Study by Numerical Simulation of the Structural and Dynamical Properties of the Fused LiCl-KCl Eutectic

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The ionic properties of the eutectic LiCl-KCl melt are examined in a large range of temperature and density. The radial distribution functions are calculated. It is shown that, although the contribution of the Coulomb energy to the thermodynamic properties decreases at high temperatures it remains always predominant and explains the temperature dependence of the specific heat at constant volume.

The diffusion coefficients of Li^+, K^+ and Cl^- are determined. The mechanism of the ionic motion is studied through the memory function formalism. Two types of motion are detected, which arise from binary collisions and from dynamical events which involve a large number of ions. Temperature and volume changes show that the lithium ions remain always surrounded by a more structured atmosphere which hinders their motion. This effect becomes more apparent at high temperature and low density.

Introduction

Our present understanding of the structural and dynamical properties of ionic liquids is based largely on the results of computer simulations using rigid ion potentials [1, 2]. The properties of a system of charged particles can be easily calculated on the assumption of a pairwise additive interaction. For most of the alkali chlorides the comparison between the calculated and the available experimental properties indicates that the simulation process gives a correct representation of the actual system [3, 4]. Then, these technics appear as a tool of investigation of electrolytes: they give detailed information on the intimate structure and atomic motion in these liquids; they can be used to obtain data in regions where experimental investigations are inaccurate or hard to carry out.

In the present work we have choosen to study the LiCl-KCl eutectic mixture (59 mol.% LiCl, 41 mol.% KCl, melting point 352 °C) at different temperatures and molar volumes. In addition to its technological interest [5] this mixture is considered particularly suitable for study because of the existing extensive data of its physico-chemical properties.

The purpose of the present work is to investigate how the diffusion coefficients and the structure of this melt are affected by varying the temperature (at constant volume) or by varying the density (at constant temperature).

Details of the Simulation

The method of the computer simulation of Molecular Dynamics is described in ref. [6]. The form of the potential function was taken to be that suggested by Tosi and Fumi [7].

$$\Phi_{ij}(r_{ij}) = z_i z_j \frac{e^2}{r_{ij}} + b_{ij} \cdot \exp B\,(\sigma_{ij} - r_{ij}) + \frac{C_{ij}}{r_{ij}^6} + \frac{D_{ij}}{r_{ij}^8}. \tag{1}$$

The parameters introduced in (1) have been deduced from the parameters given for pure salts [7] by an interpolation analogous to the combining rule indicated by Larsen et al. [8]. The used values are given in Table 1. 108 anions Cl^-, 63 cations Li^+ and 45 cations K^+ are introduced in a periodic box of length L. For experiments at constant volume the box length is $L = 18.18$ Å; it corresponds to a molar volume $V_m = 33.48\ cm^3$, which is the experimental value at about 640 K [9–10] at atmospheric pressure.

To construct a suitable starting configuration an aged liquid configuration previously used [11] is adjusted to the required temperature and volume. This system was then equilibrated for at least 5 ps before accumulating quantities for averaging. A re-

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Table 1. Repulsion and dispersion parameters of the Tosi-Fumi pair potential in the LiCl-KCl mixtures deduced from the pure salt data $B/10^{10}\,m^{-1}$: 2.941 for all pairs.

	Li-Li	Li-K	K-K	Cl-Li	Cl-K	Cl-Cl
$b/10^{-20}$ J	6.760	5.344	4.225	4.645	3.380	2.535
$\sigma/10^{-10}$ m	1.632	2.279	2.926	2.401	3.048	3.17
$C/10^{-79}$ Jm^6	− 0.073	− 1.332	− 24.30	− 2.000	− 48.0	− 116.4
$D/10^{-99}$ Jm^8	− 0.030	− 0.849	− 24.00	− 2.40	− 73.0	− 233.9

presentative time evolution of the system is obtained from 20000 successive time steps. The time step is $0.8 \cdot 10^{-14}$ s at low temperatures and $0.6 \cdot 10^{-14}$ s at 1570 K, 1946 K and 3418 K.

Structure

The equilibrium microstructure is a fundamental quantity which is required for the interpretation of both the thermodynamic and time-dependent phenomena [12−13]. We base our discussion of the structure of the melt on the six partial radial distribution functions. These rdf's are characterized (Figs. 1, 2) by the following quantities: the distance of closest approach r_c, the position r_M and height h_M of the main peak, the position r_m of the minimum following this peak. These quantities are listed in Table 2. The positions r_M of the first peak are in good agreement with the values indicated recently by Okada et al. [14] for eutectic LiCl-KCl at low temperature (669 K).

For the anion-cation rdf's, the large values of h_M reflect the predominance of the Coulomb attraction and the behaviour of r_M and h_M on isothermal expansion indicates the incipient formation of ion pairs at a separation close to the distance r_{min} corresponding to the minimum of the pair potential (for Li^+-Cl^- $r_{min} = 1.84$ Å, potential energy at that point: 613.92 kJ mole^{-1}; for K^+-Cl^- $r_{min} = 2.58$ Å, potential energy 470.21 kJ mole^{-1}). When more space is given to the set of ions r_M does not vary significantly.

As observed for many other liquids, polar or non polar, the distance of closest approach decreases with increasing temperature while the first peak becomes lower and broader [13]. Also the penetra-

Table 2. Numerical values deduced from the radial distribution functions; r_M and h_M are the position (in Å) and the height of the first peak; r_m is the position of the first minimum; r_c is the closest distance of approach.

		Constant volume $V_m = 33.48$ cm^3 mole^{-1} temperature:				Constant temperature $T = 1570$ K volume V_m/cm^3 mole^{-1}		
		706.1 K	1176.1 K	1946.0 K	3418.5 K	33.48	42.51	54.35
Li-Cl	r_c	1.70	1.67	1.54	1.33	1.60	1.53	1.55
	r_M	2.23	2.17	2.12	2.09	2.12	2.11	2.10
	h_M	5.61	4.46	3.51	2.94	3.86	4.47	5.59
	r_m	3.41	3.45	3.64	3.79	3.61	3.68	3.79
K-Cl	r_c	2.42	2.35	2.20	2.04	2.27	2.22	2.23
	r_M	3.00	2.92	2.89	2.80	2.90	2.93	2.92
	h_M	3.21	2.70	2.47	2.16	2.60	2.62	2.89
	r_m	4.32	4.47	4.47	4.46	4.47	4.54	4.58
Li-Li	r_M	3.68	3.67	3.67	3.64	3.66	3.70	3.78
	h_M	1.83	1.69	1.68	1.42	1.69	1.63	1.86
	r_m	5.30	5.30	5.42	5.49	5.42	5.46	5.52
K-Li	r_M	4.00	4.00	3.99	3.98	3.99	4.26	4.43
	h_M	2.25	1.97	1.58	1.36	1.68	1.73	1.59
	r_m	5.98	6.00	5.99	5.99	5.99	6.13	6.23
K-K	r_M	4.45	4.42	4.27	4.24	4.32	4.75	4.89
	h_M	1.92	1.54	1.54	1.25	1.56	1.48	1.48
	r_m	6.52	6.52	6.60	6.66	6.52	6.87	7.00
Cl-Cl	r_M	3.79	3.77	3.71	3.71	3.72	3.77	3.89
	h_M	2.29	1.97	1.71	1.46	1.83	1.70	1.69
	r_m	5.38	5.38	5.45	5.53	5.43	5.74	5.93

tion of the different shells increases with increasing temperature and the contribution of the Coulomb energy (negative) to the potential energy becomes smaller (Table 3). As the repulsion energy (positive) increases, these two effects (Coulomb + repulsion) contribute to decrease the potential energy (negative).

A different behaviour is observed for an isothermal volume change: at high pressure a more ordered structure appears; this is indicated by the higher values of h_M. The number of unlike ions in the vicinity of a given ion increases. If we integrate up to r_m of the rdf for Li-Cl or K-Cl (coordination numbers n) we find at 1570 K:

$$\text{for}\quad V_m = 54.35\ \text{cm}^3\,\text{mole}^{-1},\quad n_{\text{LiCl}} = 2.04\,,\quad n_{\text{KCl}} = 2.00\,,$$

$$V_m = 33.48\ \text{cm}^3\,\text{mole}^{-1},\quad n_{\text{LiCl}} = 2.51\,,\quad n_{\text{KCl}} = 2.88\,.$$

Also, as the unlike ions distance of approach does not vary very much, the increase of pressure leads to higher values of both the Coulomb and repulsion energies. As the changes of these two terms nearly neutralize one another, the volume change has no marked effect on the values of the internal energy of the salt (Table 3).

The molar heat capacity C_V (JK^{-1}) is deduced from the variation of the internal energy at constant volume ($V_m = 33.478\ \text{cm}^3$). It can be represented by the equation:

$$C_V = 68.0 - 13.5 \cdot 10^{-3}\,T + 2.01 \cdot 10^{-6}\,T^2\,. \tag{2}$$

The dependence of C_V on temperature is only due to the variation of the Coulomb energy. Indeed the contribution of the kinetic energy is constant and equal to $3R = 24.94\ \text{JK}^{-1}$; the part coming from the short-range forces is also nearly constant and equal to $(12.8 \pm 0.8)\ \text{JK}^{-1}$. Under the effect of thermal agitation the ionic arrangement becomes more random as indicated by the shape of the radial distribution functions $g_{\text{Li-Cl}}$ and $g_{\text{K-Cl}}$; this larger cancellation of Coulomb forces induces the C_V change; the contribution of the Coulomb energy to the specific heat varies from $23.2\ \text{JK}^{-1}$ at 700 K to $9.3\ \text{JK}^{-1}$ at 3400 K.

Ionic Dynamics

The study of the dynamical properties is restricted here to the single particle properties. The self-diffusion coefficients D of the ions are deduced from the linear increase of the time-dependent mean-square displacement $\langle \delta^2 \rangle$.

$$D = \frac{1}{6}\,\frac{\langle \delta^2 \rangle}{t}\,. \tag{3}$$

This relation is obeyed for times t far greater than an induction time τ_0. An order of magnitude of τ_0 is given by the brownian motion approximation. In this case the time dependence of $\langle \delta^2 \rangle$ is given by [15]:

$$\langle \delta^2 \rangle = \frac{6\,m\,D^2}{k\,T}\left\{\frac{k\,T}{m\,D}\,t - 1 + \exp\left(-\frac{k\,T}{m\,D}\,t\right)\right\}. \tag{4}$$

As expected, this formula shows that $\langle \delta^2 \rangle$ is proportional to t^2 at very short times; the induction time $\tau_0 = m\,D/k\,T$ which characterizes the apparition of the linear dependence varies according to the particle mass; here we have at 1570 K and $V_m = 33.48\ \text{cm}^3$: $\tau_0 = 0.7 \cdot 10^{-14}$ s for Li^+; $\tau_0 = 3.7 \cdot 10^{-14}$ s for K^+ and $\tau_0 = 3.4 \cdot 10^{-14}$ s for Cl^-. These times correspond to an average displacement of 0.3 Å.

An alternative route to derive the self-diffusion coefficient involves the self-correlation function for ionic velocity v_i [16] (see Figs. 3, 4):

$$D = \tfrac{1}{3}\int_0^{\infty} \langle v_i(0) - v_i(t) \rangle\, \delta t\,. \tag{5}$$

Table 3. Computed thermodynamic properties: internal energy U and resolution of the potential energy, pressure, specific heat C_V at constant volume.

Temperature/K		706.8	1176.1	1946.0	3518.5	1570.0	1570.0	1570.0
Molar volume/cm^3 mole^{-1}		33.48	33.48	33.48	33.48	33.48	42.51	54.35
Pressure/kbar		6.2	12.6	23.5	42.2	18.8	4.80	0.065
Specific heat C_V/J K^{-1} mole^{-1}		59.5	54.9	49.3	45.3	51.7		
Energy/kJ	Internal U	− 734.7	− 708.2	− 668.1	− 599.4	− 686.8	− 680.3	− 672.3
	Coulomb	− 866.2	− 857.0	− 846.0	− 832.3	− 850.2	− 826.6	− 812.6
	Dipole-dipole	− 19.4	− 20.1	− 21.6	− 23.7	− 20.9	− 16.1	− 13.6
	Dipole-quadrupole	− 3.0	− 3.3	− 3.7	− 4.4	− 3.5	− 2.6	− 2.3
	Repulsion	136.2	142.9	154.6	175.6	148.7	126.0	116.9

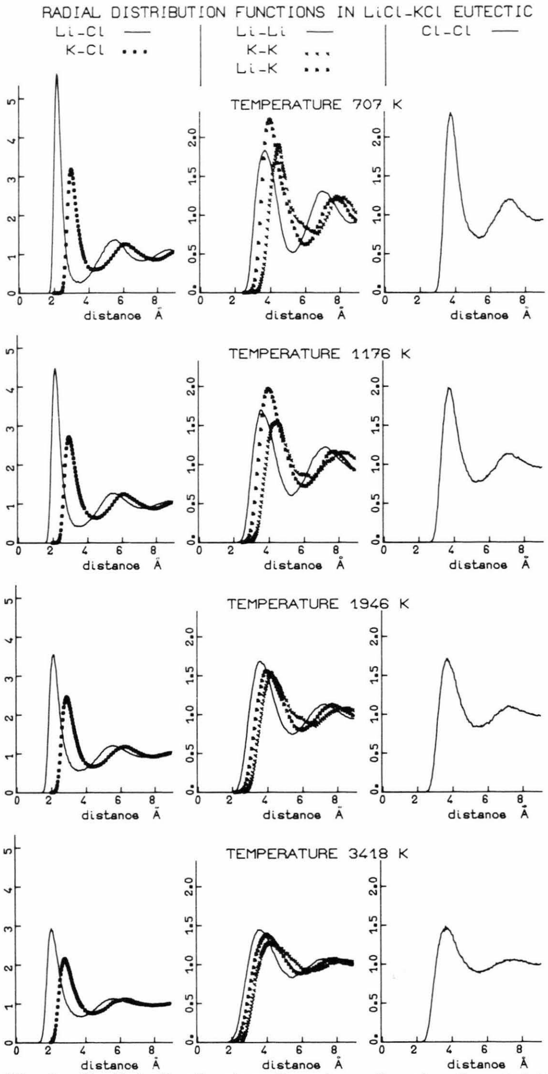

Fig. 1. Radial distribution functions for the fused LiCl-KCl eutectic mixture at constant volume $V_m = 33.48$ cm^3 mole^{-1} and different temperatures.

For an infinite system and a long time the two expressions of D are equivalent [17]. But for a run of limited duration involving a finite system they can give different results since the available dynamical information is weighted differently. In our calculations the departure between the two methods never exceeds 8 per cent; the average values of D are given in Table 4.

At constant volume the dependence of D on T is represented by the classical equation

$$D = D_0 \exp(-\Delta H/RT)\,. \qquad (6)$$

As the temperature range is very large (from 700 K to 3400 K), D_0 and ΔH are not constant; therefore two subintervals have been used. The values of the parameters D_0 and ΔH are given in Table 5. At low temperatures the diffusion coefficients of the three ions Li^+, K^+ and Cl^- are quite similar but at higher temperature the Li^+ ions become more mobile than K^+ and Cl^-.

The density effect on D is studied at 1570 K; the decrease of D which occurs when the molar volume V_m is reduced can be represented by the equation:

$$D = a + b\,V_m + c\,V_m^2\,. \qquad (7)$$

The values of the parameters a, b and c are reported in Table 5. It is also possible to derive the function $D(T)$ for the molar volume V_m corresponding to constant pressure experiments. The volumes V_m are calculated by interpolating the V_m values of the pure salts [10]; it has been shown that the excess molar volume is very small [9]. In these calculations

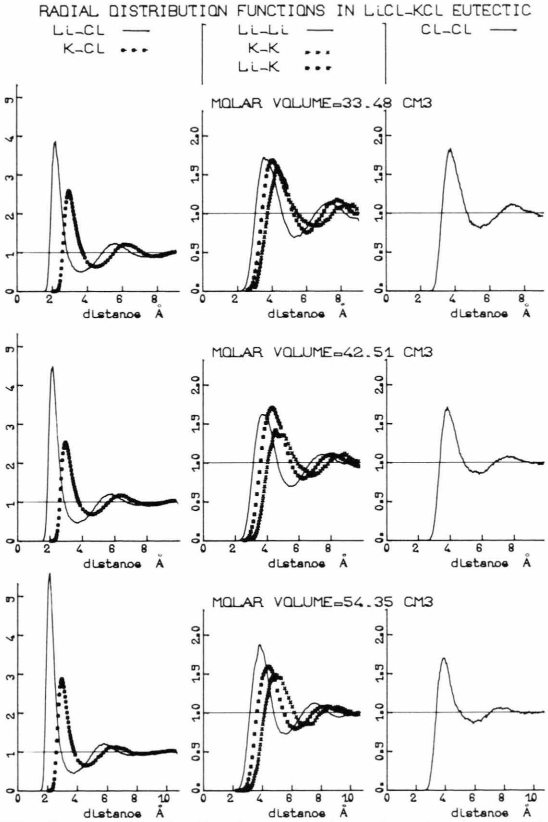

Fig. 2. Radial distribution functions for the fused LiCl-KCl eutectic mixture at constant temperature $T = 1570$ K and different molar volumes.

Table 4. Self-diffusion coefficients D in $10^{-5}\,\mathrm{cm^2\,s^{-1}}$ of Li^+, K^+ and Cl^- in the eutectic LiCl-KCl. Parameters of the memory functions $M(t) = \omega_1^2 \exp(-t/\tau_1) + \omega_2^2 \exp(-t/\tau_2)$, ω in $10^{13}\,\mathrm{s^{-1}}$ and τ in 10^{-13} s; σ: deviation between calculated and M.D. velocity autocorrelation functions (see Figs. 3 and 4).

Temperature/K		706.8	1176.1	1946.0	3418.5	1570.0	1570.0	1570.0
Molar volume/cm^3 mole^{-1}		33.48	33.48	33.48	33.48	33.48	42.51	54.35
Lithium ion	D	2.59	7.12	21.6	48.0	13.4	19.7	23.7
$m_{Li} = 7.0$ amu	ω_1	9.31	9.40	9.63	9.07	9.61	9.41	9.02
	ω_2	4.27	4.03	3.99	3.80	4.00	4.41	4.75
	τ_1	0.052	0.049	0.045	0.050	0.045	0.033	0.023
	τ_2	1.54	0.95	0.41	0.31	0.622	0.338	0.268
	σ%	4.9	3.9	3.1	2.9	3.5	3.4	4.2
Potassium ion	D	2.63	6.72	17.0	37.4	12.5	18.7	26.1
$m_K = 39.1$ amu	ω_1	2.45	2.61	3.01	3.38	2.79	2.55	2.46
	ω_2	0.72	0.95	0.55	–	0.71	0.56	–
	τ_1	0.326	0.232	0.224	0.171	0.256	0.242	0.214
	τ_2	7.27	2.39	1.36	–	1.40	0.69	–
	σ%	1.6	1.1	0.9	1.4	0.8	1.2	1.5
Chloride ion	D	2.67	6.71	16.8	35.7	12.5	18.5	24.2
$m_{Cl} = 35.45$ amu	ω_1	3.07	3.16	3.29	3.65	3.16	2.97	3.08
	ω_2	0.78	0.74	0.34	–	0.50	0.63	–
	τ_1	0.259	0.238	0.232	0.170	0.257	0.218	0.161
	τ_2	6.25	3.20	2.05	–	1.60	0.214	–
	σ%	1.5	1.2	0.7	1.2	1.0	0.8	1.7

are included the values found previously for the same system at 646 K and 1096 K. The parameters of the relation $D = D_0 \exp(-\Delta H/RT)$ are given in Table 5 for the three ions. These relations can be considered as giving the values of the self-diffusion coefficients at the atmospheric pressure. To our knowledge the self-diffusion coefficients have not yet been measured; however it has been shown [18] that in alkali halides the Li^+, K^+ and Na^+ have a similar diffusion coefficient. The values (in $10^{-5}\,\mathrm{cm^2\,s^{-1}}$) obtained here ($D_{Li} = 2.35$ and 3.24, $D_K = 2.50$ and 3.36, respectively, at 404 °C and 482 °C) can be compared to the values $D_{Na} = 1.97$ and 2.65 obtained from radio-tracer experiments in this melt at the same temperatures [19].

It is shown that a temperature change at constant pressure has the same influence on the three ions. This behaviour results from two opposite effects under the combined temperature and volume changes. Indeed at constant temperature the ions interact more easily when the volume is increased; the lithium ion with its strong electrostatic interactions moves less faster than the potassium ion. At constant volume under the effect of thermal agitation there is a decreasing influence of the electrostatic interaction and, then the lithium moves more faster than potassium ion when the temperature is increased. These observations, which are quite

Table 5. Evolution of the diffusion coefficients in the LiCl-KCl eutectic (D in $\mathrm{cm^2\,s^{-1}}$).

At constant temperature $T = 1570$ K

$D = a + b\,V_m + c\,V_m^2$ $a/10^{-5}\,\mathrm{cm^2\,s^{-1}}$		V_m = molar volume in cm^3 $b/10^{-5}\,\mathrm{cm^{-1}\,s^{-1}}$	V_m range = 33.5 – 54.4 cm^3 $c/10^{-8}\,\mathrm{cm^{-4}\,s^{-1}}$
Li^+	– 35.16	2.037	– 17.57
K^+	– 16.03	0.974	– 3.66
Cl^-	– 20.65	1.257	– 7.93

At constant volume $V_m = 33.48$ cm^3; $D = D_0 \exp^{-\Delta H/RT}$

	R range: 706 – 1570 K		T range: 1570 – 3420 K	
	$D_0/10^{-5}\,\mathrm{cm^2 s^{-1}}$	ΔH/kJ	$D_0/10^{-5}\,\mathrm{cm^2 s^{-1}}$	ΔH/kJ
Li^+	46.10	17.11	140.6	30.46
K^+	39.08	16.05	94.7	26.92
Cl^-	38.74	15.91	86.1	25.60

For the experimental V_m at the atmospheric pressure
($V_m = 29.43 + 3.194 \cdot 10^{-3}\,T + 4.725 \cdot 10^{-6}\,T^2$);
$D = D_0 \exp^{-\Delta H/RT}$

	Temperature range 646 – 1570 K	
	$D_0/10^{-5}\,\mathrm{cm^2\,s^{-1}}$	ΔH/kJ
Li^+	92.5	20.8
K^+	82.8	19.9
Cl^-	88.3	20.9

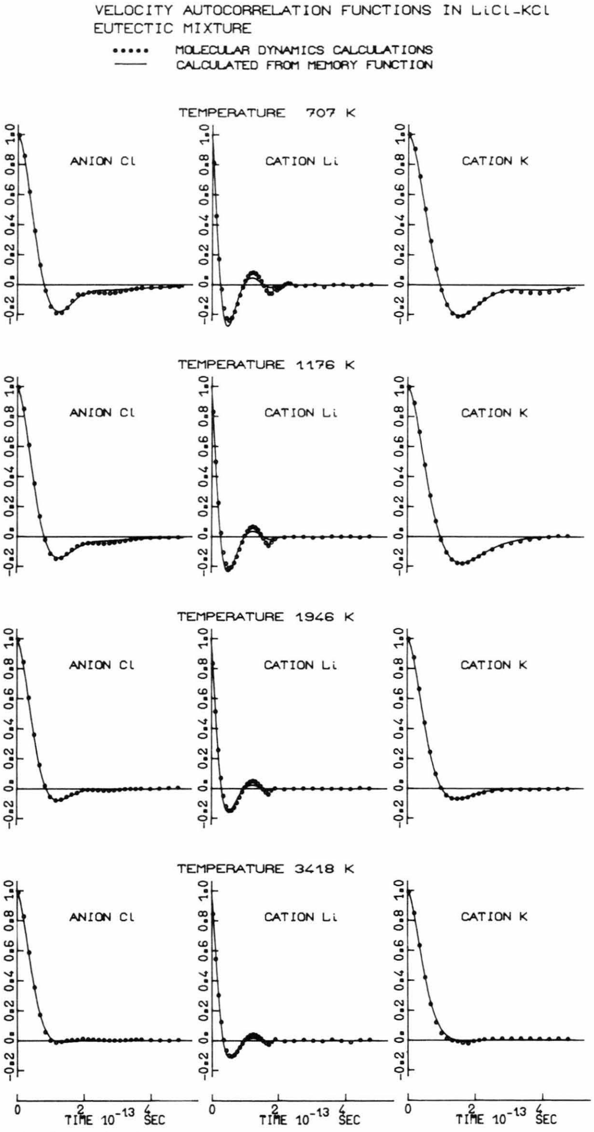

Fig. 3. Velocity autocorrelation functions for the fused LiCl-KCl eutectic mixture at constant volume $V_m = 33.48\ \mathrm{cm}^3\ \mathrm{mole}^{-1}$ and different temperatures.

general in fused alkali halides systems, are in good agreement with an analysis developed recently [20] on the same subject.

Ionic Motion and the Chemla's Effect

More details on the mechanism of ion motion can be obtained from the memory formalism which provides a link between the particle dynamics and the liquid structure. The function $M(t)$ represents the autocorrelation of the random forces acting on the particles; it can be calculated [21] from the velocity autocorrelation function according to the equation [22]

$$\dot{V}(t) = -\int_0^t M(t-t')\,V(t')\,\mathrm{d}t' .$$

As a first approximation the time evolution of $M(t)$ can be represented by the sum of two exponential functions [21]:

$$M(t) = \omega_1^2 \exp(-|t|/\tau_1) + \omega_2^2 \exp(-|t|/\tau_2) .$$

In broad terms, is seems safe to attribute the rapid decay at short times to the effect of binary collisions, whereas the tail in the memory function arises from dynamical events involving a large number of

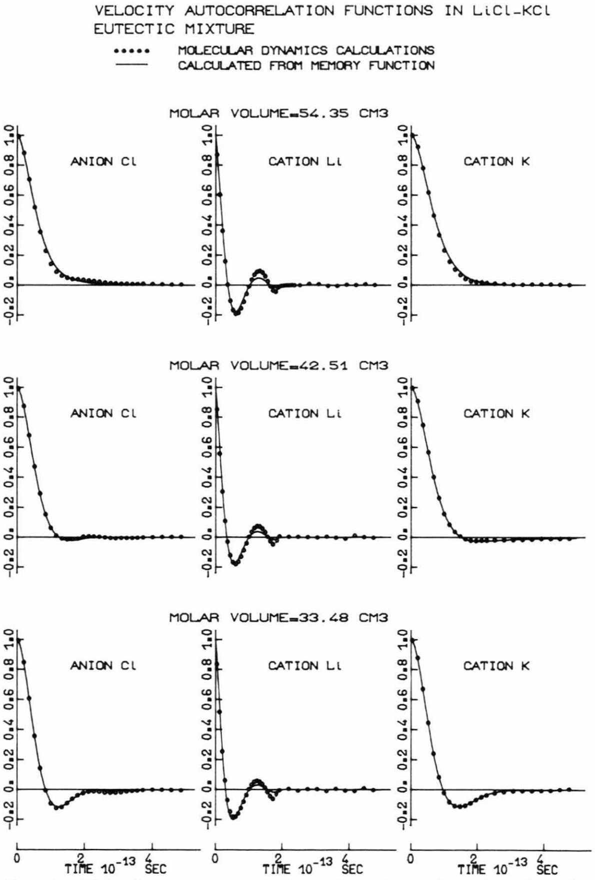

Fig. 4. Velocity autocorrelation functions for the fused LiCl-KCl eutectic mixture at constant temperature $T = 1570$ K and different molar volumes.

ions [23]. The values of the parameters τ and ω are reported in Table 4.

At constant temperature the density changes have a marked effect on the relaxation times τ_1 and τ_2. More free-space reduces the life-time of local structure (for K^+ and Cl^- ions the calculations are not so accurate to detect the value of τ_2 at low density). In general a loosening of the ionic environment is observed at low density (decreasing values of ω_1 and ω_2 for K^+) but for the Li^+ ions it seems that a significant increase of ω_2 is observed; this is attributed to a greater cohesion of the collective displacements due to the strong electrostatic field around this ion.

At constant volume the frequency of binary collisions increases as the temperatures increases. The more random distribution observed when the thermal agitation becomes greater induces a large decrease of the relaxation time τ_2 of the collective mode of motion (at 3418 K the τ_2 values for K^+ and Cl^- ions are too small to be significantly measured). The same decreasing tendency is observed for τ_1 except for the Li^+ ions; this behaviour can again be attributed to the persistance of a local order around this ion even at high temperature. As expected, under the effect of an increase of the temperature, or of the volume, the friction terms $\omega_1^2 \tau_1$ and $\omega_2^2 \tau_2$ decrease, but this influence is less pronounced for Li^+. Then, at high temperature or at low density, the lithium ion becomes less mobile than the potassium ion; as this behaviour is due to the presence of a cohesive atmosphere of negative ions, this difference between Li^+ and K^+ ions should be more apparent on the results concerning the electrical mobilities. The verification of this assertion requires the calculation of the current-current correlation functions [24]. Experimental by this behaviour has been observed by Chemla et al. for many systems such as LiBr-KBr, $LiNO_3$-KNO_3 [25, 26].

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