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Space-dependent self-diffusion processes in molten copper halides: A molecular dynamics study

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This work is concerned with single ion dynamics in molten copper halides (CuI and CuCl) which exhibit fast ionic conduction before melting. The self-dynamic structure factor of the two ionic species in each melt have been calculated by molecular dynamics simulations and the corresponding effective wavelength-dependent self-diffusion coefficients have been studied. The results have been compared with those obtained for molten alkali halides (KCl and RbCl). © 2001 American Institute of Physics. [DOI: 10.1063/1.1401827]

I. INTRODUCTION

In this work, we are concerned with molten CuI and CuCl, two copper halides that melt from superionic phase or show strong premelting phenomena that result in rather large values of the ionic conductivity before melting. In the superionic phase, the anions are closely bound to lattice sites and the cations are relatively mobile. These systems exhibit a relatively large size difference between cations and anions: the former are smaller, more disordered, and more mobile. Effective pair potentials, which allow for reduction in the effective ionic charges and introduce a very small ionic radii differences between the cation and anion motions arise solely from the mass difference. In KCl, the almost perfect symmetry between the two species, which only differ in the charge sign, implies that the dynamics of cations and anions is almost identical [see Fig. 1(a)]. Then, we shall compare the self-diffusional processes in these two alkali halides with those in two systems where the size difference plays an important role. In CuI the cations are smaller and lighter than the anions, while in CuCl the cations are smaller and heavier.

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The layout of the paper is briefly as follows. In Sec. II we outline simulated systems and definitions of the evaluated properties. In Sec. III we present the MD results obtained for KCl, RbCl, CuI, and CuCl. These are followed by relevant conclusions.

II. SIMULATED SYSTEMS AND EVALUATED PROPERTIES

We have studied molten KCl, RbCl, CuI, and CuCl near the melting point. The temperature $T$ and the ionic density $\rho = (N_+ + N_-)/V$ for each system are indicated in Table I. We have assumed the effective pair potentials of Fumi-Tosi reviewed by Sangster and Dixon\textsuperscript{15} for KCl and RbCl, and the potentials proposed by Stafford et al.\textsuperscript{4} for CuI and CuCl.

MD of the four melts has been carried out by considering systems made up of 108 cations ($N_+$) and 108 anions ($N_-$) placed in a cubic box of side $L = (N/\rho)^{1/3}$ with periodic boundary conditions.\textsuperscript{16} The positions and velocities of the ions have been computed using the Beeman’s integration algorithm with a time step of $5 \times 10^{-15}$ s. The long-range Coulomb interactions have been calculated according to the Ewald method.\textsuperscript{15}

The evaluated properties of interest in this paper are the self-intermediate scattering functions (SISF) of species $\alpha (\alpha = +, -)$,

$$F_{\alpha}^s(k,t) = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \exp[-i \mathbf{k} \cdot (\mathbf{r}_{i\alpha}(t) - \mathbf{r}_{i\alpha}(0))], \quad (1)$$

where the angular brackets represent the ensemble average, $\mathbf{r}_{i\alpha}(t)$ is the position of an ion of species $\alpha$, and $\mathbf{k} = (2 \pi / L) \mathbf{n}$ is a wave vector in the reciprocal space allowed by the periodic boundary conditions, $\mathbf{n}$ being a vector of integer components. In liquids the SISF is function of $k = |\mathbf{k}|$. Furthermore, since the SISF is an autocorrelation, it is a real and even function. The time Fourier transform of the SISF is the self-dynamic structure factor (SDSF),

$$S_{\alpha}^s(k,\omega) = \frac{1}{2 \pi} \int_{-\infty}^{\infty} F_{\alpha}^s(k,t) \exp(i \omega t) dt = \frac{1}{\pi} \int_{0}^{\infty} F_{\alpha}^s(k,t) \cos(i \omega t) dt. \quad (2)$$

Besides the above functions, we have also calculated the normalized velocity autocorrelations functions (VACF),

$$\psi_{\alpha}(t) = \frac{1}{3 u_{0\alpha}^2} \sum_{i=1}^{N_{\alpha}} \left( \mathbf{v}_{i\alpha}(t) \cdot \mathbf{v}_{i\alpha}(0) \right), \quad (3)$$

where $\mathbf{v}_{i\alpha}(t)$ is the velocity of an ion of species $\alpha$ and $u_{0\alpha} = \sqrt{k_{B} T / m_{\alpha}}$ is the thermal velocity of these ions. $k_{B}$ is the Boltzman’s constant and $m_{\alpha}$ is the mass of a $\alpha$-type ion. The self-diffusion coefficient can be evaluated by the Green–Kubo formulas,

$$D_{\alpha} = u_{0\alpha}^2 \int_{0}^{\infty} \psi_{\alpha}(t) dt. \quad (5)$$

Furthermore, we have also calculated the partial radial distribution functions $g_{\alpha\beta}(r)$ and the corresponding partial static structure factors. In the studied molten monohalides $S_{++}(k)$ and $S_{--}(k)$ present the first peak at the same wave number value, which we will indicate by $k_{\text{max}}$, while $S_{+-}(k)$ presents a minimum at this wave number. This structural feature is a reflection of the regular alternation of concentric shells of oppositely charged ions.\textsuperscript{17} The wavelength associated to $k_{\text{max}}$ corresponds to the distance between shells of like ions, $d_{\text{like}} = 2 \pi / k_{\text{max}}$, which is about twice the averaged first-neighbor distance between unlike ions. The static structure factors and corresponding radial distribution functions are available on request.

It is useful to recall that $F_{\alpha}^s(k,t)$ is the spatial Fourier transform of the van Hove self-correlation function, $G_{\alpha}^s(r,t)$, which is defined as the probability per unit volume of finding a tagged $\alpha$-type ion at a distance $r$ at time $t$ given that it was located at the origin at time zero. Since $G_{\alpha}^s(r,t) = (2 \pi)^{-3} \iiint F_{\alpha}^s(k,t) \exp(-i \mathbf{k} \cdot \mathbf{r}) d\mathbf{k}$, for a given $t$, $G_{\alpha}^s(r,t)$ can be considered as a superposition of static harmonic plane waves of wavelength $\lambda = 2 \pi / k$ and amplitude proportional to $e^{-i \mathbf{k} \cdot \mathbf{r}}$.
to $F^s_a(k,t)$. So, $F^s_a(k,t)$ gives the time evolution of the amplitude of the harmonic plane waves and $S^s_a(k,\omega)$ is its spectral distribution. Since $G^s_a(r,t)$ describes the time evolution of the averaged spatial distribution of the tagged ion, say the space-dependent self-diffusion process, it is an initially sharply peaked distribution around $r=0$ which spreads over $r$ as the ion diffuses along time. Consequently, $F^s_a(k,t)$ decays monotonically with a decay rate that increases with $k$, indicating that the shorter wavelength plane waves die out rapidly. Moreover, a more rapidly decaying of $F^s_a(k,t)$ gives a broader $S^s_a(k,\omega)$, which also decays monotonically. So, the self-diffusional processes can be described by the half-width at half-maximum of $S^s_a(k,\omega)$. Furthermore, the self-diffusional processes can also be described by the peak height of $S^s_a(k,\omega)$. Since the zero frequency moment of the SDSF is the unity, the area under $S^s_a(k,\omega)$ is the same for all wave numbers. So, the peak height becomes lower as $S^s_a(k,\omega)$ becomes broader with $k$.

In the free-particle (FP) limit ($t\to 0$, $k\to \infty$, $\omega\to \infty$) the SISF is a Gaussian in $t$ and the SDSF is a Gaussian in $\omega$,

$$[S^s_a(k,\omega)]_{FP} = \frac{1}{\sqrt{2\pi}} \frac{1}{u_{0a} k} \exp\left(-\frac{1}{2} \frac{\omega^2}{(u_{0a} k)^2}\right),$$

with a half-width at half-maximum given by

$$[\Delta \omega_a(k)]_{FP} = \sqrt{2} \ln \frac{2}{u_{0a} k},$$

which is proportional to the decay rate of the SISF.

On the other hand, in the hydrodynamic (HD) limit ($t\to \infty$, $k\to 0$, $\omega\to 0$), also called diffusion limit, the SISF decays exponentially with $t$ and the SDSF is a Lorentzian centered at $\omega=0$,

$$[S^s_a(k,\omega)]_{HD} = \frac{1}{\pi} \frac{D^a \omega_a k^2}{\omega^2 + (D^a \omega_a k)^2},$$

with a half-width at half-maximum given by

$$[\Delta \omega_a(k)]_{HD} = D^a \omega_a k^2,$$

which is the decay rate of the SISF.

Since $D^a$ is related to $[\Delta \omega_a(k)]_{HD}$, the space-dependent self-diffusion process is usually described by the following effective wavelength-dependent self-diffusion coefficient

$$D^s_a(k) = \frac{\Delta \omega_a(k)}{k^2},$$

where $\Delta \omega_a(k)$ is the half-width at half-maximum of $S^s_a(k,\omega)$. Obviously, $D^s_a(k)$ is equal to $D^a$ in the HD limit as can be seen from Eq. (9).

Moreover, the peak height of SDSF, $S^s_a(k,\omega=0)$, is usually described by the following dimensionless wave number dependent function,

$$\Sigma^s_a(k) = \frac{S^s_a(k,\omega=0)}{[S^s_a(k,\omega=0)]_{HD}} = \pi D^a \omega_a k^2 S^s_a(k,\omega=0),$$

that is, the peak height normalized to the corresponding value in the HD limit,
reached at a larger $k$ value and $\Delta_\alpha(k)$ approaches to the FP limit at larger wave numbers. In RbCl, the normalized effective self-diffusion coefficient of the heavier ions, $\Delta_{\text{Rb}}(k)$, reaches the maximum and approaches to the FP limit at lower $k$ values than that of the lighter ions, $\Delta_{\text{Cl}}(k)$. In copper halides, the normalized effective self-diffusion coefficient, which reaches the maximum and approaches to the FP limit at lower wave numbers, corresponds to the more diffusive ions, that is $\Delta_{\text{Cu}}(k)$, independently of the relative mass.

The qualitative behavior of $\Delta_\alpha(k)$ after $k_{\text{max}}$ described above can be estimated from the dynamical characteristic wave number $k_\alpha$ defined in Eq. (15) and given in Table II. For $k_\alpha$ values about twice $k_{\text{max}}$ ($\alpha=\text{Cu}^+$), the shape of $\Delta_\alpha(k)$ reminds us that in hot liquids, whereas for $k_\alpha$ values larger than three times $k_{\text{max}}$ the shape $\Delta_\alpha(k)$ is similar to that observed in simple monatomic liquids near the melting point. As $k_\alpha$ is larger, $\Delta_\alpha(k)$ approaches the FP limit at larger $k$ values and its maximum is higher and located at a larger wave number. Since the self-diffusion coefficients of the two ionic species in RbCl are very close ($D_{\text{Rb}}<D_{\text{Cl}}$), and the cations are heavier than the anions ($m_{\text{Rb}}>m_{\text{Cl}}$), the value of $k_{\text{max}}$ is lower for the cations ($k_{\text{Rb}}<k_{\text{Cl}}$). However, despite the cations are lighter than the anions ($m_{\text{Cu}}>m_{\text{Cl}}$), in CuI the value of $k_{\text{max}}$ is also lower for the cations ($k_{\text{Cu}}<k_{\text{Cl}}$) because the anions are much more diffusive than the cations ($D_{\text{Cu}}<D_{\text{Cl}}$). In CuI, where the cations are heavier and much more diffusive than the anions ($m_{\text{Cu}}>m_{\text{Cl}}$) and $D_{\text{Cu}}>D_{\text{Cl}}$, $k_\alpha$ is also lower for the cations ($k_{\text{Cu}}<k_{\text{Cl}}$). Furthermore, $k_1<k_{\text{Cl}}$ since $m_{\text{Cl}}>m_{\text{Cu}}$ and $D_{\text{Cl}}>D_{\text{Cu}}$.

We turn now to study the wave number dependence of the peak height. In Fig. 3 we have plotted $\Sigma_\alpha(k)$ for the four molten salts. As in Fig. 2, we have only shown the results for the cations in KCl. At wave numbers larger than 6 Å$^{-1}$, we have also plotted this function in FP limit, that is,

$$[\Sigma_\alpha(k)]_{\text{FP}} = \sqrt{\frac{k}{\pi k_\alpha}}.$$

As can be seen in Fig. 3, the transition from small to large wave numbers of $\Sigma_\alpha(k)$ is also determined by $k_\alpha$. In all the cases, when $\Delta_\alpha(k)$ presents a well-defined maximum (higher than unity), $\Sigma_\alpha(k)$ presents a dip. Although less pronounced, this dip was also observed in monatomic liquids near melting. Moreover, in copper halides the dimensionless peak height of the more diffusive ions, $\Sigma_{\text{Cu}}(k)$, increases monotonically as it does in monatomic dense gases or hot liquids.

### Table II. Wave numbers corresponding to the first peak of the static structure factors ($k_{\text{max}}$), and the characteristic wave numbers defined by Eq. (15).

<table>
<thead>
<tr>
<th></th>
<th>KCl</th>
<th>RbCl</th>
<th>CuI</th>
<th>CuCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{max}}$ (Å$^{-1}$)</td>
<td>1.6</td>
<td>1.5</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>$d_{\text{like}}=2\pi/k_{\text{max}}$</td>
<td>3.9</td>
<td>4.1</td>
<td>3.2</td>
<td>3.7</td>
</tr>
<tr>
<td>$k_\alpha$ (Å$^{-1}$)</td>
<td>6.4</td>
<td>8.2</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>$k_1$ (Å$^{-1}$)</td>
<td>6.6</td>
<td>11.5</td>
<td>9.8</td>
<td>17.8</td>
</tr>
</tbody>
</table>

The minimum of $\Delta_\alpha(k)$ near $k_{\text{max}}$ reminds the collective phenomenon of de Gennes narrowing observed in simple liquids. The narrowing of the width of the total dynamic structure factor around the first diffraction peak corresponds to a slowing down in the decay of the density fluctuations with these wavelengths. Physically, this phenomenon can be understood by arguing that the strong spatial correlations at these wavelengths can not easily be destroyed. Therefore, it is said that de Gennes narrowing corresponds to a structural inhibition of the diffusion mechanism. We recall that, although the SDSFs are the self-contribution to the total dynamic structure factor, their half-width at half-maximum, $\Delta\omega_\alpha(k)$, do not show any minimum. Nevertheless, the dip of $\Delta_\alpha(k)=\Delta\omega_\alpha(k)/(D_\alpha k^2)$ can be thought as the signature of de Gennes narrowing in the single ion dynamics.

After the dip, $\Delta_\alpha(k)$ shows a maximum and at large $k$ values approaches to the FP limit. The value of this maximum for the cations of CuI and CuCl, Cu$^+$, is lower than unity, $\Delta_{\text{Cu}}(k)<1$, while in all the other cases it is higher than the unity. Moreover, $\Delta_{\text{Cu}}(k)$ approaches the FP limit at lower wave numbers than $\Delta_{1}(k)$ or $\Delta_{\text{Cl}}(k)$. Despite its small maximum, the shape of $\Delta_{\text{Cu}}(k)$ reminds us of the monatomic dense gases or hot liquids. On the contrary, the shape of $\Delta_\alpha(k)$ in the other cases reminds that for monatomic liquids near melting.

The maximum of $\Delta_\alpha(k)$ found in monatomic liquids near melting has been related to the oscillatory component in the VACF. Our results confirm this relation. As we can see from Figs. 1 and 2, the maximum of $\Delta_\alpha(k)$ is higher when the corresponding VACF exhibits a more pronounced backscattering. Furthermore, as the maximum is higher it is
This behavior can be explained taking into account that in the HD limit
\( S(k) \) and its FP limit. The corresponding figures are available on request.
Taking into account that the copper

\[ k \]

diffusion reminds us of that in hot liquids. As in simple monatomic liquids, the space-dependent self-diffusion process in the four studied molten monohalides (KCl, RbCl, CuI, and CuCl) is less favorable at wavelengths related to the main spatial correlations. However, in molten monohalides these wavelengths are over
\[ d_{\text{like}} = 2\pi/k_{\text{max}} \]

which is about the radius of the second-neighboring shell of like ions and twice the first-neighbor distance between unlike ions, while in monatomic liquids these wavelengths are over the first-neighbor separation.

The main features of \( \Delta(k) \) and \( \Sigma(k) \) can be qualitatively estimated from the value of the dynamical characteristic wave number
\[ k_\alpha = (k_BT/m_\alpha)^{1/2}/D_\alpha \]

As \( k_\alpha \) is larger, \( \Delta(k) \) and \( \Sigma(k) \) approach the FP limit at larger \( k \) values. For \( k_\alpha \) values larger than three times \( k_{\text{max}} \), the self-diffusional process is similar to that observed in simple monatomic liquids near the melting point. If \( k_\alpha \) is about twice \( k_{\text{max}} \), self-diffusion reminds us of that in hot liquids.

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