

Approach to metallic behavior in metal–molten-salt solutions

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A combined molecular-dynamics density-functional simulation of concentrated $K_x(KCl)_{1-x}$ solutions with $x \leq 0.11$ has been performed. Bipolaronic structures where two spin-paired electrons are trapped in the same liquid cavity are seen to be a characteristic feature of this mixture. The bipolarons exhibit a tendency to cluster. At $x \approx 0.11$ the bipolaronic clusters tend to have an elongated percolating structure which leads to metallic behavior. Our findings are in good agreement with available experimental information.

The metal–nonmetal transition in the liquid state is a question of major theoretical interest.^{1,2} Among the systems where such a transition has been observed, metal–molten-salt solutions of the type $M_x(MX)_{1-x}$ are especially fascinating because of their complex behavior which only now is being unravelled through a combination of experiments^{2–9} and computer simulations.^{10–13} So far this effort has only allowed an understanding of the region of highly diluted concentration, and much remains to be done in order to determine the mechanism through which the metallic behavior is set up as the concentration of the metallic species is increased.

At $x \rightarrow 0$ the established picture is that the valence electrons of the added metal are released in the salt and are localized into liquid cavities that are the liquid-state counterpart of the F centers in the solid state. As the concentration is increased spin pairing occurs and a new complex which we call the bipolaron complex is formed. In the bipolaron complex electrons with opposite spins bind and localize in a cavity that closely resembles that of an F center. In other words, they sit in an anion vacancy, and surround themselves on the average by four cations. The limits of this description and the relevance of fluctuations for diffusion processes have been discussed elsewhere.^{12,13}

We here study $K_x(KCl)_{1-x}$ solutions for which much evidence is currently available. Experiments on these solutions have shown that at $x \approx 0.1$ a polarization catastrophe occurs⁴ and indirect evidence has been gathered on the possible existence of clustering effects.^{6–8} The bearing of clustering effects on the polarization catastrophe and the transition to the metallic state is, however, poorly understood. In order to clarify these issues, in this Communication we study the structural and electronic properties of these solutions for a few values of the concentration in the range $x \sim 0.1$. In particular, we show that the onset of metallic behavior is related to the formation of extended bipolaronic clusters with percolative character. It is not the aim of the present investigation to discuss critical properties, such as the critical concentration and critical indices.

Our study is based on a newly proposed method of simulation that combines molecular dynamics (MD) with the local-density approximation (LDA).¹⁴ In this approach the basic assumptions are that the motion of the system is well described by the Born–Oppenheimer (BO)

approximation and that the LDA provides an accurate description of the electronic ground state. Although the hypothesis of BO behavior when the electronic excitation energy becomes comparable to the thermal energy—as it is the case here—is questionable, our results appear to give a consistent and meaningful picture of the physics of the system. This provides an *a posteriori* justification for the approximation used.

In LDA the electronic density is expanded in a set of occupied Kohn–Sham (KS) orbitals.¹⁴ These orbitals are our variables together with the positions of the ions which are treated as classical entities. The BO evolution of this system could in principle be obtained by minimizing at every time step the LDA energy functional. Even using efficient minimization schemes,¹⁵ this approach is very costly. We therefore prefer to describe the evolution of our mixed classical quantum mechanical system by Newton's equation for the ions and a time-dependent effective Schrödinger equation for the KS orbitals.^{12,13} If the motion of the system is adiabatic, this time evolution is equivalent to the BO. However, if nonadiabatic transitions occur, our equations of motion become inconsistent. Thus, periodic intervention is needed in order to monitor the adiabaticity. This is done by calculating the projection P_0 of the electronic state given by our time evolution onto the instantaneous ground state Φ_0 . When sizable departures are observed the electrons are brought back to Φ_0 . Even so this approach is computationally convenient because it greatly reduces the number of LDA minimizations.

We have studied systems of N_e electrons, $108 K^+$ and $(108 - N_e) Cl^-$ ions, with $N_e = 6$ and 12 . These correspond to a metal concentration of $x = 0.06$ and $x = 0.11$, respectively. In each case the temperature was $T \sim 1300$ K and the molar volume was taken equal to the corresponding experimental value.¹⁶ The electronic orbitals were expanded in plane waves on a mesh of $(16)^3$, leading to a spatial resolution of 2.44 a.u. Explicit calculations were performed with a smaller mesh in order to check the adequacy of this choice. The model used to describe the ion–ion and electron–ion interaction was the same as Refs. 10–13. At variance with Ref. 13, LDA and not the local-spin-density approximation was used to handle the electron–electron interaction. Neglect of spin-dependent effects is justified by explicit tests performed on smaller

systems, by previous results,^{11,13} and by experimental findings⁷ that show a strong tendency towards spin pairing. Every 5000 time steps, minimization of the LDA energy functional was performed by a very efficient conjugated gradient method.¹⁵ Whenever P_0 was smaller than 0.9, the electrons were brought back to Φ_0 as in Ref. 12. The latter operation had to be done more frequently for $x=0.11$. In this case, the average time interval between successive interventions was 40000 time steps, which corresponds to about 5×10^{-13} s, that is an interval larger than a typical ionic time.

The results obtained at the two different concentrations showed remarkable similarities for several static properties. In Fig. 1, we plot the ion-ion and electron-ion pair correlation functions for the $x=0.11$ case; the corresponding quantities for the $x=0.06$ case are practically indistinguishable on the same scale. Furthermore, they show a great similarity to the two-electron case, suggesting the existence in these melts of bipolaronic structures similar to those described in Ref. 13. This conclusion is further strengthened by a more detailed analysis, aimed at localizing the bipolaronic structures. This is a nontrivial and costly task since one has to locate, in a complicated three-dimensional structure the existence of pockets of electronic charge, surrounded by cations. The procedure followed by us was to define the function

$$\rho_c(\mathbf{r}) = \rho_e(\mathbf{r}) + \rho_{K^+}(\mathbf{r}), \quad (1)$$

where $\rho_e(\mathbf{r})$ is the electronic charge density and $\rho_{K^+}(\mathbf{r})$ the cationic charge obtained by giving to each ionic charge a Gaussian distribution of radius equal to the electron-cation pseudopotential core radius $r_c = 3.7$ a.u. The many local minima of $\rho_c(\mathbf{r})$ define positions in space where there is an excess of electronic charge in a liquid cavity. A simulated annealing procedure¹⁷ that used

$\rho_c(\mathbf{r})$ as cost function was employed to locate the local minima of $\rho_c(\mathbf{r})$ on the $(16)^3$ points of the real-space mesh used in the Fourier transforms. At each concentration this analysis was performed on 30 uncorrelated configurations generated by our dynamical scheme. We found that the number of minima is on average 3 and 7.1 for $N_e = 6$ and $N_e = 12$, respectively. We plot in Fig. 2 the average pair-correlation function between these entities and the ions. The local environment in either case is very close to that of the bipolaron. On the same graph we also plot the average radial charge distribution $\rho_b(r)$ as seen from the minima. This shows the existence of a localized state, which approximately contains two electrons in a cavity surrounded by four cations. This is the signature of the bipolaronic complex. In the $x=0.11$ case there appears to be some tendency towards a greater delocalization as indicated by a tail at larger distances and a lower value of the charge density at the origin. Also our finding of an average number of minima of 7.1 indicates that the bipolarons are spread at times over several localization centers. Still, our data provide a clear indication that these complexes are a characteristic motif of the melt, which tends to preserve the molten salt structure by replacing the missing Cl^- ions with bipolaronic complexes. This tendency may explain the stability of the molten salt ionic structure to the addition of metal. Experiments show that the ionic molten salt structure persists up to $x \cong 0.75$.¹⁸

Although the local structure is remarkably similar in the two cases, differences in the electronic properties arise from the different spatial arrangement of the bipolaronic complexes. Typical electronic arrangements are displayed in Fig. 3. In either case, a tendency to clustering is observed. However, for $x=0.06$ one finds mostly localized clusters, while for $x=0.11$ the dominant structure is a percolating electronic charge distribution, i.e., an elongated distribution extending from one side to the other of our

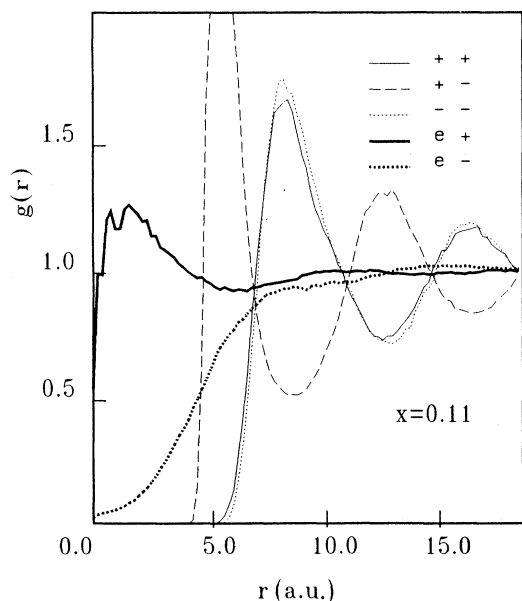


FIG. 1. Ion-ion (+ +, + -, -) and electron-ion (e +, e -) radial pair-correlation functions for $x=0.11$.

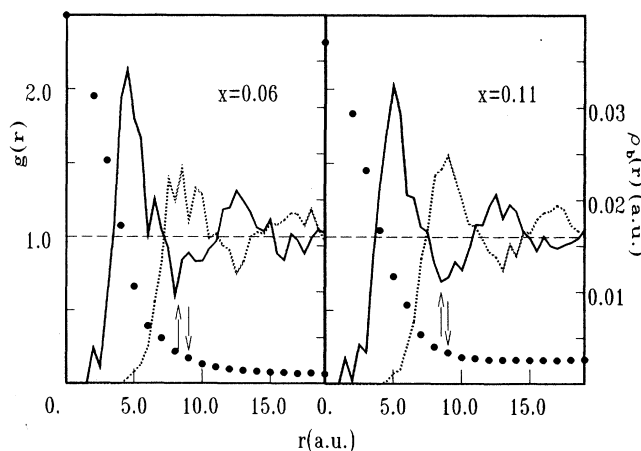


FIG. 2. Radial pair correlation function between the bipolaron and the K^+ (full line) and Cl^- (dotted line) ions. The up arrow is where the bipolaron-cation coordination is 4. The dots indicate the spherically averaged electronic charge density ρ_b as seen from the center of the bipolaron. The down arrow is where the integral of ρ_b is 2.

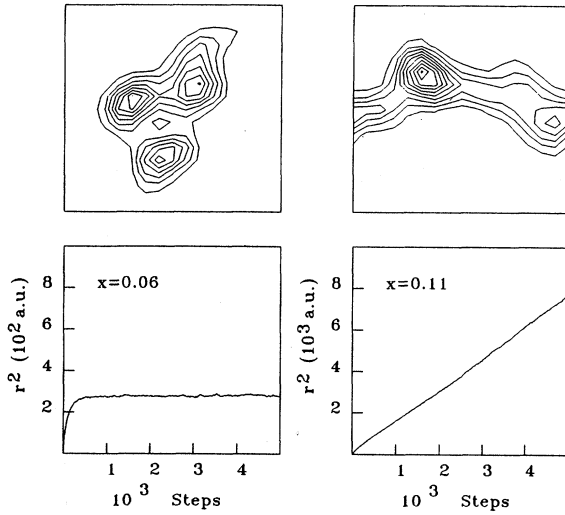


FIG. 3. Upper panels: typical electronic charge distribution on a (001) section of the MD cell for $x=0.06$ (left) and $x=0.11$ (right). Lower panels: corresponding mean-square displacement r^2 as a function of the number of steps in the random walk.

MD cell. One can quantitatively distinguish between percolating and nonpercolating structures by monitoring the mean-square displacement r^2 of a set of random walkers which move on the subset of real-space mesh points where the electronic charge density $\rho_e(\mathbf{r})$ is greater than some threshold value ρ_t and are reflected when they arrive at a site where ρ_e is below ρ_t . Percolating structures in which there is a connected path between one side and the other of the cell will display a diffusive behavior of r^2 , while in nonpercolating structures r^2 will eventually saturate to a constant value. This contrasting behavior is illustrated in the lower part of Fig. 3, where we have taken ρ_t to be $\frac{1}{10}$ of the maximum value of $\rho_e(\mathbf{r})$. This analysis shows that $\sim 10\%$ and $\sim 70\%$ of the structures are percolative at $x=0.06$ and $x=0.11$, respectively.¹⁹ Reasonable variations of ρ_t gave qualitatively similar results.

The appearance of percolating paths has important consequences for the electric properties of the system as shown in Fig. 4 where we plot the equivalent optical conductivity

$$\Lambda(\omega) = \sigma(\omega)/n^e, \quad (2)$$

where n^e is the excess electron density and the conductivity $\sigma(\omega)$ is calculated as a configurational average of

$$\sigma(\omega, \{R_j\}) = \frac{\pi e^2}{m^2 \omega} \frac{1}{\Omega} \sum_{v,c} |\langle \phi_v^0 | \hat{p} | \phi_c^0 \rangle|^2 \delta(E_c - E_v - \hbar\omega), \quad (3)$$

where $\phi_v^0(\phi_c^0)$ and $E_v(E_c)$ are eigenfunctions and eigenvalues of the occupied (empty) electronic BO states calculated for the ionic configuration $\{R_j\}$. In the calculation of $\sigma(\omega, \{R_j\})$ we use the single-particle KS states and eigenvalues, thus introducing an additional approximation beside the Franck-Condon (FC) approach implicit in the use of BO states in Eq. (3). We find that $\Lambda(\omega)$ is very similar in the two cases but for the low- ω region where it

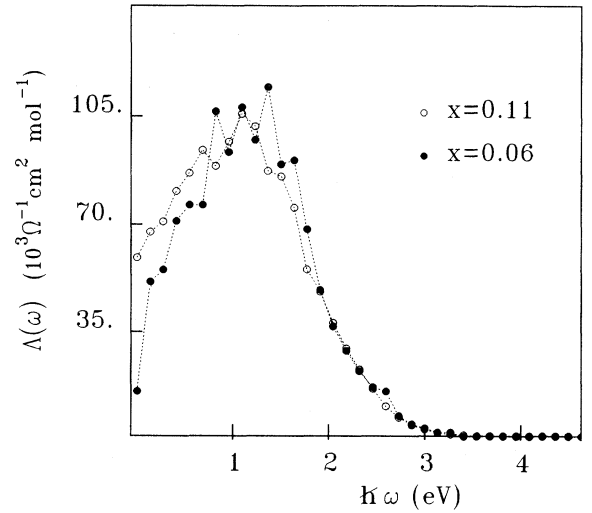


FIG. 4. Equivalent optical conductivity obtained by averaging over 30 uncorrelated configurations. Both spectra satisfy the f -sum rule to better than 90%. Dots and circles are calculated values, the lines are just a guide for the eye.

tends to a much larger value when $x=0.11$. The value that we obtain for the static conductivity $\sigma(0)$ by extrapolating our results to zero frequency is about $100 (\Omega \text{ cm})^{-1}$ at $x=0.11$ in qualitative agreement with experiments,^{3,8} while at $x=0.06$, $\sigma(0) \sim 0$ within our numerical uncertainty. Two different effects conspire to produce this change, one is that the energy gap is reduced from an average value of 0.13 eV for $x=0.06$ to an average value of 0.046 eV for $x=0.11$, and the other is that for $x=0.06$ the transition matrix elements $\langle \phi_v^0 | \hat{p} | \phi_c^0 \rangle$ are tiny for all those states whose energy difference ($E_c - E_v$) is small. The increase of the transition matrix element for $x=0.11$ is due to the greater delocalization of the high-energy KS states.¹⁹ These two effects are expected to vary smoothly with concentration between $x=0.06$ and $x=0.11$. Non-FC effects alter this picture only quantitatively. In particular for $x=0.06$, as well as for $x \rightarrow 0$,¹² they lead to a finite although small electronic mobility. However, we expect that these non-FC contributions do not alter the finding that at $x=0.11$ new conduction channels are operative that are related to the formation of conducting paths of percolative character. This picture is reminiscent of the Jortner and Cohen model²⁰ for metal-ammonia solutions. In $\text{K}_x(\text{KCl})_{1-x}$ these percolating structures appear to optimally compromise between two contrasting tendencies. On one side is the drive to reduce the electronic kinetic energy via the formation of delocalized states, on the other, the strong tendency to form localized bipolaronic states which optimize the electron-ion interaction preserving the charge ordered structure of the molten salt.

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- ¹N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis Ltd, London, 1974).
- ²For a general review, see W. W. Warren, Jr., in *The Metallic and Non-Metallic States of Matter: An Important Facet of the Chemistry and Physics of The Condensed State*, edited by P. P. Edwards and C. N. R. Rao (Taylor and Francis, London, 1985).
- ³M. A. Bredig, in *Molten Salt Chemistry*, edited by M. Blander (Interscience, New York, 1964).
- ⁴W. Freyland, K. Garbade, H. Heyer, and E. Pfeiffer, *J. Phys. Chem.* **88**, 3745 (1984); W. Freyland *et al.*, *Phys. Rev. Lett.* **51**, 1304 (1983).
- ⁵W. W. Warren, Jr., S. Sotier, and G. F. Brennert, *Phys. Rev. B* **30**, 65 (1984); *Phys. Rev. Lett.* **50**, 1505 (1983).
- ⁶N. Nicoloso and W. Freyland, *J. Phys. Chem.* **87**, 1997 (1983).
- ⁷N. Nicoloso and W. Freyland, *Z. Phys. Chem.* **135**, 39 (1983).
- ⁸D. Nattland, H. Heyer, and W. Freyland, *Z. Phys. Chem.* **149**, 1 (1986).
- ⁹W. W. Warren, Jr., B. F. Campbell, and G. F. Brennert, *Phys. Rev. Lett.* **58**, 941 (1987).
- ¹⁰M. Parrinello and A. Rahman, *J. Chem. Phys.* **80**, 860 (1984).
- ¹¹M. Parrinello and A. Rahman (unpublished).
- ¹²A. Selloni, P. Carnevali, R. Car, and M. Parrinello, *Phys. Rev. Lett.* **59**, 823 (1987).
- ¹³E. S. Fois, A. Selloni, M. Parrinello, and R. Car, *J. Phys. Chem.* **92**, 3268 (1988).
- ¹⁴See, for instance, *Theory of Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), and references therein.
- ¹⁵I. Štich, R. Car, M. Parrinello, and S. Baroni (unpublished).
- ¹⁶K. Garbade and W. Freyland, *Z. Phys. Chem* **156**, 169 (1988).
- ¹⁷S. Kirkpatrick, G. D. Gelatt, and M. P. Vecchi, *Science* **220**, 671 (1983).
- ¹⁸J. F. Jal, P. Chieux, and J. Dupuy, in *Molten Salts*, edited by G. Mamantov *et al.* (The Electrochem. Society, Pennington, 1981); J. F. Jal, Ph.D. thesis, Université Claude Bernard, Lyon, 1981 (unpublished).
- ¹⁹For each configuration a similar analysis was performed on the square moduli of the various KS orbitals. Typically, when ρ_e is percolating, one (or more) of the high-energy KS states is also percolating, whereas the low-energy states are always well localized.
- ²⁰J. Jortner and M. H. Cohen, *Phys. Rev. B* **13**, 1548 (1976).