Instability due to long range Coulomb interaction in a liquid of polarizable particles (polarons, etc.)

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The interaction Hamiltonian for a system of polarons a la Feynman in the presence of long range Coulomb interaction is derived and the dielectric function is computed in mean field. For large enough concentration a liquid of such particles becomes unstable. The onset of the instability is signaled by the softening of a collective optical mode in which all electrons oscillate in phase in their respective self-trapping potential. We associate the instability with a metallization of the system. Optical experiments in slightly doped cuprates and doped nickelates are analyzed within this theory. We discuss why doped cuprates metallize whereas nickelates do not.

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An electron moving in a highly polarizable lattice can distort the environment and create a potential which self-traps the electron. The resulting object can move by dragging the distortion resulting in a heavy particle called polaron. Apart from its motion as a whole the polaron has an extra degree of freedom which can be thought as the electron oscillating in the self-trapping potential. Because of this internal mode a polaron can be polarized in an external electric field.

In this Letter a model Hamiltonian that takes into account the interactions due to mutual polarization is derived. It is shown that a polaron liquid or more generally a liquid of polarizable particles becomes unstable for high enough concentrations due to the dipole-dipole interaction. The onset of the instability is indicated by a softening of the internal mode of the polaron which can be measured in optical experiments. Recent experimental results in cuprates and nickelates are analyzed within this scenario.

For simplicity the present treatment is semiclassical (in the spirit of the Drude model) however we expect that the same effect will show up in a fully quantum mechanical computation.

We concentrate on the case of dielectric polarons but we believe our results are valid also for other kinds of heavily dressed particles in solids as long as they have a polarizable internal degree of freedom.

Consider an electron in a dielectric with static dielectric constant $\varepsilon_0$ dominated by lattice polarization. If the electron is not allowed to move it will generate a radial polarization of the lattice towards itself. This distortion implies that some ionic positive charge ($q$) will accumulate in the vicinity of the electron. The charge induced in the lattice can be estimated as

$$q = e \left(1 - \frac{1}{\varepsilon_0}\right).$$

Now let us free the electron. If the electron binds to the induced lattice charge we have a dielectric polaron. In this case for the electron to move it has to drag the distortion of the lattice.

To describe this situation we use Feynman’s effective model for the polaron. The effect of the distortion is mimicked by a heavy fictitious particle of mass $M$. The electron, of mass $m$, is coupled to the heavy particle with a harmonic potential. The result is a composite particle. The non-interacting Hamiltonian for a liquid of such particles reads $H_0 = \sum_i H_i$ with

$$H_i = \frac{p_i^2}{2m} + \frac{P_i^2}{2M} + \frac{k}{2} |r_i - R_i|^2.$$

The first term in $H_i$ is the kinetic energy of the electron. The second term is the kinetic energy of the heavy mass representing the surrounding deformation. The third term is the coupling between the electron and the distortion. $p_i$, $r_i$ ($P_i$, $R_i$) are the momentum and position of the electron (fictitious mass) $i$.

In the original formulation by Feynman the action corresponding to Eq. (3) is regarded as an effective action for the dynamics of a polaron. The parameters are obtained variationally from the Fröhlich model of a dielectric polaron. Here we take as granted that $H_0$ is a first approximation to describe the dynamics of a polaron liquid and explore the consequences of adding a Coulomb term.

To derive the interaction Hamiltonian consider two fixed electrons in the dielectric at $r_1, r_2$. As before each electron will induce a close-by charge in the lattice of magnitude $+q$. The total electrostatic energy can be computed as usual. One gets self-energy terms plus the interaction term:

$$E_{\text{int}} = \frac{e^2}{\varepsilon_0 |r_1 - r_2|}.$$

This energy includes the vacuum electrostatic energy between charges plus the elastic energy stored in the dielectric.
\[ E_{\text{int}} = E_{\text{Coul}} + E_{\text{ela}}. \]  
(4)

The former is:

\[ E_{\text{Coul}} = \frac{e^2}{|r_1 - r_2|} \]  
(5)

i.e. the electrostatic energy between the screened charges. Eq. (4) can be solved for the elastic energy:

\[ E_{\text{ela}} = \frac{e^2}{|r_1 - r_2|} \left( 1 - \frac{1}{\epsilon_0} \right). \]  
(6)

The factors with the dielectric constant in Eq. (6) ensure that the elastic energy is zero for an infinitely rigid lattice \((\epsilon_0 \to 1)\) or an infinitely soft lattice \((\epsilon_0 \to \infty)\).

Suppose now that we move the electrons from the equilibrium position keeping ions fixed so that the distortion does not move. i.e. \(r_i \neq R_i\). Since the elastic energy depends only on the configuration of the lattice we should replace in Eq. (6) \(r_i \to R_i\). So that in general the elastic energy is:

\[ E_{\text{ela}} = \frac{(e - q)q}{|R_1 - R_2|} \]  
(7)

where we eliminated \(\epsilon_0\) using the definition of the induced lattice charge \(q [\text{Eq. (1)}]\).

The Coulomb energy can be decomposed into elementary Coulomb interactions. For general position of charges and distortions it reads:

\[ E_{\text{Coul}} = \frac{e^2}{|r_1 - r_2|} - \frac{eq}{|r_1 - R_2|} - \frac{eq}{|R_1 - r_2|} + \frac{q^2}{|R_1 - R_2|} \]  
(8)

which reduces to Eq. (6) for \(r_i = R_i\).

Adding again the elastic and Coulomb energy we can write the interaction Hamiltonian for a liquid of such particles:

\[ H_{\text{int}} = \sum_{ij, i \neq j} \left( \frac{1}{2} \frac{e^2}{|r_i - r_j|} - \frac{eq}{|r_i - R_j|} + \frac{1}{2} \frac{eq}{|R_i - R_j|} \right) \]  
(9)

where indexes \(i, j\) run over particles.

A similar argument can be used to derive the interaction Hamiltonian with an external electric field. The Coulomb contribution of the induced charge cancels with the elastic part and one obtains,

\[ H_E = \sum_i e(r_i - R_i)E. \]  
(10)

The many-particle Hamiltonian is \(H = H_0 + H_{\text{int}} + H_E\).

It is convenient to change to center of mass variables, \(\rho_i = (r_i - m + R_iM)/(M + m)\), \(u_i = r_i - R_i\). Making a Taylor expansion for small \(u_i\) we obtain the following interacting Hamiltonian in the dipole approximation,

\[ H_{\text{int}} = \sum_{ij, i \neq j} \left( \frac{1}{2} \frac{e^2}{|r_i - r_j|} - \frac{eq}{|r_i - R_j|} + \frac{1}{2} \frac{eq}{|R_i - R_j|} \right) \]  
(9)

where we have defined the matrix \(\Phi_{\mu\nu}(\rho) = \delta_{\mu\nu}/\rho^3 - 3\rho_{\mu}\rho_{\nu}/\rho^5\) and \(\mu, \nu\) are Cartesian indexes.

Hamiltonian Eq. (3) have the essential ingredients to treat the interacting polaron problem at concentrations such that the interparticle distance exceeds the polaron radius.

Now we compute the dielectric constant of such a system. To obtain equations of motion for one particle in the mean field of the others we compute the forces \(F_{u_i} = -\partial H/\partial u_i\) and \(F_{\rho_i} = -\partial H/\partial \rho_i\). The former is the force that polarizes particles and the latter is the force acting on the center of mass. The equations of motion in mean field read,

\[ \mu \ddot{u} = -k u + 4\pi L n e q u - \frac{e}{1 + m/M} E \]  
(12)

\[ (m + M) \ddot{\rho} = -e E \]  
(13)

where \(u \equiv < u_i >\), etc. \(n\) is the density of particles, \(1/\mu = 1/m + 1/M\), and \(L\) is a geometric factor discussed below.

A crucial point in the derivation is the evaluation of the force due to dipole-dipole interactions \(F_L = e q u < \sum_{j, i \neq i} \phi(\rho_i - \rho_j) >\). This is the well known Lorentz-Lorenz local field i.e. the dipolar field at \(\rho_i\) due to dipoles at positions \(\rho_j\) averaged over the position of the dipoles. Using well known results from the theory of dielectrics we obtain the second term in Eq. (12). Either for a random isotropic distribution of dipoles or for a cubic array \(L = 1/3\). For other distributions \(L\) can be computed using the results of Ref. [12] (see below).

By putting \(E = 0\) we solve for the dipole moment \(\Pi\) and compute the polarization vector \(P \equiv n\Pi\) where in the original variables the dipole moment is \(\Pi_i \equiv -e r_i + q R_i\).

Finally from the relation between \(P\) and \(E\) one obtains the following dielectric function for the interacting polaron liquid

\[ \epsilon(\omega) = 1 + \frac{\Omega_p^2}{\omega^2 + i\gamma_p \omega} - \frac{\omega_p^2 - \Omega_p^2}{\omega^2 - \Omega_c^2 + i\gamma_p \omega} \]  
(14)

where we have introduced phenomenological inverse relaxation times \(\gamma, \gamma'\) and defined the bare plasma frequency \(\omega_p^2 \equiv 4\pi n e^2/m\) and the polaron plasma frequency \(\Omega_p^2 \equiv 4\pi n e(e - q)/(M + m) = 4\pi n e^2/\epsilon_0(M + m)\). In the latter \(M + m\) can be identified with the polaron effective mass. We have also defined the renormalized frequency of the internal mode.
\[ \omega_{\text{coll}}^2 = \omega_0^2 - \frac{q}{e} L (1 + \frac{m}{M}) \omega_p^2 \]  

(15)

where \( \omega_0 \equiv \sqrt{E/\mu} \) is the frequency of the internal mode of an isolated polaron.

The dielectric function Eq. (14) takes a very simple form: the sum of a Drude term plus a collective excitation at frequency \( \omega_{\text{coll}} \). The latter consists of all electrons oscillating in phase inside their respective self-trapping potentials. In this oscillation polarons develop time-dependent in-phase dipole moments. The dipole-dipole interaction tends to soften this mode and the effect increases as interparticle distance decreases i.e. density increases \((\propto \omega_p^2)\). Eq (14) can be seen as a generalization of both Drude model and Clausius-Mossotti equation \( \Box \).

Notice that the f-sum rule is exactly satisfied.

At some critical density given by \( 4 \pi n_c / e^2 m = \omega_0^2 / e L (1 + m/M) \) the energy cost to displace the electrons away from the respective lattice distortion vanishes and an instability occurs. Within this simplified model we cannot describe the new phase that arises for \( n > n_c \). In fact we assumed above that electron and distortion are bound and, even more, that the binding potential is harmonic. Both approximations will break down close to \( n_c \). Interestingly, if a positive quartic term were present in the distortion-electron potential, the system would become a liquid crystal of ferroelectric polarons above the critical density.

A less exotic possibility is that polarons start to dissociate. This can occur either abruptly or in a continuous way. In the former case all polarons collapse at \( n_c \) whereas the latter case can be realized by a two component system of coexisting polarons and free electrons \( \Box \).

Recently the softening of a polaron band has been observed as a function of doping \( \Box \) in the Nd$_2$CuO$_4$-\( y \) system. We have used Eqs. (14), (15) to analyze those data.

Slightly doped cuprates show a polaronic band, phonon bands, a mid-IR band and a charge transfer band \( \Box \) (we neglect much weaker magnetic bands \( \Box \)). Following Calvani and collaborators we fitted reflectivity data \( \Box \) on Nd$_2$CuO$_4$-\( y \) with a Drude-Loewntz model for the dielectric constant (a sum of Lorentzians plus a Drude term, see Ref. \( \Box \)). The model dielectric function is of the same form as in Eq. (14) but for the addition of phonons and of high energy electronic contributions, and with an appropriate \( \epsilon_{\infty} \) replacing 1. Because of the electronic screening \( \omega_p \) and \( \Omega_p \) in Eq. (14) should be considered screened plasma frequencies. Two Lorentzians were used above \( 10^4 \text{ cm}^{-1} \) to fit the charge transfer band and higher energy contributions. Four Lorentzians were used below \( 800 \text{ cm}^{-1} \) to model the TO phonons, one Lorentzian above \( 5000 \text{ cm}^{-1} \) (depending on sample) were used to fit the mid-IR band (MIR) and finally one Lorentzian below \( 2000 \text{ cm}^{-1} \) were used to fit the internal mode of polarons. In Fig. (1) we show the resulting optical conductivity \( \sigma(\omega) = \text{Im}(\epsilon(\omega)\omega/4\pi) \), excluding the electronic contributions and the phonons. Neither \( n \) nor \( y \) are well controlled variables so we use \( \omega_p^2(\propto n) \) as our control parameter which can be determined directly by adding the polaron and the Drude oscillator strength [Eq. (14)]. In the inset of Fig. (1) we show \( \omega_{\text{coll}}^2 \) vs. \( \omega_p^2 \). Both quantities are obtained from the fits.

As found by Lupi et al. \( \Box \) in this doping range we see a rapid decrease of the internal mode energy. To estimate the rate of decrease we neglect the higher doping point (it is in the region where our approximations break down) and we do a linear regression. We obtain a slope of \(-0.55 \).

![FIG. 1. Optical conductivity obtained from the fit of the model dielectric function to reflectivity \( \Box \) data at 300K as explained in the text. Only Drude and internal mode polaron contributions have been included. The upper curves have larger doping \( y \) or equivalently larger density of particles \( n \). The area under the curves is proportional to \( \omega_p^2 \). The maximum of the broad structure approximately corresponds to \( \omega_{\text{coll}} \). Inset: The parameter \( \omega_{\text{coll}}^2 \) vs. \( \omega_p^2 \) from the fits. The error bars reflect uncertainties in the fit. The line is a linear regression excluding the higher doping point.

To get a theoretical estimate of the slope in Eq. (13) we need the Lorentz-Lorenz local field factor \( L \). Using the results of Ref. \( \Box \) we estimate \( L = 0.6 \) for Nd$_2$CuO$_4$-\( y \) and for the electric field of the radiation parallel to the Cu-O plane.

Also the induced charge in the lattice will not be given any more by Eq. (13). In fact Eq. (13) gives the total induced charge but part of this charge which we call \( q_e \) is induced in the electronic degrees of freedom. This should be subtracted from \(+q\) and added to \(-e\) since it will follow antiadiabatically the electron and hence is positioned at \( r_1 \), not at \( r_2 \). This effect is taken into account by replacing \( q/e \) by \( (q - q_e)/(e - q_e) \) in Eq. (13). \( q_e \) can be estimated, using long wave length Lyddane-Sachs-Teller like arguments \( \Box \), to be of the order of \( q_e = e(1 - 1/\epsilon_{\infty})(1/2)(\epsilon_0/(1/2)) \). Using \( \epsilon_0 = 30 \) and \( \epsilon_{\infty} = 5 \) \( \Box \) one gets \( (q - q_e)/(e - q_e) = 0.91 \). Finally, as a first approximation, we can take \( (1 + M/m) \sim 1 \) so we obtain for the slope -0.55 in excellent agreement with the experiment. The linear regression extrapolates
to $\omega_{\text{coll}} = 0$ at a critical value $\omega_{p,c}^2 = 7.6 \times 10^6 \text{ cm}^{-2}$.

For $n > n_c$, a sudden increase of Drude weight is observed (not shown), that we associate with metalization. This occur at much lower doping than the insulator superconducting transition observed at lower temperatures [24]. We believe that more complicated phenomena like charge ordering may change the picture at low temperatures [2]. Quantum corrections will also be important close to $n_c$ and at low temperatures.

Lupi et al. find that the collective mode subsists at a small finite frequency for $n > n_c$ and then monotonously decreases as doping is increased at a much slower rate [2]. This suggests a scenario where the polarons stabilize at a concentration slightly below $n_c$ and added carriers go to free states. Different versions of such two-fluid model has been considered in the literature [14–17]. Interestingly, this coexistence implies that for a finite doping range the system is at the verge of a dielectric anomaly with a soft electronic mode. At larger doping, polarons are expected to become unstable due to short-range interactions and screening and a first order transition will occur to a one component Fermi liquid. We speculate that this scenario can explain the phase diagram of cuprates. In fact the soft collective mode can explain many of the anomalous Fermi liquid properties [21] that these systems show at optimum doping levels including pairing formation and superconductivity due to exchange of the soft mode boson. At overdoping the experimental optical conductivity shows a single component Drude behavior which suggest a first order transition [2]. A related scenario including the softening of an optical electronic mode associated with matallization has been proposed previously [22].

The present theory also explains why a material like doped La$_2$NiO$_4$ never becomes metallic. In this system the observed energy of the internal mode of small doping is roughly by a factor of 3 larger than in Nd$_2$CuO$_4$ [39]. Then if we assume that the slopes of $\omega_{p,c}^2$ vs. $\omega_p^2$ are similar in the two systems we expect, according to Eq. (13), that the critical plasma frequency $\omega_{p,c}$ in the nickelate is by a factor of 9 larger than in the cuprate. On the other hand, the observed spectral weight in this system reaches a maximum and decreases again as a function of doping [30]. We estimate the maximum $\omega_p^2$ by integrating the fitted line shapes in Ref. [39] to be roughly $9 \times 10^6 \text{ cm}^{-2}$ which is almost by an order of magnitude smaller than the estimated $\omega_{p,c}^2$. This means that on undimensionalized scales ($\omega_{p,c}^2/\omega_f^2$ vs. $\omega_p^2/\omega_f^2$) only the first $\sim 10\%$ of the curve in the inset of Fig. 1 is physically accessible and the system never reaches the point in which it should metalize. Meaningfully a modest softening of the internal mode is actually observed [48] in this relatively small $\omega_p^2/\omega_{p,c}^2$ variation range consistent with Eq. (13).

To conclude we have derived a many body Hamiltonian that takes into account dipole-dipole interactions in a polaron system in a general way. We obtained the dielectric constant in mean field for a liquid of such particles and showed that the system becomes unstable for large concentration. We argue that the theory explains a rapid softening of the internal mode of the polaron recently observed in cuprates [4] and discussed the doping-induced matallization of cuprates and nickelates. We speculate that the same framework can be used to explain the occurrence of matallization or not as a function of doping in a wide range of materials where the electron phonon interaction dominates.

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