Theory of linear response applied to the lithium isotope effects on the mobilities in molten LiCl

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Expressions in terms of group-velocity time-correlation functions for the ionic mobilities of molten ^{6}LiCl,^{7} LiCl and (^{6}Li,^{7} Li)Cl are derived, taking the time-averaged zero momentum of inertia of each of the three groups of ions into account. MD-simulations have been performed for ^{6}LiCl and ^{7}LiCl, yielding agreement between the simulated and the published experimental reduced isotope effect, although the temperature - volume conditions of the simulations did not conform with natural LiCl.

According to the theory of linear response [1] the ionic mobilities of a molten salt can be obtained from an MD-simulation of the melt in its equilibrium state. This is because the ions follow the faster the forces exerted on them by the fluctuating internal electric field, the more mobile they are, and the time auto- and cross-correlations of their species-averaged velocities, i.e. their group-velocities, which can be extracted from an MD-simulation, are related to their mobilities [2,3]

We consider additive binary systems (1,2)3 consisting of two monovalent cations 1 and 2 and one monovalent anion 3 because the mobilities of many such systems have been measured [4]. If the simulations reproduce such experimental results, they will give new quantitative information about the dynamics in the melts and will allow for predictions in p, T-regions inaccessible by experiments.

According to the theory, the internal mobilities b_{13} and b_{23} are given by (cf. (10), (12), and (15) in [2])

$$b_{i3} = \frac{e}{kT} \int_0^\infty K_{i3}(t) \mathrm{d}t, \; i = 1, 2 \tag{1}$$

with e the elementary charge and

$$\begin{aligned} K_{13} &= -(1 + x_1)C_{13} - x_2 C_{23} \\ &\quad + x_2 C_{12} + x_1 C_{11} + C_{33}, \\ K_{23} &= -(1 + x_2)C_{23} - x_1 C_{13} \\ &\quad + x_1 C_{12} + x_2 C_{12} + C_{33}, \end{aligned} \tag{2}$$

where x_1 and $x_2 = 1 - x_1$ are the mole fractions of 1 and 2 and the C_{ij} are group-velocity time-correlation functions

$$\begin{aligned} C_{ij}(t) &= N_3 < \overline{\boldsymbol{v}_i(t)} \cdot \overline{\boldsymbol{v}_j(0)} >, \\ C_{ij}(t) &= C_{ji}(t); \; i, j = 1, 2, 3. \end{aligned} \tag{3}$$

N_3 is the number of anions in the periodic cube of the simulation and $\overline{\boldsymbol{v}_k(t)} (k = i, j)$ is the average velocity of the ions k. The brackets mean “ensemble average”, which in the simulation is the average over different starting times $t = 0$ of the correlations. The larger N_3, the smaller is the value of the ensemble average, while the product of the two remains constant.

Since the moments of inertia of the three groups of ions are and remain zero in the ensemble average, one has the three relations

$$\begin{aligned} x_1 m_1 C_{11} + x_2 m_2 C_{21} + m_3 C_{31} &= 0, \\ x_1 m_1 C_{12} + x_2 m_2 C_{22} + m_3 C_{32} &= 0, \\ x_1 m_1 C_{13} + x_2 m_2 C_{23} + m_3 C_{33} &= 0, \end{aligned} \tag{4}$$

where $m_i (i = 1, 2, 3)$ are the ionic masses. These relations allow to eliminate three correlation functions in (2). If one choosen to eliminate the autocorrelation functions, one obtains

$$\begin{aligned} K_{13} &= \alpha_{13} C_{13} + \alpha_{23} C_{23} + \alpha_{12} C_{12}, \\ K_{23} &= \beta_{13} C_{13} + \beta_{23} C_{23} + \beta_{12} C_{12} \end{aligned} \tag{5}$$

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with

$$\begin{aligned}
\alpha_{13} &= -\left[1 + x_1\Big(1 + \frac{m_1}{m_3}\Big) + \frac{m_3}{m_1}\right],\\
\alpha_{23} &= -\big(1 - x_1\big)\Big(1 + \frac{m_2}{m_3}\Big),\\
\alpha_{12} &= \big(1 - x_1\big)\Big(1 - \frac{m_2}{m_1}\Big),\\
\beta_{13} &= -x_1\Big(1 + \frac{m_1}{m_3}\Big),\\
\beta_{23} &= -\left[1 + \big(1 - x_1\big)\Big(1 + \frac{m_2}{m_3}\Big) + \frac{m_3}{m_2}\right],\\
\beta_{12} &= x_1\Big(1 - \frac{m_1}{m_2}\Big).
\end{aligned} \tag{6}$$

In case of a single salt (1 → +, 3 → −), one obtains

$$b_{+-} = \frac{e}{kT}\int_0^\infty K_{+-}(t)\mathrm{d}t, \tag{7}$$

$$K_{+-}(t) = \alpha_{++}C_{++} = \alpha_{--}C_{--} = \alpha_{+-}C_{+-} \tag{8}$$

with

$$\begin{aligned}
\alpha_{++} &= \Big(1 + \frac{m_+}{m_-}\Big)^2,\\
\alpha_{--} &= \Big(1 + \frac{m_-}{m_+}\Big)^2,\\
\alpha_{+-} &= -\Big(1 + \frac{m_+}{m_-}\Big)\Big(1 + \frac{m_-}{m_+}\Big).
\end{aligned} \tag{9}$$

One may now ask, in what respect the information from such calculations exceeds the information got from the experimental internal mobilities. In case of a single salt the simulation yields the time-dependent function $K_{+-}(t)$, while the experiment gives only the time-independent mobility b_{+-}. Thus from the simulation one learns something about the duration of the correlations. For additive binary systems (1,2)3 this is also true but, more important, the simulation gives three functions, e.g. $C_{13}(t), C_{23}(t)$ and $C_{12}(t)$, while the experiment gives only the two values of b_{13} and b_{23}. One may compare the functions $C_{13}(t)$ and $C_{23}(t)$ with the corresponding functions for the single salts, while the function $C_{12}(t)$ gives information about the correlation between the movements of the cations 1 and 2 in the mixture.

The dynamics in a molten salt depends on both the interionic forces and the ionic masses. These two dependencies are partly singled out in system like (^{150}Nd,^{150}Sm)Cl$_3$ and (^{204}Tl,^{206}Tl)Cl. While systems of the former type are rare and have never been studied, neither experimentally nor by MD-simulations with variation of their m_+/m_--ratio, systems of the latter type are abundant and their mobilities have in many cases been measured [4].

For the present MD-study we have chosen the system (^{6}Li,^{7}Li)Cl. The experimental results for $x_1 = 1, x_1 = 0.079$ (natural mixture) and $x_1 = 0$ are reported in [5].

The case $x_1 = 0.079$ would require a large periodic box in order to have sufficient ^{6}Li-ions in the box. Therefore we decided to simulate instead the case $x_1 = 0.5$. To get reliable results, we also had to enlarge the difference of the lithium masses. For reasons given the Appendix A, the simulations were done with $m_1 = 4.25$ and $m_2 = 9.32$. With these cationic masses, the anionic mass $m_3 = 35.45$ and $x_1 = 0.5$, the coefficients in (6) and (9) become

$$\begin{aligned}
&\alpha_{13} = -9.796,\ \alpha_{23} = -0.633,\ \alpha_{12} = -0.597,\\
&\beta_{13} = -0.561,\ \beta_{23} = -5.388,\ \beta_{12} = +0.272.
\end{aligned} \tag{10}$$

and

$$\begin{aligned}
&\alpha^{(1)}_{++} = 1.254,\ \alpha^{(1)}_{--} = 87.105,\ \alpha^{(1)}_{+-} = -10.453,\\
&\alpha^{(2)}_{++} = 1.595,\ \alpha^{(2)}_{--} = 23.078,\ \alpha^{(2)}_{+-} = -6.066,
\end{aligned} \tag{11}$$

respectively. Please note that, in case of a single salt, the larger are the masses of the ions involved, the smaller are their thermal velocities, the smaller are the absolute values of their velocity-correlation functions, and the larger are the absolute values of the coefficients α.

As a first step we have simulated the isotopic LiCl salts ($+^{(1)}-$) and ($+^{(2)}-$) with the masses $m^{(1)}_+ = 4.25$, $m^{(2)}_+ = 9.32$ and $m_- = 35.45$. These simulations are described in the Appendix B. The resulting functions $K^{(1)}_{+-}(t)$ and $K^{(2)}_{+-}(t)$, together with the corresponding running intergrals are shown in Figure 1. The values of $\int_0^\infty K_{+-}(t)\mathrm{d}t$ were approximated by averaging over the running integrals from $t = t_0$ to $t = t_0+240\,\delta t$,. where t_0 is the time where the function $K_{+-}(t)$ becomes zero for the second time and $\delta t = 0.5\cdot 10^{-14} s$ is the time step of the simulation. These averages are shown in Fig. 1 as horizontal lines. The ratio q of their ordinates amounts to 1.30. Thus, according to (7), the result is

$$q = (b_{+-})_{m_+=4.25}/(b_{+-})_{m_+=9.32} = 1.30. \tag{12}$$

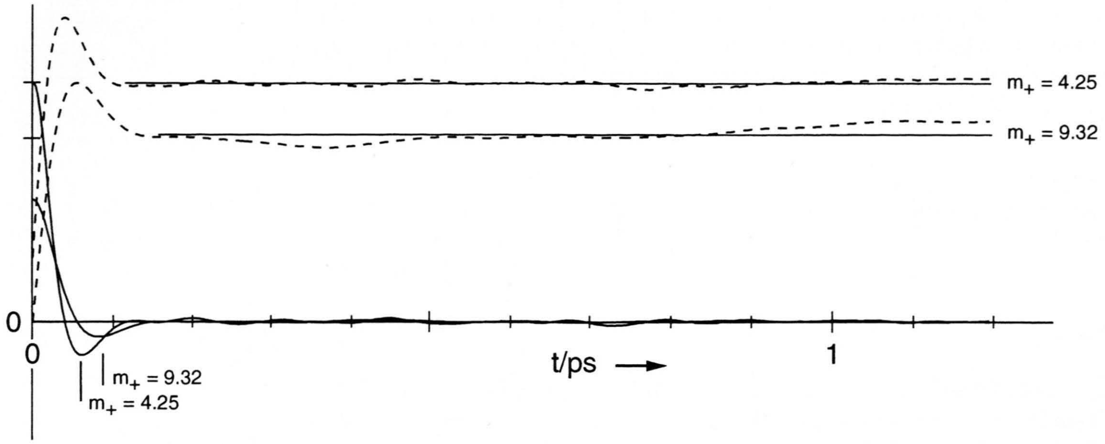

Fig. 1. The functions $K_{+-}(t)_{m_+=4.25}$ and $K_{+-}(t)_{m_+=9.32}$ (solid lines) and the corresponding running integrals (broken lines) both in arbitrary units.

The masses $m_+ = 4.25$ and $m_+ = 9.32$ were chosen such (see Appendix A), that

$$-1.29\frac{q-1}{\sqrt{q}} = \left(\frac{\mathrm{d}\ln b_{+-}}{\mathrm{d}\ln m_+}\right)_{m_+=6.5, m_-=35.45}$$

Thus the simulation has yielded

$$\left(\frac{\mathrm{d}\ln b_{+-}}{\mathrm{d}\ln m_+}\right)_{m_+=6.5, m_-=35.45} = -0.342. \qquad (13)$$

The simulation was performed for a periodic box containing $N_3 = 108$ chlorine ions with a density corresponding to the experimental molar volume of LiCl at 1023 K.

The measurement of the conductivities of ^{6}LiCl and ^{7}LiCl at 1023 K had yielded [5]

$$\mu_+^0 = \left(\frac{\mathrm{d}\ln b_{+-}}{\mathrm{d}\ln m_+}\right)_{m_+=6.5, m_-=35.45} = -0.335. \qquad (14)$$

Since a temperature of about 1570 K resulted from the simulations (see Appendix B), whereas the size of the periodic box and the experimental reduced cation-isotope effect on the mobilities (μ_+^0) corresponded to 1023 K, one may wonder why the experimental μ_+^0 was so well reproduced by such simulations. The answer is, that in our case the value of μ_+^0 resulting from the simulations is independent of the temperature in the box.

This follows from (8), which shows that the relations between the three group velocity time correlation functions do not change with temperature. Since μ_+^0 is a quotient of such correlation functions, it will stay constant on varying, ceteris paribus, the temperature.

The experimental temperature-dependence of μ_+^0 will result from simulations with boxes whose sizes correspond to experimental molar volumes at different temperatures. Experimentally the dependence of μ_+^0 on temperature was found to be linear within error-margins. Therefore it would be sufficient to perform two simulations for the two lithium masses and the same box -size, and two other simulations for the same masses and an other box-size, the box-sizes corresponding to experimental molar volumes at given temperatures.

Figure 1 shows that, on the average, the movement of an ion at a given time is independent of its movement at some minimal time before. This relaxation time is, according to (8), the same for the Li^+ and Cl^- ions. In case of $m_+ = 4.25$ it amounts to 0.118 ps, and in case of $m_+ = 9.32$ to 0.156 ps.

One may ask, what distance the ions move on the average during this time. If they move with their average one-dimensional thermal velocity $\sqrt{kT/m}$, which at $T = 1570$ K is 1.75 km/s for $m_+ = 4.25$, 1.18 km/s for $m_+ = 9.32$ and 0.60 km/s for $m_- = 35.45$, the distances are in $\mathrm{LiCl}_{m_+=4.25}$ 2.06 Å for Li^+ and 0.71 Å for Cl^-, and in $\mathrm{LiCl}_{m_+=9.32}$ 1.84 Å for Li^+ and

0.94 Å for Cl^-. These distances may be compared with the diameter 3.8 Å of the chlorine ions.

By further simulations we intend to obtain the dependence of μ_+^0 on the temperature, and also μ_+ for a 1 to 1 mixture of ^6LiCl and ^7LiCl.

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Appendix A

In order to obtain sufficiently accurate MD-results for ^6LiCl and ^7LiCl, the simulations had to be performed for an enlarged difference of the lithium masses. Since the dependence of b_{+-} on m_+ is not linear, however, a too large difference would involve an error when interpolating linearly to obtain $d\ln b_{+-}/d\ln m_+$ at $m_+ = 6.5$. Therefore we have interpolated according to the known nonlinear dependence of b_{+-} on $r = m_+/m_-$ of an ionic gas.

In a completely dissociated gasified salt only two-body collisions have to be taken account of, and therefore one has [4]

$$b_{+-} = a\left(\frac{m_+ m_-}{m_+ + m_-}\right)^{-1/2}, \tag{A1}$$

where a depends on the forces, the molar volume and the temperature, but not on the masses. For $m_+ \ll m_-$ and $m_+ \gg m_-$ the relation (A1) is also valid for a liquid salt because then the respective heavy ions are practically immobile. In our case m_- is fixed, and we write (A1) in the form

$$b_{+-} = a(m_-)^{-1/2}(1 + r^{-1})^{1/2}. \tag{A2}$$

The dependence of b_{+-} on r according to (A2) is shown in Fig. A1, where $a\cdot(m_-)^{-1/2}$ is set to be unity. In this figure some straight lines are drawn which are parallel to the tangent of the curve at $r_0 = 6.5/35.45 = 0.183$. On the assumption that the curve for the liquid has about the same curvature as the curve for the gas it was decided to obtain the tangent of the imagined curve for the liquid at r_0 from the values of $(b_{+-})_{r_1}$ and $(b_{+-})_{r_2}$ obtained from the simulation with $r_1 = 4.25/35.45 = 0.120$ and $r_2 = 9.32/35.45 = 0.263$. One then has

$$\left(\frac{d\ln b_{+-}}{d\ln m_+}\right)_{r_0} = \frac{r_0}{(b_{+-})_{r_0}}\,\frac{(b_{+-})_{r_1} - (b_{+-})_{r_2}}{r_1 - r_2}, \tag{A3}$$

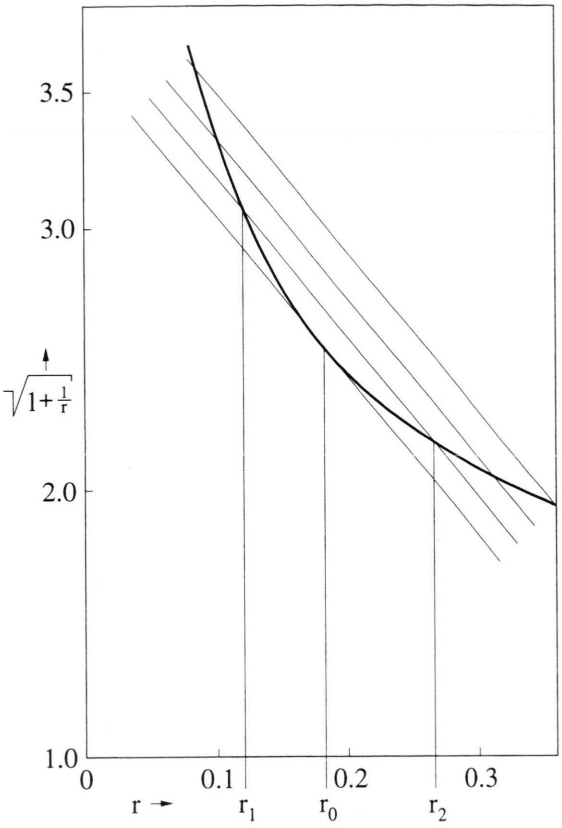

Fig. A1. The dependence of the internal mobility $b_{+-} = a\,(m)^{-1/2}\sqrt{1+\frac{1}{r}}$ in units $a\,(m_-)^{-1/2}$ on $r = m_+/m_-$ for the ionic gas. The value $r_0 = 0.183$ for the average of ^6LiCl and ^7LiCl, and the values $r_1 = 0.12$ and $r_2 = 0.263$ chosen for the simulations are indicated.

where according to (A2)

$$(b_{+-})_{r_0} = \frac{\sqrt{1 + r_0^{-1}}}{\sqrt[4]{1 + r_1^{-1}}}\sqrt{(b_{+-})_{r_1}(b_{+-})_{r_2}},$$

i.e.

$$(b_{+-})_{r_0} = 0.983\,\sqrt{(b_{+-})_{r_1}(b_{+-})_{r_2}}. \tag{A4}$$

With (A4) and the values of r_0, r_1, and r_2, (A3) becomes

$$(d\ln b_{+-}/d\ln m_+)_{r_0} = -1.289\,\frac{q-1}{\sqrt{q}} \tag{A5}$$

with

$$q = (b_{+-})_{r_1}/(b_{+-})_{r_2}. \tag{A6}$$

Appendix B

We used Born-Mayer-Huggins pair potentials

$$\phi_{ij}(r) = \frac{e^2}{r} + b\,B_{ij}\exp\left(\frac{\sigma_{ij}-r}{\varrho}\right) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}$$

with the parameters for LiCl suggested by Tosi and Fumi [6]:

ij	B_{ij}	σ_{ij} 10^{-8}cm	C_{ij} 10^{-60}erg cm^6	D_{ij} 10^{-76}erg cm^8
++	1.250	1.632	0.073	0.03
+-	1.375	2.401	2.000	2.40
--	0.750	3.170	111.000	223.00

$b = 0.33810^{-12}$ erg/mol, $1/\rho = 2.92\,10^8$ cm^{-1}, e elementary charge.

108 cations and 108 anions were placed randomly with zero total momentum of inertia in a cubic periodic box having an edge-length S of 17.365 Å corresponding to the molar volume 29.2 cm^3/mol of LiCl at 1023 K [7]. Ewald's method with $\eta = 0.175\ S$ Å^{-1} was applied to determine the Coulomb energy. The time step was $5 \cdot 10^{-3}$ ps.

After equilibrium was reached, 52500 time steps were performed for each Li mass. The resulting averaged internal energies (U) temperatures (T) and pressures (P) with the corresponding standard deviations were:

Li mass	U J/mol	T K	P kbar
4.25	-825331.2 ± 66.5	1571 ± 62	-0.16 ± 2.2
9.32	-825458.7 ± 14.8	1569 ± 60	-0.21 ± 2.1

The internal energy at 1023 K, resulting from the experimental values of the lattice energy at 298 K [8], the heat capacities of the crystal and the melt, and the heat of fusion [9], amounts to -750 810 J/mol, i.e. it is by 9% smaller than the internal energy got from the simulations. This indicates that the repulsive forces resulting from the pair potentials used are too small as compared to the resulting attractive forces.

The kinetic energy fluctuated by 4% and amounted to 4.7% of the internal energy, while the internal energy fluctuated by only about 5 ‰.

The standard deviation of the pressure amounted to ± 2 kbar. The reason for this behaviour might be the rigidity and small size of the periodic box, which prevents large scale density fluctuations, while in the natural melt such fluctuations, extending over more than 17 Å, do exist.

For these reasons it was not possible to obtain realistic mobilities but only the mobility ratio, which amounted to $q = 1.30 \pm 0.076$.

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