

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

Olga Alcaraz and Joaquim Trullàs

Citation: *The Journal of Chemical Physics* **115**, 7071 (2001); doi: 10.1063/1.1401827

View online: <http://dx.doi.org/10.1063/1.1401827>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/115/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[A molecular dynamics examination of the relationship between self-diffusion and viscosity in liquid metals](#)
J. Chem. Phys. **136**, 214505 (2012); 10.1063/1.4723683

[Self-diffusion coefficient in smoothed dissipative particle dynamics](#)
J. Chem. Phys. **130**, 021101 (2009); 10.1063/1.3058437

[Molecular dynamics simulation of imidazolium-based ionic liquids. II. Transport coefficients](#)
J. Chem. Phys. **130**, 014703 (2009); 10.1063/1.3042279

[Effect of bending and torsion rigidity on self-diffusion in polymer melts: A molecular-dynamics study](#)
J. Chem. Phys. **123**, 114901 (2005); 10.1063/1.2035086

[Molecular dynamics simulations of aqueous NaCl and KCl solutions: Effects of ion concentration on the single-particle, pair, and collective dynamical properties of ions and water molecules](#)
J. Chem. Phys. **115**, 3732 (2001); 10.1063/1.1387447



2014 Special Topics

PEROVSKITES

2D MATERIALS

MESOPOROUS MATERIALS

BIOMATERIALS/
BIOELECTRONICS

METAL-ORGANIC
FRAMEWORK
MATERIALS

AIP | APL Materials

Submit Today!

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

Olga Alcaraz and Joaquim Trullàs^{a)}

Departament de Física i Enginyeria Nuclear, UPC, Campus Nord, 08034 Barcelona, Spain

(Received 7 May 2001; accepted 19 July 2001)

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.^{1–3} Effective pair potentials, which allow for reduction in the effective ionic charges and introduce a very small ionic radii ratio, have been proposed for molten copper halides.⁴ These potentials are quite successful in accounting for the main structural trends observed in molten CuCl by neutron diffraction experiments.^{5–7} While the anion–anion and cation–anion structure qualitatively resemble those of molten alkali halides, the cation–cation structure is less marked and presents a deep penetration of the cations into the first coordination shell of anions.

Molecular dynamics simulations (MD) of molten copper halides⁸ show that, for a given melt, the self-diffusion coefficient of the small ions (D_+) is much higher than that of the large ones (D_-), which was also experimentally observed in molten CuCl.⁹ For this reason, it is said that copper halides retain in the liquid state some of the “superionic” features that characterize their high-temperature solid phase. Moreover, MD shows that the velocity autocorrelation function (VACF) of the large ions is always oscillatory while the VACF of the small ones exhibits only a weak backscattering (see Fig. 1). Although Cu⁺ are lighter than I[−], their VACF in CuI does not present oscillations, as it would be expected from molten alkali halides results.¹⁰ The oscillatory VACF corresponds to I[−]. These results suggest that the large ions experience a “rattling” motion in the relatively long-lived cage formed by the neighboring like ions, while the small ones diffuse through the packed structure of slowly diffusing unlike ions. This picture contrast with that given for molten

alkali halides where the “rattling” motion is experienced by the lighter ions in the neighboring cage of unlike ions.¹¹

In a recent work, we confirmed the above picture for copper halides.¹² We showed that the averaged microscopic motion of the small ions is mainly determined by the first-neighboring shell of unlike ions, whereas the nearest shell of like ions (the second-neighboring shell) also affects the dynamics of the large ions. Moreover, we showed that the difference between the cation and anion sizes encourages the backscattering and oscillations of the VACF of the large ions, whereas the mass difference encourages the vibrational motion of the light ions. However, the size difference effects prevail in the hydrodynamics regime and the self-diffusion coefficient of the small ions is higher than that of the large ones (see Table I). In copper halides, size difference effects are much more important than mass difference effects. On the other hand, in alkali halides, where the cation and anion sizes are very similar, D_+ and D_- are very close.

The aim of this article is to gain further insight into the dynamical processes associated with diffusional motion of single ions in copper halides. To this end, we have calculated by MD the self-intermediate scattering functions (SISF) of the two ionic species in CuI and CuCl, and the corresponding self-dynamic structure factor (SDSF). These functions describe the physical process of space-dependent diffusion of a tagged ion in the reciprocal space. While there are many studies about the SDSFs of monatomic liquids,^{13,14} to our knowledge, there is not yet any MD study about the SDSFs in molten salts. For this reason, we have also calculated the SDSFs in molten KCl and RbCl. In RbCl, the symmetry of the cation–cation and anion–anion interactions implies that the 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.

^{a)}Author to whom correspondence should be addressed. Electronic mail: quim.trullas@upc.es

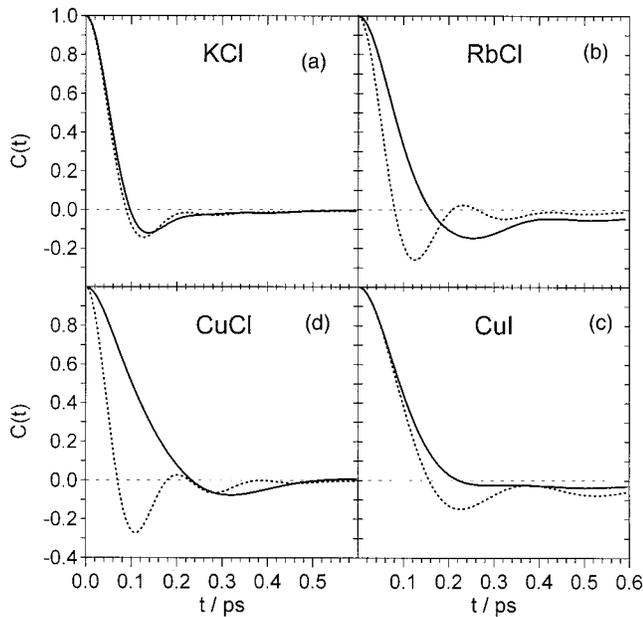


FIG. 1. Normalized velocity autocorrelation functions for (a) KCl, (b) RbCl, (c) CuI, and (d) CuCl. Solid lines are for the cations and dotted lines are for the anions.

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, CuCl, and CuI. 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 Dixon¹⁵ for KCl and RbCl, and the potentials proposed by Stafford *et al.*⁴ for CuI and CuCl.

MD of the four melts have 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.¹⁶ The positions and velocities of the ions have been computed using the Beeman's integration algorithm with a time step of 5×10^{-15} s. The long-range Coulomb interactions have been calculated according to the Ewald method.¹⁵

TABLE I. Temperature (T), ionic densities (ρ), and self-diffusion coefficients (D_α) of the simulated molten salts.

| | KCl | RbCl | CuI | CuCl |
|---------------------------------------|--------|--------|--------|--------|
| T (K) | 1173 | 1023 | 938 | 773 |
| ρ (\AA^{-3}) | 0.0235 | 0.0221 | 0.0282 | 0.0443 |
| D_+ (10^{-5} cm ² /s) | 7.8 | 3.8 | 9.5 | 9.3 |
| D_- (10^{-5} cm ² /s) | 7.9 | 4.2 | 2.5 | 2.4 |

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

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

where the angular brackets represent the ensemble average, $\mathbf{r}_{i\alpha}(t)$ is the position of an ion of species α , 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),

$$\begin{aligned} S_\alpha^s(k, \omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} F_\alpha^s(k, t) \exp(i\omega t) dt \\ &= \frac{1}{\pi} \int_0^{\infty} F_\alpha^s(k, t) \cos(i\omega t) dt. \end{aligned} \quad (2)$$

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

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

where $\mathbf{v}_{i\alpha}(t)$ is the velocity of an ion of species α and

$$u_{0\alpha} = \sqrt{\frac{k_B T}{m_\alpha}} \quad (4)$$

is the thermal velocity of these ions. k_B is the Boltzman constant and m_α is the mass of a α -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_{\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.¹⁷ The wavelength associated to k_{\max} corresponds to the distance between shells of like ions, $d_{\text{like}} = 2\pi/k_{\max}$, 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, $G_\alpha^s(\mathbf{r}, t)$, which is defined as the probability per unit volume of finding a tagged α -type ion at a distance r at time t given that it was located at the origin at time zero. Since $G_\alpha^s(\mathbf{r}, t) = (2\pi)^{-3} \iiint F_\alpha^s(\mathbf{k}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{k}$, for a given t , $G_\alpha^s(\mathbf{r}, t)$ can be considered as a superposition of static harmonic plane waves of wavelength $\lambda = 2\pi/k$ and amplitude proportional

to $F_\alpha^s(k, t)$. So, $F_\alpha^s(k, t)$ gives the time evolution of the amplitude of the harmonic plane waves and $S_\alpha^s(k, \omega)$ is its spectral distribution. Since $G_\alpha^s(r, t)$ 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, $F_\alpha^s(k, t)$ 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 $F_\alpha^s(k, t)$ gives a broader $S_\alpha^s(k, \omega)$, which also decays monotonically. So, the self-diffusional processes can be described by the half-width at half-maximum of $S_\alpha^s(k, \omega)$. Furthermore, the self-diffusional processes can also be described by the peak height of $S_\alpha^s(k, \omega)$. Since the zero frequency moment of the SDSF is the unity, the area under $S_\alpha^s(k, \omega)$ is the same for all wave numbers. So, the peak height becomes lower as $S_\alpha^s(k, \omega)$ becomes broader with k .

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

$$[S_\alpha^s(k, \omega)]_{\text{FP}} = \frac{1}{\sqrt{2\pi}} \frac{1}{u_{0\alpha}k} \exp\left(-\frac{1}{2} \frac{\omega^2}{(u_{0\alpha}k)^2}\right), \quad (6)$$

with a half-width at half-maximum given by

$$[\Delta\omega_\alpha(k)]_{\text{FP}} = \sqrt{2 \ln 2} u_{0\alpha}k, \quad (7)$$

which is proportional to the decay rate of the SISF.

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

$$[S_\alpha^s(k, \omega)]_{\text{HD}} = \frac{1}{\pi} \frac{D_\alpha k^2}{\omega^2 + (D_\alpha k^2)^2}, \quad (8)$$

with a half-width at half-maximum given by

$$[\Delta\omega_\alpha(k)]_{\text{HD}} = D_\alpha k^2, \quad (9)$$

which is the decay rate of the SISF.

Since D_α is related to $[\Delta\omega_\alpha(k)]_{\text{HD}}$, the space-dependent self-diffusion process is usually described by the following effective wavelength-dependent self-diffusion coefficient

$$D_\alpha(k) = \frac{\Delta\omega_\alpha(k)}{k^2}, \quad (10)$$

where $\Delta\omega_\alpha(k)$ is the half-width at half-maximum of $S_\alpha^s(k, \omega)$. Obviously, $D_\alpha(k)$ is equal to D_α in the HD limit as can be seen from Eq. (9).

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

$$\Sigma_\alpha^s(k) = \frac{S_\alpha^s(k, \omega=0)}{[S_\alpha^s(k, \omega=0)]_{\text{HD}}} = \pi D_\alpha k^2 S_\alpha^s(k, \omega=0), \quad (11)$$

that is, the peak height normalized to the corresponding value in the HD limit,

$$[S_\alpha^s(k, \omega=0)]_{\text{HD}} = \frac{1}{\pi} \frac{1}{D_\alpha k^2}. \quad (12)$$

III. MD RESULTS

As it was expected, the SDSFs obtained for the four molten salts decay monotonically and their half-width at half-maximum, $\Delta\omega_\alpha(k)$, increases with k while the peak height, $S(k, \omega=0)$, decreases. At the lowest accessible wave number (0.3 \AA^{-1}) the SDSFs approach to Eq. (8) considering the self-diffusion coefficient obtained by Eq. (5) and given in Table I. At the highest wave number that we have considered (about 6 \AA^{-1}) the SDSFs are close to the FP limit given by Eq. (6). Then, at small wave numbers $\Delta\omega_\alpha(k)$ increases proportionally to k^2 , as predicted by Eq. (9), whereas at large wavenumber it increases linearly with k , as predicted by Eq. (7). However, transition from small to large wave numbers is not the same for all the different molten salts, as we will see below.

As it is usually done in the studies of monatomic systems, we will describe the diffusional processes of single ions by the effective wavelength-dependent self-diffusion coefficients $D_\alpha(k)$ normalized to D_α , that is,

$$\Delta_\alpha(k) = \frac{D_\alpha(k)}{D_\alpha} = \frac{\Delta\omega_\alpha(k)}{D_\alpha k^2}. \quad (13)$$

Obviously, $\Delta_\alpha(k)$ goes to the unity in the HD limit. Moreover, it is easy to see from Eqs. (7) and (13) that in the FP limit $\Delta_\alpha(k)$ decreases with $1/k$,

$$[\Delta_\alpha(k)]_{\text{FP}} = \sqrt{2 \ln 2} \frac{u_{0\alpha}}{D_\alpha} \frac{1}{k} = \sqrt{2 \ln 2} \frac{k_\alpha}{k}, \quad (14)$$

where

$$k_\alpha = \frac{u_{0\alpha}}{D_\alpha} \quad (15)$$

is a dynamical characteristic wave number that relates the thermal velocity, which characterizes the ionic motion in the FP limit, with the self-diffusion coefficient, which characterizes the ionic motion in the HP limit. In Fig. 2 we have plotted $\Delta_\alpha(k)$ for the four molten salts. We have also plotted the $[\Delta_\alpha(k)]_{\text{FP}}$ prediction at wave numbers larger than 6 \AA^{-1} . For the sake of clarity, we have only plotted the results for the cations in KCl. Due to the almost perfect symmetry between the two ionic species of KCl $\Delta_{\text{K}^+}(k)$ and $\Delta_{\text{Cl}^-}(k)$ are almost identical.

In the four studied systems, $\Delta_\alpha(k)$ for each ionic species goes through a minimum near k_{max} . In monatomic simple liquids near the melting point, the normalized effective self-diffusion coefficient also presents a dip near the first peak position of the static structure factor, which wavelength is close to the averaged first-neighbor distance. For this reason, it is said that diffusion over a distances equal to the averaged first-neighbor separation is less favorable because of the strong spatial correlations with these neighbors.¹³ Then, for the studied molten salts, we can say that diffusion is less favorable over a distance equal to $d_{\text{like}} = 2\pi/k_{\text{max}}$, which is about the radius of the second-neighboring shell of like ions and twice the first-neighbor separation between unlike ions.

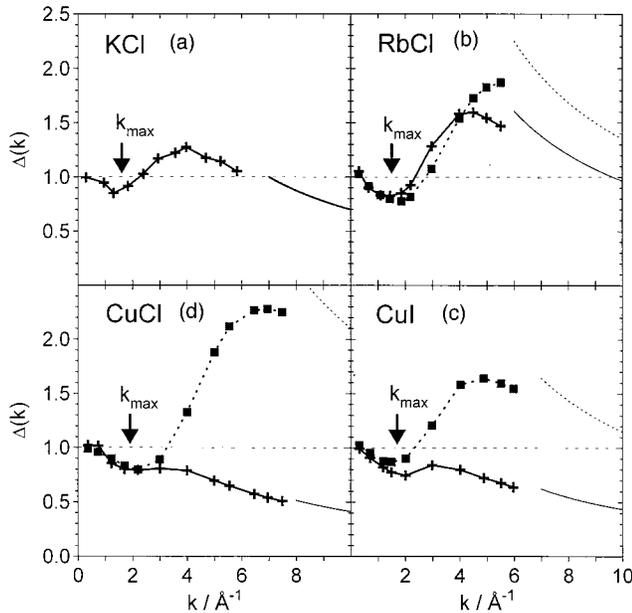


FIG. 2. Normalized effective self-diffusion coefficients, $\Delta_\alpha(k)$, for (a) KCl, (b) RbCl, (c) CuI, and (d) CuCl. Crosses are for the cations and squares are for the anions. The solid and dotted lines at k values lower than 6 \AA^{-1} are plotted to guide the eye. The lines at k values larger than 6 \AA^{-1} correspond to the free-particle approximation of $\Delta_\alpha(k)$. Solid lines are for the cations and dotted lines are for the anions.

The minimum of $\Delta_\alpha(k)$ near k_{\max} reminds the collective phenomenon of de Gennes narrowing observed in simple liquids.^{11,18} 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.¹⁸ 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 $\Delta_{\text{I}^-}(k)$ 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.¹⁹ 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.¹³ 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 back-scattering. Furthermore, as the maximum is higher it is

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

| | KCl | RbCl | CuI | CuCl |
|-----------------------------------|-----|------|-----|------|
| $k_{\max} (\text{\AA}^{-1})$ | 1.6 | 1.5 | 1.7 | 1.9 |
| $d_{\text{like}} = 2\pi/k_{\max}$ | 3.9 | 4.1 | 3.2 | 3.7 |
| $k_+ (\text{\AA}^{-1})$ | 6.4 | 8.2 | 3.7 | 3.5 |
| $k_- (\text{\AA}^{-1})$ | 6.6 | 11.5 | 9.8 | 17.8 |

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_{\max} described above can be estimated from the dynamical characteristic wave number k_α defined in Eq. (15) and given in Table II. For k_α values about twice k_{\max} ($\alpha = \text{Cu}^+$), the shape of $\Delta_\alpha(k)$ reminds us that in hot liquids, whereas for k_α values larger than three times k_{\max} the shape $\Delta_\alpha(k)$ is similar to that observed in simple monatomic liquids near the melting point. As k_α 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 ($D_{\text{Rb}^+} \approx D_{\text{Cl}^-}$), and the cations are heavier than the anions ($m_{\text{Rb}^+} > m_{\text{Cl}^-}$), the value of k_α is lower for the cations ($k_{\text{Rb}^+} < k_{\text{Cl}^-}$). However, despite the cations are lighter than the anions ($m_{\text{Cu}^+} < m_{\text{I}^-}$), in CuI the value of k_α is also lower for the cations ($k_{\text{Cu}^+} < k_{\text{I}^-}$) because the anions are much more diffusive than the cations ($D_{\text{Cu}^+} > D_{\text{Cl}^-}$). In CuCl, 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_α is also lower for the cations ($k_{\text{Cu}^+} < k_{\text{Cl}^-}$). Furthermore, $k_{\text{I}^-} < k_{\text{Cl}^-}$ since $m_{\text{I}^-} > m_{\text{Cl}^-}$ and $D_{\text{I}^-} \approx D_{\text{Cl}^-}$.

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 \AA^{-1} , we have also plotted this function in FP limit, that is,

$$[\Sigma_\alpha(k)]_{\text{FP}} = \sqrt{\frac{\pi}{2}} \frac{k}{k_\alpha}. \quad (16)$$

As can be seen in Fig. 3, the transition from small to large wave numbers of $\Sigma_\alpha(k)$ is also determined by k_α . 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.¹⁹ 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.

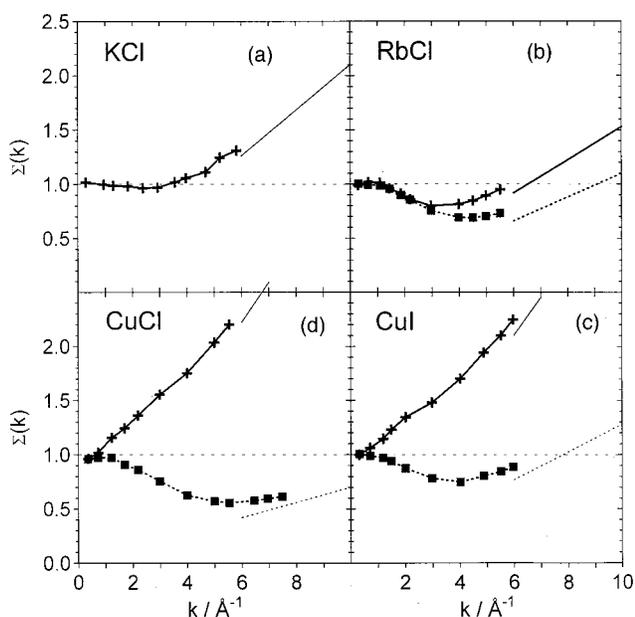


FIG. 3. Same as in Fig. 2 except for dimensionless peak heights $\Sigma_{\alpha}(k)$.

Furthermore, we have also studied $1/\Sigma_{\alpha}(k)$ and its FP limit. The corresponding figures are available on request. Taking into account that in the HD limit $S_{\alpha}^s(k, \omega=0)$ is related to $1/D_{\alpha}$ through Eq. (12), $1/\Sigma_{\alpha}(k)$ could be thought as a second effective wavelength-dependent self-diffusion coefficient normalized to D_{α} . Obviously, $1/\Sigma_{\alpha}(k)$ goes to the unity in the HD limit and decreases with $1/k$ in the FP limit as $\Delta_{\alpha}(k)$ does. The transition to the FP limit is determined by k_{α} in a similar way of the transition of $\Delta_{\alpha}(k)$ described above. However, $1/\Sigma_{\alpha}(k)$ does not present any dip around k_{\max} . As it has been observed describing the behavior of $\Delta_{\alpha}(k)$, for the ions with an oscillatory component in the VACF, $1/\Sigma_{\alpha}(k)$ presents a maximum which is higher as the oscillations are more pronounced. This maximum is lower and located at smaller wave numbers than that for $\Delta_{\alpha}(k)$. This behavior can be explained taking into account that $[1/\Sigma_{\alpha}(k)]_{\text{FP}}$ is smaller than $[\Delta_{\alpha}(k)]_{\text{FP}}$.

IV. CONCLUSIONS

The resulting $\Delta_{\alpha}(k)$ and $\Sigma_{\alpha}(k)$ for molten copper halides show that these systems are made up of two species that have very different behaviors. The characteristic features of $\Delta_{-}(k)$ and $\Sigma_{-}(k)$ for the anions are similar to those found in simple liquids near the melting point, such as rare gas liquids, metal liquids or molten alkali halides. On the contrary, the shape of $\Delta_{+}(k)$ or $\Sigma_{+}(k)$ for the cations, which are smaller and more diffusive than the anions, reminds that found for monatomic dense gases or hot liquids. This result can be understood by taking into account that the copper

halides melt from a superionic phase. The superionic solid phase led to the idea of the cations sublattice melting. So, in the liquid phase, when the anions sublattice has melt, the behavior of anions is close to that of particles of a liquid near the melting point, while the behavior of cations is closer to that of particles in a hot liquid.

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 $d_{\text{like}} = 2\pi/k_{\max}$, 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 $k_{\alpha} = (k_B T / m_{\alpha})^{1/2} / D_{\alpha}$. As k_{α} is larger, $\Delta(k)$ and $\Sigma(k)$ approach the FP limit at larger k values. For k_{α} values larger than three times k_{\max} , the self-diffusional process is similar to that observed in simple monatomic liquids near the melting point. If k_{α} is about twice k_{\max} , self-diffusion reminds us of that in hot liquids.

ACKNOWLEDGMENTS

The authors thank J. A. Padró for useful discussions and suggestions. The authors gratefully acknowledge the financial support of DGICYT of Spain (Grant No. PB96-0170-C03-02) and DGUR of the Generalitat of Catalonia (Grant No. 1997SGR-00149).

- ¹M. P. Tosi, D. L. Price, and M. L. Saboungi, *Annu. Rev. Phys. Chem.* **44**, 173 (1993).
- ²M. Rovere and M. P. Tosi, *Rep. Prog. Phys.* **49**, 1001 (1986).
- ³J. E. Enderby and G. W. Neilson, *Adv. Phys.* **29**, 323 (1980).
- ⁴A. J. Stafford, M. Silbert, J. Trullàs, and A. Giró, *J. Phys.: Condens. Matter* **2**, 6631 (1990).
- ⁵I. D. Page and K. Mika, *J. Phys. C* **4**, 3034 (1971).
- ⁶S. Eisenberg, S. F. Jal, J. Dupuy, P. Chieux, and W. Knoll, *Philos. Mag. A* **46**, 195 (1982).
- ⁷Y. Shirakawa, M. Saito, S. Tamaki, M. Inui, and S. Takeda, *J. Phys. Soc. Jpn.* **60**, 2678 (1991).
- ⁸J. Trullàs, A. Giró, and M. Silbert, *J. Phys.: Condens. Matter* **2**, 6643 (1990).
- ⁹J. C. Poignet and M. J. Barbier, *Electrochim. Acta* **26**, 1429 (1981).
- ¹⁰G. Ciccotti, G. Jacucci, and I. R. McDonald, *Phys. Rev. A* **13**, 426 (1976).
- ¹¹J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- ¹²O. Alcaraz and J. Trullàs, *J. Chem. Phys.* **23**, 10635 (2000).
- ¹³J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, London, 1982).
- ¹⁴U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon, Oxford, 1994).
- ¹⁵M. J. L. Sangster and M. Dixon, *Adv. Phys.* **25**, 247 (1976).
- ¹⁶M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ¹⁷N. H. March and M. P. Tosi, *Coulomb Liquids* (Academic, London, 1984).
- ¹⁸R. L. McGreevy, *Solid State Phys.* **40**, 247 (1987).
- ¹⁹D. Levesque and L. Verlet, *Phys. Rev. A* **2**, 254 (1970).