Monte Carlo Computations on Molten Caesium Bromide

Chiara Margheritis and Cesare Sinistri

Centro di studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi del CNR
Institute of Physical Chemistry, University of Pavia, Italy

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Molten CsBr was computer simulated tat 1 atm and four different temperatures using the Monte Carlo method. Structural and thermodynamic properties of the melt were obtained on the basis of pair potentials. In particular, radial distribution functions, volume, and energy with its coulomb, dipole-dipole, and repulsive components were determined. Separately, the polarization energy was also evaluated: this quantity increases with increasing temperature and ranges between 2 and 4% of the total energy.

Monte Carlo (MC) methods have recently been shown to be very useful for computer simulation of structural and thermodynamic properties of ionic systems.

For molten potassium chloride, Woodcock and Singer[1] used an NVT ensemble: they assumed pair interactions described by Born-Huggins-Mayer type potentials with an exponential repulsive term. Calculations carried out on an NPT ensemble of molten KCl using a Pauling repulsive potential[2] (i. e. an inverse power function) yielded much less satisfactory results.

In the present work structural and thermodynamic properties of molten CsBr were computer simulated at 1573 (boiling point), 1133, 1021 and 910 K (melting point). For comparison, also solid CsBr at the m.p. was simulated.

The pair potential used for the calculations was the following:

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

where r is the distance between ions i and j having charge z_i and z_j; c_{ij} is the coefficient for the dipole-dipole dispersion energy; a_{ij} and b are characteristic constants of the repulsive term which were obtained previously[3] using properties of the crystal at different temperatures.

In view of future research on molten mixtures and for direct comparison with the experimental data, an NPT ensemble at $P = 1$ atm was preferred. For computer calculations on this type of ensemble the variable volume of the system prevents the use of tabulated values for the exponential function, whereas this is achievable through the inverse power function. In order to restrict the computing time, different procedures were tested. It was found convenient to use potential (1), with the exponential repulsive function, to calculate the energy which initiates the MC chain. Within the chain a proper inverse power repulsive function was instead used: it should be noted that in the chain only energy variations are requested. Further problems were found in the evaluation of the polarization energy of the system. Being a many-body interaction energy, this quantity needs to be evaluated in the MC loop, a very time consuming computation: it was decided to compute this energy only for every 5000th configuration.

Calculations

a) The Pair Potential

The constants used in the pair potential (1) were: $z_i z_j = 2.3067 \cdot 10^{-11}$ erg Å; $a_{++} + a_{--} = 0.590 \cdot 10^{-8}$, $a_{+-} = 0.881 \cdot 10^{-9}$ erg/molecule, $b = 2.35$ Å^{-1} (see Ref.[3]); $c_{--} = 0.242 \cdot 10^{-9}$, $c_{+-} = 0.257 \cdot 10^{-9}$, $c_{++} = 0.512 \cdot 10^{-9}$ erg Å^{6} (see Reference[4]).

In order to obtain explicit values of a_{++} and a_{--} the Huggins model was used along with Fumi-Tosi data[5]: a ratio $a_{--}/a_{++} = 1/2$ was thus assumed in the calculations. In general it was proved that the value of this ratio is not a critical one for the thermodynamic properties of the system: by varying this ratio, only slight variations in the volume and in the energy were observed. As regards structural properties, it was noted that the general features of the radial distribution functions are independent of this ratio, even though the distance of closest approach of like ions depends on it.

Reprint requests to Prof. Cesare Sinistri, Istituto di Chimica Fisica Università di Pavia, *I-27100* Pavia (Italien).

Within the MC chain the inverse power repulsive function

$$^{\mathrm{R}}\varphi_{ij}(r) = a_{ij}\, r^{-b} \qquad (2)$$

was used. This potential was periodically tested against the exponential one and it was found that the difference between the two repulsive energies did not exceed 0.5%. Typical values for the liquid were: $a_{++} + a_{--} = 0.302 \cdot 10^{-7}$, $a_{+-} = 0.640 \cdot 10^{-8}$ and $b = 8.20$ to obtain $^{\mathrm{R}}\varphi_{ij}(r)$ in erg/molecule.

Spears[6] reported repulsive potentials for all alkali cation and halide anion pairs: his values were mainly deduced from data on the gaseous state. Spears' repulsive potentials are sensitively harder than those obtained from data on the solid, particularly for the $\mathrm{Cs^+} - \mathrm{Br^-}$ pair. By using Spears' potentials in a MC chain, data in total disagreement with the experimental ones were obtained (see further on).

b) The Model

The model[7] consists of a cubic box containing N ions (for the liquid $N = 216$, i.e. 108 $\mathrm{Cs^+}$ and 108 $\mathrm{Br^-}$; for the solid $N = 128$) which interact according to pair potential (1). The box is surrounded on all sides by periodic replicas of itself. Successive configurations, which constitute the MC chain, are generated by randomly choosing an ion which is then randomly moved to a new position. At the same time the volume of the box is randomly changed by a maximum amount of 3%. Configurations are accepted or rejected so that, provided the MC chain is sufficiently long, the factor

$$V_i^N \exp\{-(E_i + P\,V_i)/R\,T\} \qquad (3)$$

is proportional to the frequency with which the i-th configuration of volume V_i and potential energy E_i occurs in the chain.

After equilibration (which requires about 150000 configurations) appropriate averages are taken over about 200000 configurations to estimate the equilibrium properties of the system. Among these, the molar volume V and the molar potential energy E, with its coulomb ($^{\mathrm{C}}E$), van der Waals ($^{\mathrm{W}}E$) and repulsive ($^{\mathrm{R}}E$) components, are particularly significant. The evaluation of the radial distribution function (RDF) is also noteworthy from a structural viewpoint.

Further details on the calculations (e.g. the use of the Ewald method in the computation of the total coulomb energy) can be found in Reference [1].

Two different Fortran programs were used: they were mainly run on the 6030 Honeywell computer of the University of Pavia. The first program, devised for the equilibration of the system, generates about 120000 configurations per hour. It does not contain refinements such as the evaluation of the polarization energy, of the RDF and of the Fourier part of the coulomb energy; besides, the error function part of the Ewald summation is truncated at one half cell length. The second program, which is complete, was used to calculate the mean values of the thermodynamic properties: when devoid of the RDF computation it generates about 30 – 40000 configurations per hour.

c) Thermodynamic Properties

Table 1 reports the results obtained for the molar volume, the internal energy and the coulomb, repulsive, dipole-dipole dispersion and polarization energies of the liquid at the four examined temperatures and of the solid at the melting point. The internal energy U can be obtained from the mean configurational energy E by:

$$U = E + 3\,R\,T \qquad (4)$$

The experimental volumes shown in the table are by Johnson et al.[8] for the solid and by Yaffe and van Artsdalen[9] for the liquid. The experimental value $V = 67.7\ \mathrm{cm^3\,mole^{-1}}$ is also reported in the litera-

	at 1573 K (b. p.)	1133 K	1021 K	910 K liquid (m. p.)	910 K solid (m. p.)
V_{calc}	89.7	74.4	71.7	67.5	58.8
V_{exp}	(90.4) *	74.5	71.0	67.9	53.4
U_{calc}	−132.2	−138.8	−140.1	−141.8	−144.3
U_{exp}	−129.0	−133.9	−135.7	−137.5	−143.1
$^{\mathrm{C}}E$	−154.2	−159.0	−159.9	−161.0	−162.9
$^{\mathrm{R}}E$	28.8	31.4	32.1	32.6	33.0
$^{\mathrm{W}}E$	−16.2	−18.0	−18.4	−18.8	−19.8
$^{\mathrm{P}}E$	−5.1	−4.2	−3.9	−3.4	−2.6

Table 1. Thermodynamic properties of CsBr. The volumes are in $\mathrm{cm^3\,mole^{-1}}$, the energies in $\mathrm{kcal\,mole^{-1}}$. The largest standard deviations on V_{calc} and U_{calc} values are ±0.9% and ±0.06% respectively (* extrapolated value).

ture[10] for the liquid at the melting point; the value at the boiling point was calculated by extrapolating the results given[9] in the range 910 – 1133 K.

Uncertainties on the crystal energy at 298 K and also on the C_P values affect the experimental internal energy data. The figures reported in Table 1 were calculated from Cubicciotti's crystal energy[11] along with the estimated C_P values[12]. For the liquid, the differences between experimental and calculated values are very small for the volume and about 3% for the energy. The calculated heat capacity is 14 – 15 e. u. while literature[12] reports 16 e. u. The heat of fusion obtainable from Table 1 (2.5 kcal/mole) should be compared with the experimental value[13] 5.6 kcal/mole.

It is interesting to observe that the dipole-dipole interaction energy is a rather important quantity for CsBr: in the liquid at the m. p. the coulomb, repulsive and van der Waals energies are in the ratio 100 : 19.9 : 11.7. When fusion occurs the absolute value of all these quantities decreases.

By using Spears' potentials[6] for the computation of the thermodynamic properties of the liquid at the m. p. the following values were obtained:

$V_{\text{calc}} = 139$ (exp $= 67.9$) cm^3 mole^{-1};
$E_{\text{calc}} = -115$ (exp $= -143$),
${}^{\text{C}}E = -128$, ${}^{\text{R}}E = 18$, ${}^{\text{W}}E = -5$,
${}^{\text{P}}E = -2$ kcal mole^{-1}.

These values should be taken as merely indicative since the equilibration of the system was not completed. Nevertheless, the system is clearly strongly relaxed.

d) Polarization Energy

The evaluation of the polarization energy (${}^{\text{P}}E$) was done in the MC chain on a single configuration every 5000. The method used to compute ${}^{\text{P}}E$ is based on the evaluation of the electrostatic field acting on each ion and is fully described in Reference[14]. The ionic polarizabilities used were: $\alpha_{\text{Cs}^+} = 2.94$, $\alpha_{\text{Br}^-} = 4.25$ Å^3 which are averages of many values reported in the literature[15]. The ${}^{\text{P}}E$ value thus calculated was never taken into account for the evaluation of the total potential energy E_i, and therefore it does not affect factor (3).

For solid CsBr at the m.p. the polarization energy is -2.6 kcal mole^{-1} which is a surprisingly high value and is due to the non perfect crystal state of the solid. For liquid CsBr the polarization energy is about 2 – 3% of the coulomb energy and its absolute value increases with temperature.

e) Radial Distribution Function

On the basis of the histograms of the ionic pair distances, the RDF of like ions $g_1(r)$ $[= 1/2(g_{--} + g_{++})]$, of unlike ions $g_u(r)$ $(= g_{+-})$ and of all ions $g_{\text{tot}}(r)$ $[= 1/2(g_u + g_1)]$ has been evaluated.

Figure 1 reports the RDFs of liquid CsBr at 1573 and 910 K. The most significant features of these functions appear in Table 2, where the quantities reported are: 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 ($r^{\min}$) of the functions $g(r)$ and the coordination number (n). Since the two functions $g_{++}(r)$ and $g_{--}(r)$ practically coincide, only their mean value $g_1(r)$ is reported in Fig. 1 and in Table 2. As already pointed out for KCl[1], the RDFs show a remarkable "penetration" of like ions into the first coordination sphere. For liquid CsBr at 910 K there are 0.2 like ions on a total coordination of 3.9 (about 5% penetration); at 1573 K the penetration is 9% (0.3 like ions on 3.4 total coor-

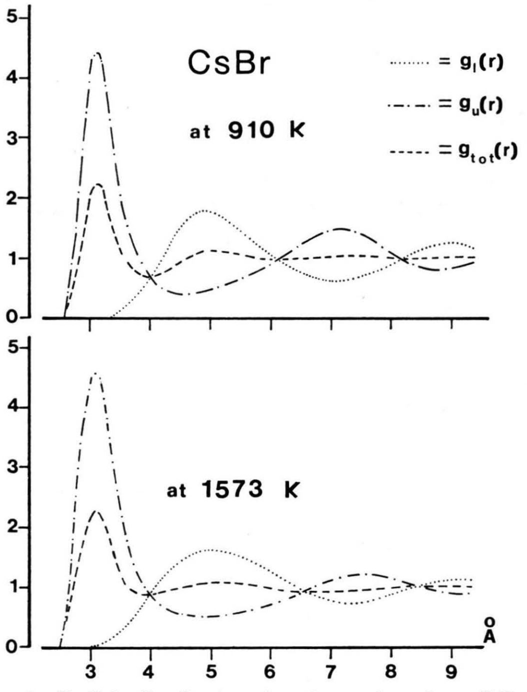

Fig. 1. Radial distribution functions of molten CsBr at 910 (m. p.) and at 1573 K (b. p.) for like ions (g_1), for unlike ions (g_u) and for all ions (g_{tot}).

Table 2. RDF characteristics for molten CsBr as calculated by the MC method (all distances in Å).

	at 1573 K	910 K
d_u	2.48	2.58
r_u^{max}	3.10	3.15
r_u^{min}	4.9	4.6
n_u	4.1	4.5
d_l	3.11	3.31
r_l^{max}	5.0	4.9
r_l^{min}	7.3	7.1
n_l	10.7	13.1
r_{tot}^{max}	3.10	3.15
r_{tot}^{min}	4.0	3.9
n_{tot}	3.4 *	3.9 **

* of which 0.3 are like ions, ** of which 0.2 are like ions.

dination). Among other RDF features which are also in agreement with those observed for liquid KCl, the following are particularly noteworthy: the distance d decreases as T increases, the value of r^{max} is almost independent of T, the first peak of $g_l(r)$ tends to become flatter with increasing T. The shape of $g_u(r)$ and $g_l(r)$ shows that the internal structure of the melt appears statistically formed by shells of alternate charges up to fairly long distances.

The results reported in Table 2 can be compared with those obtained by Levy et al.[16] by X-ray and neutron diffraction. These authors find a first shell with 4.6 – 4.7 neighbours centered at 3.55 Å and a second one with 7.9 – 8.3 neighbours between 4.05 and 5.7 Å.

Final Remarks

The results obtained by computer simulation of the thermodynamic properties of liquid CsBr are fairly good and give support to the used pair potential (1).

The evaluation of the polarization energy brings into evidence some conflicting results: this energy is a sensitive contribution which cannot be neglected without evident variations of the properties of the system (see Reference[14]). On the other hand the thermodynamic properties of CsBr can be calculated without taking into account the ^{P}E contribution.

One might suppose that the polarization energy is somehow included in pair potential (1). Thus the repulsive term $a_{ij} \exp(-b\,r)$ should be considered as a semiempirical function accounting for whatever is not coulomb nor van der Waals energy.

These considerations might partially justify the negative results obtained when using Spears' repulsive potentials for this type of calculations.

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