Polarization catastrophe in doped cuprates and metal-ammonia solutions: an analogy.

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Abstract

On doping polar dielectrics, such as the cuprates or liquid ammonia, the long range polarization leads to the formation of bound states (polarons or solvated electrons). However, the exact role of such entities in the metal-insulator transition (MIT) still remains unclear. We suggest that the driving mechanism of the MIT is a polarization catastrophe that occurs due to their unscreened Coulomb interaction. This phenomenon is associated to a negative static dielectric constant, which could be the origin of both the superconducting transition in the cuprates — where the doping ions are frozen in the lattice structure — and the phase separation observed in liquid metal-ammonia solutions — where the counter-ions are mobile.

The aim of this paper is to propose an analogy between high-$T_c$ cuprate superconductors (HTSC) and metal-ammonia solutions (MAS). The analogy starts with the simple observation that for both systems, the MIT is accompanied with a special instability. For cuprates, there is an insulator-to-superconductor transition, while for metal-ammonia solutions the MIT is related with phase separation. In recent works we have studied the melting of a Wigner crystal of polarons as a function of both temperature and doping density (the full details are presented in ref. [1]). Starting from the insulating phase at low density, an insulator-to-metal transition takes place upon increasing the density. There are several important results to underline: (i) when the electron-phonon coupling is strong enough, the melting toward a polaron liquid is not possible; (ii) rather, the melting of the polaron Wigner crystal is driven by a polarization catastrophe leading to polaron dissociation above the MIT; (iii) at the critical density, the static dielectric constant becomes negative. The last point indicates that the existence of a mixed phase of free electrons coexisting with localized polarons above the polarization catastrophe could lead to a superconducting instability [2]. The glue for the superconductivity in this scenario would be due to the vibrations of the residual localized electrons inside their polarization potential-wells, which are able to overscreen the Coulomb interaction between mobile electrons and induce their pairing.

The generic phase diagram of the doped cuprates is sketched on Fig.1a, and can be roughly divided in three different regions. (I) is the low density regime where all the doping charges form polarons, and interact through the unscreened long-range Coulomb interactions. (III) is the region where the formation of dielectric polarons is completely prevented due to the screening of the interactions. There is no more superconductivity at such high densities, and the system tends to an ordinary metal. The straight line represents the onset of the pseudo-gap phenomenon. This can be extended down to zero temperature, well inside the superconducting region, by applying a strong magnetic field [3], indicating that the insulator-to-metal crossover takes place in the region (II) around optimal
doping. In our picture, the region (II) corresponds to a mixed phase of free electrons and localized polarons occurring above the polarization catastrophe.

The phase diagram of liquid metal-ammonia solutions is sketched on Fig.1b. As for the cuprates, there are three well defined regions. On doping pure ammonia with alkali metals (e.g. with Na), the metal atoms dissociate yielding two species in solution: the electrons, and the metal ions that are solvated by the ammonia molecules. At low density (I), the electrons are also solvated by ammonia molecules yielding entities – the solvated electrons – which are equivalent to Fröhlich polarons in oxides. A simple model for solvated electrons was first proposed by Jortner [5] and confirmed later by path integral calculations [6] and numerical (molecular dynamics) simulations [7]. The short range repulsion between the electron and the ammonia molecules creates a small cavity (of radius about 3 Å) in which the electron localizes (see Fig.2). The attractive forces giving rise to localization come from the long range polarization due to the orientational degrees of freedom of the ammonia molecules. Equivalently, the formation of (Fröhlich) polarons in oxides comes from the polarization field created by the longitudinal optical phonons of the underlying lattice. In both cases, the long-range asymptotic potential felt by the electrons is Coulombic: $V(r) \sim e/\varepsilon r$, with $\varepsilon^{-1} = \varepsilon_\infty^{-1} - \varepsilon_s^{-1}$. Here $\varepsilon_\infty$ is the optical dielectric constant ($\approx 4$ for undoped cuprates, and $\approx 2$ for pure ammonia), determined by the response of the ion cores, while $\varepsilon_s$ is the static dielectric constant ($\approx 30$ for undoped cuprates, and $\approx 22$ for ammonia). The difference between $\varepsilon_\infty$ and $\varepsilon_s$ originates from the polarizability related to the lattice deformation (in the cuprates), or the orientation of ammonia molecules (which carry a permanent dipole moment), and indicates that both systems are strongly polarizable.

When the coupling of electrons to the polarization degrees of freedom is strong, the potential-well which surrounds each electron has at least two localized levels: the ground-state (1s) and one excited state (2p). The transition energy is given by $\hbar \omega_0 = E_{2p} - E_{1s}$, and can be measured by optical experiments. In the cuprates, $\omega_0 \approx 0.1 - 0.15 eV$ [8], while in metal-amonia solutions $\omega_0 \approx 0.8 - 0.9 eV$ [9]. The polarization vibrates at a much lower frequency, and therefore is not able to screen such transition.

Starting from the low density limit, we can calculate the dielectric constant as we did for the
the pressure forces in the particle fluid. To evaluate the dielectric constant, we use the expression of electrons and of the ions (and cavities). The terms containing gradients of the density correspond to \( \eta \) of all other fluid particles, is related to the macroscopic field in the medium by the Lorentz formula:

\[
\mathbf{E} = \frac{e}{\varepsilon} \nabla \phi + \frac{\mathbf{J}}{\varepsilon_c} - \nabla \phi_c.
\]

We propose here a simple hydrodynamic (and classical) model able to incorporate some important aspects of the many body problem. For the sake of simplicity, we only consider three kinds of particles in solution [10]: the solvated metal ions with mass \( M^+ \) and charge +e, the neutral cavities with mass \( M_0 \) (we take \( M_0 = M^+ \equiv M \)), and the electrons with mass \( m_e \) and charge \(-e\). Each electron is linked to a neutral cavity through a harmonic oscillator with spring constant \( K \).

Figure 2: Left: Jortner’s model [5]; the electron is localized inside a cavity, to form a solvated electron. The lowest energy levels in the potential-well are \( E_{1s} \) (ground state) and \( E_{1p} \) (excited state). The transition energy is \( \hbar \omega_0 = E_{1p} - E_{1s} \). Right: The three fluid model for metal-ammonia solutions consists of: the solvated metal ions (Na+) with velocity \( V^+ \), the neutral cavities (circles) with velocity \( V_0 \), and the electrons (e-) with velocity \( V^- \), which are linked to the cavities by springs of strength \( K \).

Solvated electrons exist [5,6,7], but the many solvated-electrons problem has been poorly studied to our knowledge. We propose here a simple hydrodynamic (and classical) model able to incorporate some important aspects of the many body problem. For the sake of simplicity, we only consider three kinds of particles in solution [10]: the solvated metal ions with mass \( M^+ \) and charge +e, the neutral cavities with mass \( M_0 \) (we take \( M_0 = M^+ \equiv M \)), and the electrons with mass \( m_e \) and charge \(-e\). Each electron is linked to a neutral cavity through a harmonic oscillator with spring constant \( K = m_e \omega_0^2 \) [11] (see figure 2). The basic equations of motion are:

\[
\begin{align*}
-n^- m_e \dot{V}^- &= -n^- e \mathbf{E}_{\text{loc}} - n^- m_e \omega^2 (\mathbf{R}^- - \mathbf{R}_0) - n^- m_e \Gamma_e \dot{V}^- \\
n^+ M \dot{V}^+ &= +n^+ e \mathbf{E}_{\text{loc}} - k_B T \nabla n^+ - n^+ M \Gamma V^+ \\
n_0 M \dot{V}_0 &= +n_0 \eta M \omega_0^2 (\mathbf{R}^- - \mathbf{R}_0) - k_B T \nabla n_0 - n_0 M \Gamma V^+.
\end{align*}
\]

where \( \eta = m_e/M \) is the mass ratio (\( \eta \ll 1 \)), \( \Gamma_e \) and \( \Gamma \) are respectively the damping constants of the electrons and of the ions (and cavities). The terms containing gradients of the density correspond to the pressure forces in the particle fluid. To evaluate the dielectric constant, we use the expression of the current density:

\[
\mathbf{j} = i \omega [\varepsilon_\infty - \varepsilon(k, \omega)] \mathbf{E}(k, \omega) = -e \bar{n} [\mathbf{V}^-(k, \omega) - \mathbf{V}^+(k, \omega)]
\]

(\( \bar{n} \) is the average electron density). The local field, which takes into account mean field the effect of all other fluid particles, is related to the macroscopic field in the medium by the Lorentz formula:

\[
\mathbf{E}_{\text{loc}} = \frac{\varepsilon(k, \omega) + 2\varepsilon_\infty}{3\varepsilon_\infty} \mathbf{E}(k, \omega).
\]

Using the standard conservation equation for mass and expanding in powers of the mass ratio \( \eta \), one gets an approximate expression for the real part of the dielectric constant (details of the calculations will be published elsewhere):

\[
Re[\varepsilon(k, \omega)] \approx \varepsilon_\infty + \frac{\omega_p^2 [-\omega^2 + (k_B T/m_e) k^2 + (\omega_0^2 - \omega_p^2/3\varepsilon_\infty)]}{[(k_B T/m_e) k^2 + (\omega_0^2 - \omega_p^2/3\varepsilon_\infty) - \omega^2]^2 + \Gamma^2 \omega^2} \left\{ 1 + \eta C_1(k, \omega) + O(\eta^2) \right\}.
\]

The coefficients \( C_1 \) of the expansion are bound quantities, so that when the density satisfies \( \omega_p^2/3\varepsilon_\infty \rightarrow \omega_0^2 \), the uniform \((k = 0)\) dielectric constant diverges as \( 1/\Gamma^2 \) when \( \omega \) tends to zero. The above condition defines the critical density for the polarization catastrophe. At the same time, the static dielectric constant becomes negative [12]. These results generalize to metal-ammonia solutions what we already obtained for the Wigner crystal of polarons [1,2]. In both cases, a transfer of the static dielectric constant becomes negative.

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spectral weight from high to low frequency is expected when approaching the instability, in agreement with the “color change” observed in both metal-ammonia solutions and high-$T_c$ superconductors [13].

Experiments indicate that the electrons added by doping beyond this critical density do not form bound states, but rather remain free. The properties of the resulting mixed phase now depend on the behavior of both the electrons, and of the compensating positive charges which also feel a negative dielectric constant. If the latter are free to move, as is the case in liquids, they naturally tend to produce phase separation. On the contrary, if they are frozen in a structure as in the doped cuprates, phase separation is prevented, and the overscreening due to the negative sign of the dielectric constant can induce pairing of the free electrons [14].

The present discussion remains of course qualitative. It presents some conjectures about what happens beyond the instability of the insulating phase of a polarizable medium. The real situation is certainly more complicated than expected in the present scenario. For example, multipolaronic states arranged along strings could appear as proposed by Kusmartsev [15]. However, we wish to emphasize the following points: (i) the role of polarons in the MIT has been underestimated up to now; (ii) the long range Coulomb forces may be fundamental for the understanding of systems such as the superconducting cuprates (see e.g. ref.[16]) or the metal-ammonia solutions.

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