Hot electrons and the approach to metallic behaviour in $K_x(KCl)_{1-x}$

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Abstract. – The approach to the metallic phase of molten $K_x(KCl)_{1-x}$ mixtures is studied using *ab initio* molecular dynamics based on finite-temperature density functional theory. The finite electronic temperature is found to result in new and unexpected effects. In particular, we observe a thermally induced lowering of the predicted DC conductivity, which greatly improves the agreement with the experiment, and a widening of the HOMO-LUMO energy gap. We expect that these are genuinely new physical effects which could be observed also in other systems.

By adding metal to molten-salt solutions of the type M_x $(MX)_{1-x}$, the liquid may be made to undergo a transition from an insulator to a metal. These systems have been studied extensively through experiments [1]-[7], computer simulations [8]-[11] and theory [12]-[14].

The established picture is that at very low x the valence electrons of the added metal are released in the salt and are localized into liquid cavities (F-centres). As the concentration is increased spin-paired states (bipolarons) and higher aggregates are formed. The onset of metallic behaviour is related to the formation of percolating bipolaronic clusters.

The approach to metallic regime in $K_x(KCl)_{1-x}$ has been studied numerically by Fois *et al.* [11]. Their simulations were carried out using *ab initio* Molecular Dynamics (MD). In such simulations, density functional theory (DFT) in the local-density approximation (LDA) is used to compute the ground-state electronic properties of the system. Moreover, the method of ref. [11] is based on the Born-Oppenheimer (BO) approximation, namely it is assumed that the electrons adiabatically follow the nuclear motion. However, at the temperatures of interest, the electronic excitation energy becomes comparable to the thermal energy k_BT as the metal concentration is increased. This leads to fractional occupation numbers and to a finite probability of occupation of the excited states so that the hypothesis of BO behaviour

is questionable. Therefore the possibility exists that conventional *ab initio* MD provides a poor description of the physics of the system. Indeed, by performing a simulation at $x = 0.11$, Fois *et al.* [11] obtained a DC electrical conductivity considerably larger than the experimental value. Furthermore, they had severe difficulties in maintaining the system on the BO energy surface.

Recently, an alternative formulation of the density-functional–based MD, which is able to circumvent these problems, has been proposed by Alavi *et al.* [15]. It is based on a density functional which shares the same *stationary* point as the finite-temperature functional of Mermin [16], and incorporates consistently the effects of thermal electronic excitations and fractionally occupied states. Here we apply this method to study the metal–non-metal transition in $K_x(KCl)_{1-x}$. We find, as expected, that close to the metal–non-metal transition non-BO effects are important. These lead not only to a better agreement between theory and experiment, but also to an increase in the HOMO-LUMO energy gap E_g due to the finite temperature of the electrons.

We have studied systems of N_e electrons, 108 K^+ and $(108 - N_e)$ Cl^- ions, with $N_e = 2$, 6, 12, 16, 18, 24, corresponding to an excess metal concentration of $x = 0.02$, 0.06, 0.11, 0.15, 0.17, 0.22, respectively. In each case the temperature was $T \sim 1300$ K and the molar volume was taken equal to the corresponding experimental value [7]. The electronic orbitals, at the Γ-point of the Brillouin zone, were expanded in plane waves on a mesh of $(16)^3$, leading to a spatial resolution of 2.44 a.u. Previous tests [11] established the adequacy of this choice made possible by the use of smooth pseudopotentials [8]-[11] to model the ion-ion and the electron-ion interaction. For a given configuration of ions, the electronic density $n(\mathbf{r})$ was computed by minimizing the free-energy functional $\mathcal{F}$ of the electron gas. This is defined as

$$\mathcal{F} = \Omega + \mu N + E_{II}, \tag{1}$$

where

$$\Omega[n(\mathbf{r})] = -\frac{2}{\beta} \ln \det \left(1 + \exp[-\beta(\mathcal{H} - \mu)]\right) - \int d\mathbf{r}\, n(\mathbf{r}) \left(\frac{\phi(\mathbf{r})}{2} + \frac{\delta\Omega_{xc}}{\delta n(\mathbf{r})}\right) + \Omega_{xc}, \tag{2}$$

$\beta = 1/k_B T$ is the inverse electronic temperature, μ is the chemical potential, $\mathcal{H} = -1/2\nabla^2 + V(\mathbf{r})$ is the one-electron Hamiltonian with the effective potential $V(\mathbf{r}) = \sum_I V_{eI}(\mathbf{r} - R_I) + \phi(\mathbf{r}) + \delta\Omega_{xc}/\delta n(\mathbf{r})$, $\phi(\mathbf{r})$ is the Hartree potential of an electron gas of density $n(\mathbf{r})$, Ω_{xc} the LDA exchange correlation energy, and E_{II} the classical Coulomb energy of the ions. The functional Ω_{xc} is approximated by its $T = 0$ expression, since its finite-temperature corrections are negligible [17] at the temperature and the electronic densities of our systems.

$\mathcal{F}$ reproduces the exact finite-temperature density of the Mermin functional [16] and was optimized for each ionic configuration using a self-consistent diagonalization method, as in [15]. The electronic density so computed, together with the Hellmann-Feynman theorem, enables the calculation of the ionic forces. In this approach the electrons are allowed to be in thermal equilibrium with the ions and we refer to them as *hot electrons*. In contrast, in the BO approximation, the electrons are kept artificially *cold*.

The ionic degrees of freedom were integrated using a time step of 20 a.u. (~ 0.5 fs). The first part of each simulation was the preparation of a well-equilibrated liquid of K^+ and Cl^- ions in a neutralizing uniform background (~ 2 ps), then the uniform background was removed and, for each ionic configuration, $\mathcal{F}$ was self-consistently optimized by using as the electronic temperature the average ionic temperature, namely 1300 K. After an equilibration of 0.5 ps a production run of 2 ps was performed. This procedure was repeated for each metal concentration x.

TABLE I. – *Average occupation numbers, for the* HOMO *and* LUMO, *as a function of the excess metal concentration x.*

x	f_{HOMO}	f_{LUMO}
0.02	0.91	0.09
0.06	0.64	0.36
0.11	0.61	0.34
0.15	0.58	0.40
0.17	0.56	0.42
0.22	0.57	0.42

In order to appreciate the effect of the finite electronic temperature, we report in table I the average occupation numbers of the orbitals which would, in a BO simulation, be called the HOMO and LUMO. Notice that, using the BO approximation, one would assume that $f_{\text{HOMO}} = 1$ and $f_{\text{LUMO}} = 0$. For most concentrations we have performed parallel runs, with cold and hot electrons. The pair correlation functions appear to be almost insensitive to the approach chosen and they are in good agreement with the previous work of Fois *et al.* [11]. The same is also true for most of the other properties studied but for the remarkable exception of the DC electrical conductivity σ, particularly at $x = 0.11$. As in ref. [11] we compute σ by extrapolating to zero frequency the results given by the Kubo-Greenwood formula

$$\sigma = \sigma(0) = \lim_{\omega \to 0} \sigma(\omega) , \tag{3}$$

with $\sigma(\omega)$ computed as a configurational average of

$$\sigma(\omega, R_{\text{I}}) = \frac{2\pi e^2}{3m^2\omega} \frac{1}{V_{\text{b}}} \sum_{i,j} (f_i - f_j) |\langle \psi_i | \hat{p} | \psi_j \rangle|^2 \times \delta(E_j - E_i - \hbar\omega) , \tag{4}$$

where e and m are the electronic charge and mass, V_{b} is the simulation box volume, $\hat{p}$ is the momentum operator and ψ_i, E_i, are the electronic DFT eigenstates and eigenvalues (with their corresponding occupation numbers f_i), calculated for the ionic configuration $\{R_{\text{I}}\}$. Of course, the use of the single-particle DFT states and eigenvalues, instead of the true many-body eigenfunctions and eigenvalues, introduces an approximation in the calculation of σ. In spite of this limitation, eq. (4) has been successfully used, in *ab initio* MD simulations, to study insulator-metal transitions [18]. Moreover, our computed hot-electron DC conductivity gives a consistent and meaningful picture of the physics of the system and is able to reproduce the insulator-metal transition observed in the experiments [5], [19]. This provides an *a posteriori* justification for the approximation used. Since the emphasis here is on the approach to the metallic phase, rather than the true metal, a more thorough k-point sampling is not expected to affect the observed trends, although it may lead to slightly different numbers. As earlier studies [10], [11] used the same Γ-point approximation, we can compare our results directly with those calculations.

The behaviour of σ as a function of x is shown in fig. 1. The cold-electron results are affected by larger statistical errors and this reflects the lower efficiency in optimizing the energy functional in the BO approach. However, we took this into account by performing longer simulations. As can be seen from fig. 1, *the hot-electron simulations predict a value of σ which is lower than that estimated using cold electrons, and in better agreement with the experiments.* This effect is particularly evident for $x = 0.11$. The fact that the hot-electron
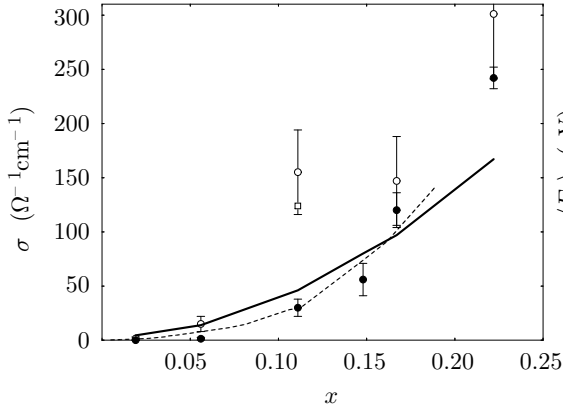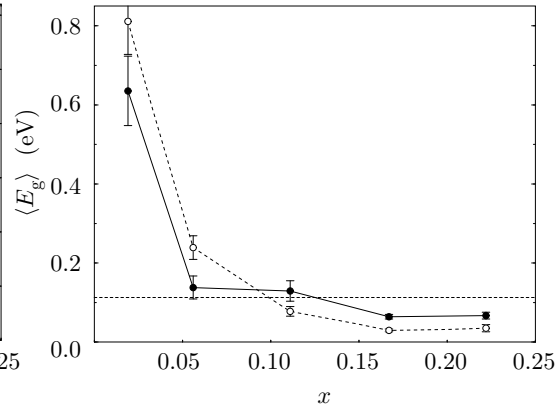
Fig. 1.

Fig. 2.

Fig. 1. – DC electrical conductivity σ as a function of the excess metal concentration x. The solid and dashed lines connect points taken from two sets of experimental data [5], [19] obtained at slightly different experimental conditions. The full circles (with their error bars) are the simulation results computed using the hot-electron approach, while the open circles were obtained by making use of the BO approximation (cold electrons). The open square represents the result reported by Fois *et al.* [11] for $x = 0.11$, again in the BO approximation.

Fig. 2. – Averaged HOMO-LUMO energy gap, $\langle E_{\text{g}} \rangle$, as a function of the excess metal concentration x. The full circles are the simulation results computed using the hot-electron approach, while the open circles were obtained by making use of the BO approximation (cold electrons). The solid and dashed lines are just a guide for the eye. The dotted line indicates the $k_{\text{B}}T$ value.

runs gave a lower conductivity is somewhat counterintuitive. In fact, by allowing the electrons to spread on the excited levels, one would expect the conductivity to increase. We have observed the same phenomenon also by performing simulations with a much smaller system, consisting of 32 K^+ and $(32 - N_{\text{e}})$ Cl^- ions. In this case, due to finite-size effects, the transition to metallic regime occurs at a concentration significantly higher than the experimental one, so that only with $N_{\text{e}} = 8$, corresponding to $x = 0.25$, the conductivity σ is appreciable. At this excess metal concentration the hot-electron approach gives $\sigma \sim 200 \ \Omega^{-1}\text{cm}^{-1}$, again in qualitative agreement with the experiment, while, using cold electrons, $\sigma \sim 1400 \ \Omega^{-1}\text{cm}^{-1}$.

In order to gain a better understanding of the physical mechanism behind the hot-electron effect on the DC conductivity, we have monitored the behaviour of the various quantities involved in the calculation of σ. We find that, for excess metal concentrations at which σ is not negligible, the matrix elements $|\langle \psi_i | \hat{p} | \psi_j \rangle|$, for hot and cold electrons, have comparable values. Therefore the large difference in the computed DC conductivities has to be mainly related to the difference in the occupation numbers of the electronic states E_i. In particular (see eq. (4)), contributions to $\sigma(\omega)$, for $\omega \sim 0$, come entirely from pairs of states (i, j) for which $(E_j - E_i)$ is small on the scale of $k_{\text{B}}T$, provided that $(f_i - f_j) \neq 0$. Hence, in the BO approximation, essentially only the HOMO-LUMO pair can contribute. In this case $(f_{\text{HOMO}} - f_{\text{LUMO}}) = 1$, irrespective of the value of the HOMO-LUMO energy gap $E_{\text{g}} = E_{(N_{\text{e}}/2+1)} - E_{(N_{\text{e}}/2)}$. In contrast, using hot electrons, $f_i = (\exp[(E_i - \mu)/k_{\text{B}}T] + 1)^{-1}$, therefore, whenever the two energy levels come very close to each other, $(f_{\text{HOMO}} - f_{\text{LUMO}}) \sim E_{\text{g}}/(4k_{\text{B}}T) \ll 1$. Of course, in the hot-electron scheme, other pairs of states may contribute to the DC conductivity, and indeed, in the full metallic regime, when there are many closely spaced energy levels around μ, the large number of their contributions compensates the small values of their weights $(f_i - f_j)$.

However, in the metal–non-metal transition region, only a few pairs of states occasionally get close to each other and give a finite contribution to σ, so that the effect of fractional occupation numbers becomes very important. This qualitatively explains the fact that the discrepancy between hot-electron and cold-electron DC conductivities is dramatic at $x = 0.11$, while it turns out to be less pronounced at higher concentrations.

Of course, σ is sensitive also to the spacing between the energy levels, particularly to the HOMO-LUMO gap E_{g}. Its configurational average, $\langle E_{\mathrm{g}} \rangle$, is shown in fig. 2. E_{g} undergoes large fluctuations during the MD simulation, however, for $x \geq 0.11$, a *statistically significant enhancement of $\langle E_{\mathrm{g}} \rangle$ can be observed in the hot-electron simulations.* This is another important cause of the lowering of the hot-electron DC conductivity, since the larger $\langle E_{\mathrm{g}} \rangle$ is, the smaller the probability becomes that the HOMO, LUMO levels come close to each other. The origin of this novel thermally induced effect can be explained as follows. At the temperature and the metal concentration of our system the Fermi distribution function, while still being far from the classical Boltzmann limit, goes from 1 to 0 in an energy interval comparable with E_{g}. Under these conditions there is a relevant energetic gain in increasing E_{g}. For by lowering the $E_{(N_{\mathrm{e}}/2)}$ level (the HOMO), the system gains energy not only because the energy is lowered but also because its occupation number is increased, while the increase in energy of $E_{(N_{\mathrm{e}}/2+1)}$ (the LUMO) is offset by the fact that its occupation number is decreased. As a result, the hot electrons induce an effective repulsion between the HOMO and the LUMO.

For $x = 0.02$ and $x = 0.06$, $\langle E_{\mathrm{g}} \rangle$ turns out to be smaller with hot electrons. As we have verified, this is related to the fact that for hot electrons the charge is more delocalized than for cold electrons. Consequently, also the configurations of the surrounding ions are quite different and the energy gap behaviour can no longer be explained by our simple energetic argument. For higher x values the difference in the electronic localization, using hot and cold electrons, becomes less pronounced so that the expected energy gap enlargement takes place.

In conclusion, we have shown that non-BO effects are important in this system in describing the transition region between non-metallic and metallic behaviour, giving rise to fractional occupation numbers and to an effective HOMO-LUMO repulsion. These two effects lead to a lowering of the predicted DC conductivity which, as a function of the excess metal concentration, exhibits a much smoother behaviour than in the BO approximation, in good agreement with the experimental curves. Indeed our computed hot-electron DC conductivities are quite close to the experimental values. In view of the crudeness of the pseudopotentials used, the good quantitative agreement with experiment may be partly fortuitous, but we expect that the same qualitative thermally induced phenomena will be operative in all systems for which $\langle E_{\mathrm{g}} \rangle \sim k_{\mathrm{B}}T$. Indeed, in a preliminary simulation of laser-heated crystalline silicon, we have observed a significant widening of the HOMO-LUMO energy gap, as a result of increasing the electronic temperature from 300 K to 15 000-30 000 K.

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