Monte Carlo Calculations on Molten TlCl, TlBr and TlI

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Molten TlCl, TlBr and TlI were computer simulated at two different temperatures using the interionic pair potentials obtained by Mayer on the corresponding solids. The calculated molar volumes in comparison with the experimental ones show that the simulated molten TlCl and TlBr are only slightly relaxed (1–2, 2–3%, respectively). On the contrary, molten TlI is strongly relaxed (23–27%) and behaves as if an important cohesive force like the homopolar one would be lacking.

In recent years, the Monte Carlo (MC) method in computer simulation has proved to be a very useful tool for the derivation of thermodynamic and structural properties of melts.

The method is designed to produce a canonical ensemble of configurations and involves no time scale. Statistical mechanics assumes that the time average of a configurational property in a dynamic system is equal to the average over an ensemble of static configurations: thus a complete MC calculation can be regarded as a computer "experiment" which yields physical properties of macroscopic system based on microscopic pair potentials. From this point of view, the method is a valid test for the interionic potentials used, the degree of adequacy of the ion pair potentials being clearly shown by the results.

The present paper reports the results obtained by MC calculations on thallous molten halides using an NPT ensemble at $P=1$ with an interionic pair potential of the type:

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

where r is the distance between ions i and j having charge z_i and z_j; c_{ij} and d_{ij} are the coefficients for the dipole-dipole and dipole-quadrupole dispersion energy, respectively; and a_{ij} and b_{ij} are the coefficients of the repulsive term. On these salts at the solid state, Mayer [1] reported a complete set of values for all the coefficients in (1). More recently, the coefficients of the van der Waals term, i.e., c_{ij} and d_{ij}, were also given by Ladd [2]. Since the repulsive coefficients reported by Mayer were obtained on the basis of his dispersion term, it was thought proper to use all Mayer's coefficients.

For solid thallium halides, Mayer [1] stated that the homopolar contribution to the lattice energy is "practically insignificant", and analogous conclusions were reached by Ladd [2]. On the other hand, Hafner and Nachtrieb [3] reported a degree of covalency equal to 0.033 for TlCl, 0.051 for TlBr and 0.095 for TlI and stated that the degree of covalency should increase in the molten state by about a factor of 2.

Calculations

The interionic pair potential is assumed to be given by (1) with the following Mayer's values:

1) for TlCl:

$c_{++} = 268$ $c_{+-} = 179$ $c_{--} = 133$ 10^{-12} erg Å^6;
$d_{++} = 500$ $d_{+-} = 346$ $d_{--} = 268$ 10^{-12} erg Å^8;
$a_{++} = 1.27$ $a_{+-} = 2.43$ $a_{--} = 4.49$ 10^{-9} erg;
$b_{++} = 2.65$ $b_{+-} = 2.77$ $b_{--} = 2.90$ Å^{-1};

2) for TlBr:

$c_{+-} = 222$ $c_{--} = 208$ 10^{-12} erg Å^6;
$d_{+-} = 460$ $d_{--} = 475$ 10^{-12} erg Å^8;
$a_{+-} = 3.30$ $a_{--} = 8.32$ 10^{-9} erg;

3) for TlI:

$c_{+-} = 307$ $c_{--} = 437$ 10^{-12} erg Å^6;
$d_{+-} = 720$ $d_{--} = 1228$ 10^{-12} erg Å^8;
$a_{+-} = 5.95$ $a_{--} = 26.93$ 10^{-9} erg.

For TlBr and TlI the constants $c_{++}, d_{++}, a_{++}, b_{++}, b_{+-}$ and b_{--} are the same as for TlCl. Moreover is $|z_i z_j| = 2.3067 \cdot 10^{-12}$ erg Å. The model and the computer programs used were the same as in [4].

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Results

The results obtained are summarized in Table 1. Each salt was simulated at two different temperatures, i.e. at the melting point (702, 732 and 713 K for TlCl, TlBr and TlI, respectively) and at 1000 K. Table 1 reports the results obtained on the liquid at the temperatures examined for the molar volume V, the internal energy U, along with the coulomb, ${}^{\mathrm{C}}E$, van der Waals, ${}^{\mathrm{W}}E$ and repulsive, ${}^{\mathrm{R}}E$, energies. Next to the volume and internal energies figures, the corresponding experimental values are also given in parentheses. The experimental values V_{exp} were obtained from the results reported by Klemm [5] for TlCl and by Grothe et al. [6] for TlBr and TlI. The U_{exp} values can be obtained from the crystal energy at 298 K (U_{298}) with the molar heat capacity and the transition and fusion enthalpies. The U_{298} values used were those by Mayer [1]: it should be noted that the corresponding absolute values reported by Ladd [2] are about 4.5% larger. However, owing to the uncertainties affecting the U_{exp} values, particularly the U_{298} ones, the comparison between the calculated and experimental energy values is less indicative than that concerning the volumes.

The last column in Table 1 reports the polarization energies evaluated as in previously investigated systems [7] on one configuration out of 5000. The ionic polarizabilities used were:

$$\alpha_{\mathrm{Tl}^+} = 5.20\,, \quad \alpha_{\mathrm{Cl}^-} = 3.05\,, \quad \alpha_{\mathrm{Br}^-} = 4.25\,, \quad \alpha_{\mathrm{I}^-} = 6.45 \quad \text{Å}^3$$

which are the averages of many values reported in the literature [8].

As it can be noted, the simulated molten structure of TlCl and TlBr is slightly relaxed, the difference between the experimental and the calculated volumes being in the range of 1–2% for TlCl and 2–3% for TlBr. On the contrary, the simulated TlI is strongly relaxed, the same difference amounting to 23–27%.

One may conclude that the MC simulation of these melts based on Mayer's constants for the coefficients in (1) yields satisfactory results for molten TlCl and TlBr, whilst the results obtained for TlI are not acceptable.

The behaviour of molten thallium iodide suggests the lack of an important cohesive force, which might be identified with the homopolar one, in analogy with previous findings on AgBr [9].

Finally, as regards the relative values of the different contributions to the system energy it can be noted that at 1000 K the coulomb, repulsive and van der Waals energies are in the ratio, respectively:

$$100:21.0:13.2 \quad \text{for TlCl}$$

and

$$100:21.3:13.7 \quad \text{for TlBr}.$$

Table 1. Thermodynamic properties of molten thallium halides, as obtained by MC calculations. The figures reported in parentheses are experimental values: temperatures are in K, volumes in ml mol^{-1}, energies in kcal mol^{-1}.

		V	U	${}^{\mathrm{C}}E$	${}^{\mathrm{W}}E$	${}^{\mathrm{R}}E$	${}^{\mathrm{P}}E$
TlCl	at 702	43.2 (42.6)	− 159 (− 161)	− 176.6	− 25.0	38.8	− 3.3
	at 1000	48.1 (47.1)	− 154 (− 156)	− 173.2	− 22.8	36.4	− 4.3
TlBr	at 732	49.0 (47.5)	− 152 (− 155)	− 169.4	− 24.1	37.2	− 3.6
	at 1000	52.4 (51.6)	− 148 (− 150)	− 166.3	− 22.8	35.5	− 4.4
TlI	at 713	66.4 (53.8)	− 139 (− 151)	− 155.8	− 20.1	32.7	− 3.3
	at 1000	74.1 (58.6)	− 134 (− 146)	− 151.9	− 18.4	30.5	− 4.3

Table 2. RDF characteristics for molten TlCl and TlBr (all distances in Å).

	TlCl: g_{l}		TlCl: g_{u}		TlBr: g_{l}		TlBr: g_{u}	
	at 702	at 1000	at 702	at 1000	at 732	at 1000	at 732	at 1000
d	2.92	2.82	2.50	2.46	3.01	2.90	2.54	2.52
$r^{\max}$	4.30	4.40	2.95	2.95	4.50	4.60	3.10	3.10
$r^{\min}$	6.75	6.85	4.50	4.50	6.95	7.00	4.70	4.70
h	1.87	1.73	4.70	4.43	1.96	1.75	4.85	4.22
n	17.0	16.1	5.9	5.4	16.4	16.0	5.8	5.7

An outstanding feature of the MC method also lies in the possibility of visualizing the intimate structure of the melt. The radial distribution function (RDF) of like ions, $g_1(r) = \frac{1}{2}(g_{--} + g_{++})$, of unlike ions, $g_u(r) = g_{+-}$, and of all ions, $g_{tot}(r) = \frac{1}{2}(g_u + g_1)$ can be evaluated on the basis of the histograms of the ion pair distances.

The characteristics of these functions obtained for molten TlCl and TlBr at the two temperatures studies are summarized in Table 2: 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, $r^{\min}$, and the height of the main peak, h, are reported along with the apparent coordination number, n. The two functions g_{++} and g_{--} are very similar: as predicted on theoretical grounds and previously confirmed, their first peaks almost coincide because of the charge ordering effect produced by the electrostatic forces. A large penetration of like ions into the first coordination sphere is also found: for TlCl there are 0.3 like ions on a total coordination of 4.8 at 702 K and 0.4 like ions on a total coordination of 4.5 at 1000 K. The corresponding figures for TlBr are 0.3 on 4.9 at 732 K and 0.6 on 5.1 at 1000 K.

Other features are in agreement with previous findings on ionic melts: as the temperature increases, the distance d decreases while the first peak of g_1 tends to become flatter and $r^{\max}$ is almost temperature independent. The melt shows alternations of positive and negative shells, oscillations of g_u and g_1 being observable up to 10 Å.

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[1] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).
[2] M. F. C. Ladd, Z. Physik. Chem. N. F. **95**, 307 (1975).
[3] S. Hafner and N. Nachtrieb, J. Chem. Phys. **40**, 2891 (1964).
[4] C. Margheritis and C. Sinistri, Z. Naturforsch. **30a**, 83 (1975).
[5] W. Klemm, Z. Anorg. Chem. **152**, 235 (1926).
[6] R. H. Grothe and L. Schrader, Hannover Naturwiss. **57** (10), 496 (1970).
[7] C. Margheritis, G. Flor, and C. Sinistri, Z. Naturforsch. **31a**, 615 (1976).
[8] J. Deltour, Physica **51**, 292 (1971) and J. R. Tessman and A. H. Kahn, Phys. Rev. **92**, 890 (1953).
[9] C. Margheritis and C. Sinistri, Z. Naturforsch. **33a**, 38 (1978).