidences the presence of a cohesive homopolar energy much more than the solid does. This must be related to the decrease of the unlike ions interionic distances on going from solid to liquid;

c) to obtain first approximation results in the simulation processes it is necessary to reduce the interionic repulsive potentials by about 40%.

Acknowledgement

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