Ferroelectrics with Low-energy Electronic Excitations

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Abstract

We formulate a general theory of the dielectric response of a lattice with a structural transition and a polarisation instability due to a soft-optic mode coupled to low energy electronic excitations by the electromagnetic fields. The electronic excitations considered are in two-limits; those of a low density of free-electrons or those of a low density of strongly localised electrons in the Coulomb-glass phase. The ferroelectric transition in the absence of the electronic-excitations and the low energy dielectric properties are shown to be strongly modified.
I. INTRODUCTION

In the last few years there has been an enormous revival in the study of ferroelectric and ferroelectric materials [1], [2], [3]. In a large part it is due to the investigation of complex materials with very large number of atoms per unit cell and substantial disorder. The disorder also introduces low-energy electronic states. Such materials display what has come to be known as ‘relaxor-ferroelectric’ properties. This term appears to cover all properties, not seen in simple ferroelectrics- for example $\text{BaTiO}_3$. Generally these materials do not have a ferroelectric transition but do have a very large dielectric-constant, the polarization displays complicated hysteresis loops and has a strong frequency and history dependence at low energies.

Various ideas for the form of disorder and its effect on the ferroelectric transition have been proposed [4], [5], [6]. But to our knowledge, the important effect of low-energy particle-hole excitations due to shallow electronic levels has not been treated. Ferroelectricity (like superconductivity) is rather special because the order parameter, the polarization, couples to the low-energy electronic excitation through the electromagnetic-fields. In this paper we study such effects. The effects of disorder are neglected here by adopting a virtual-crystal approximation. In fact both effects, disorder and low-energy electronic excitations are important; we hope to treat them together in the future.

This paper is organised as follows. In Section 2, we present a general Lagrangian for a polarization instability coupled to electronic excitations through the electromagnetic fields. The generalization to the disordered case is also indicated. In section 3, we consider the simple case that the low energy excitations are due to a low density of free electrons. While it is common-place knowledge that free-electrons will screen the electric field so that macroscopic fields cannot arise, it is worthwhile to precisely derive the conditions for this and see the condition for the formation of ferroelectric domains at low enough charge density. The domain walls in this case may be charged. We also derive the low energy charge and current response functions for this case. In Sec. 4 we take up the more interesting problem of localised electrons in a Coulomb glass phase and derive the charge response functions.

II. THE LAGRANGIAN FOR SOFT OPTIC MODES IN PRESENCE OF LOW-ENERGY ELECTRONIC EXCITATIONS

We consider the following Lagrangian density (at imaginary times), $L = L_{\text{ferro}} + L_{\text{EM}} + L_{\text{int}} + L_{\text{e}}$, where

$$L_{\text{ferro}} = \frac{1}{2\chi} \left[ \frac{\partial \vec{P}}{\partial \tau} \right]^2 + \omega_0^2 \vec{P}^2 + \gamma (\nabla \vec{P})^2 + \frac{1}{4} u \vec{P}^4, \quad (1a)$$

is a Langrangian describing the polarization vector $\vec{P}$. For $\omega_0^2 = \alpha (T - T_c)$ Eq. (1a) describes an instability of the system (in the absence of coupling to electric fields) when $T \to T_c$.

$$L_{\text{EM}} = \frac{1}{8\pi} \left[ \frac{1}{c} \left( \frac{\partial \vec{A}}{\partial \tau} \right)^2 + (\nabla \phi)^2 \right] + \frac{1}{8\pi} (\nabla \times \vec{A})^2 \quad (1b)$$
is the usual Lagrangian for EM fields in terms of vector potential $\vec{A}$ and scalar potential $\phi$ in the Coulomb gauge, $\nabla \cdot \vec{A} = 0$. In the microscopic theory, $\omega_0$ is the frequency of the zone-center transverse optic phonon. The polarization vector $\vec{P}$ couples to the electric field $\vec{E}$ through the usual Lagrangian $L_{int}$, where
\[
L_{int} = \vec{P} \cdot \vec{E} = -\vec{P} \cdot \left[ \frac{1}{c} \frac{\partial \vec{A}}{\partial \tau} + \nabla \phi \right]. \tag{1c}
\]

In the presence of charges, the EM potentials pick up additional terms in their Lagrangian. In the Coulomb gauge they are
\[
L_e = -\frac{1}{2} \left[ \chi_L \phi^2 + \left( \frac{1}{c} \right)^2 \chi_T A^2 \right], \tag{1d}
\]
where $\chi_L$ and $\chi_T$ are the longitudinal and transverse response functions of the electrons to scalar and vector potentials $\phi$ and $\vec{A}$, respectively. In Eqs. (1), $\vec{P}, \phi$ and $\vec{A}$ depend on the position $r$. For the translational invariant case, this may be directly Fourier-transformed. In the case of disorder, they are random functions of position and the response functions $\chi_L$ and $\chi_T$ are functions of two co-ordinates. In what follows, we shall assume an effective translational invariant approximation, where disorder is considered averaged over at the outset.

In the Coulomb gauge, the Lagrangian can be separated into longitudinal and transverse parts, $L = L_L + L_T + L_u$. We obtain after Fourier transforming,
\[
L_L = \frac{1}{2} \left( v(q)^{-1} - \chi_L \right) \phi^2 - \frac{1}{2\chi}(i\omega)^2 - (\omega_0^2 + \gamma^2 q^2)]\vec{P}_L \cdot \vec{P}_L - i(\vec{P}_L \cdot \vec{q}) \phi, \tag{2a}
\]
where $v(q) = 4\pi/q^2$ is the Coulomb potential, and
\[
L_T = -\frac{1}{8\pi c^2} [(i\omega)^2 - c^2 q^2 + 4\pi \chi_T] \vec{A}^2 - \frac{1}{2\chi}(i\omega)^2 - (\omega_0^2 + \gamma^2 q^2)]\vec{P}_T \cdot \vec{P}_T - i\vec{P}_T . \left( \frac{i\omega \vec{A}}{c} \right), \tag{2b}
\]
where we have divided the polarization vector $\vec{P}$ into longitudinal and transverse parts $\vec{P} = \vec{P}_L + \vec{P}_T$, and
\[
L_u = \frac{u}{4} (\vec{P}_L + \vec{P}_T)^4, \tag{2c}
\]
is the fourth-order term in $L_{ferro}$. Notice that $L_u$ mixes the longitudinal and transverse parts of $\vec{P}$.

To study the ferroelectric instability, we take the $i\omega = 0$ limit and first minimize the free energy with respect to the $\phi$ and $\vec{A}$ fields. We obtain
\[
\phi(q) = \frac{i\vec{q} \cdot \vec{P}_L}{v(q)^{-1} - \chi_L(q)} \tag{3}
\]
\[
\frac{\vec{A}}{c} = -4\pi i \left( \frac{i\omega \vec{P}_T}{(i\omega)^2 - c^2 q^2 + 4\pi \chi_T(q)} \right) \rightarrow 0.
\]
Substituting these back into Eq. (2), we obtain an effective free energy in terms of $\vec{P}$ only,
\[
f = \frac{1}{2\chi} (\omega_c^2 + \gamma^2 q^2) [\langle P_L \rangle^2 + \langle P_T \rangle^2] + \frac{1}{2} \left[ \frac{(\vec{q} \cdot \vec{P}_L)^2}{[\varphi(q) - 1 - \chi_L]} + \frac{u}{4} \right].
\]

In an infinite medium, \( P_T \) decouples from the EM field completely in the static limit, as is required by Faraday’s Law that \( \vec{B} = \nabla \times \vec{E} \neq 0 \) when a transverse electric field exists. This is not true in a finite sample, where a macroscopic \( P_T \), if it exists, is discontinuous at the surface. A surface charge - density \( \sigma = \vec{P} \cdot \hat{n} \) is then generated leading to an electric field.

**III. FREE ELECTRONS**

For free electrons, we may use the fact that

\[
(v(q)^{-1} - \chi_L(q,0))^{-1} \rightarrow \frac{4\pi}{q^2 + q_{sc}^2}
\]

in the small \( q \) limit. In Eq.(5), \( q_{sc} \) is the static screening length, given in terms of density by the Thomas-Fermi length at low temperatures and by the Debye length in the classical regime at high temperatures, i.e.

\[
q_{sc}^2 \sim q_{TF}^2 = 6\pi n_0 e^2 / E_f = 4(3/\pi)^{1/3} n_0^{1/3} / a_0
\]

for \( T \ll E_f \). Here \( n_0 \) is the density of electrons, \( E_f \) their Fermi-energy and \( a_0 \) the Bohr radius, and

\[
q_{sc}^2 \sim q_D^2 = 4\pi n_0 e^2 / kT.
\]

at high temperature. For most problems of interest in ferroelectrics, the density is low enough that near room temperature the Debye Screening is applicable.

In the absence of free electrons, an instability develops in \( \vec{P}_T \) field in the \( q \rightarrow 0 \) limit as \( T \rightarrow T_c \) (or \( \omega_0 \rightarrow 0 \)) always before any possible instability in \( \vec{P}_L \). This instability occurs at \( T_c \), where the transverse optic phonon frequency \( \rightarrow 0 \). The magnitude of \( T_c \) will in general change in the presence of free electrons due to microscopic effects not treated here. The presence of free electrons bring the transition in \( \vec{P}_T \) and \( \vec{P}_L \) to the same temperature \( T_c \) because of screening, i.e. in infinite samples, no uniform electric-field can be produced due to a macroscopic \( \vec{P} \) because the electric field sets up by the ions oscillation is screened. The electric field in the ordered state of the system with \( < \vec{P}_T > \neq 0 \) is given by

\[
\vec{E} = -\nabla < \phi > = \lim_{q \rightarrow 0} \left( \frac{q^2 \sigma}{v(q)^{-1} - \chi_L} \right).
\]

Here \( \sigma \) is the surface charge density at the surface of the sample at which \( \vec{P}_T \) has a normal component \( \vec{P}_T \cdot \hat{n} \neq 0 \). \( \vec{E} \) goes to zero as long as \( \chi_L(q,0) \) is finite, i.e. \( < \vec{P}_T > \neq 0 \) does not lead to uniform electric field in the presence of free electrons. This does not necessarily mean that ferroelectricity is destroyed by arbitrarily small density of electrons. As shown below a domain structure of electric-fields is still possible provided the charge density is low enough.
At temperatures $T < T_c$, it is easy to minimize the energy to show that $< \vec{P} > = \vec{P}_o = \sqrt{-\frac{\omega_0^2}{\chi}}$. The Langrangian can be written as $L = L(P_o) + L(P')$, where $P'$ are fluctuations around $\vec{P} = \vec{P}_o$. We find that to second order in $P'$, $L(P') = L_L(P'_L) + L_T(P'_T)$, where

$$L_L(P'_L) = -\frac{1}{2} \left[ \frac{1}{\chi} ((i\omega)^2 - (-2\omega_0^2 + \gamma^2q^2)) - \frac{4\pi q^2}{q^2 + q_{sc}^2} \right] (\vec{P}'_L)^2$$

and

$$L_T(P'_T) = -\frac{1}{2} \left[ \frac{1}{\chi} ((i\omega)^2 - (-2\omega_0^2 + \gamma^2q^2)) - \frac{4\pi (i\omega)^2}{(i\omega)^2 - c^2q^2 + 4\pi \chi_T} \right] (\vec{P}'_T)^2.$$ (8a, 8b)

Notice that the only difference between $T > T_c$ and $T < T_c$ in the quadratic fluctuations in $\vec{P}$ is that $\omega_0^2$ is replaced by $-2\omega_0^2$ as temperature decreases from $T > T_c$ to $T < T_c$.

IV. DOMAIN WALL FORMATION

For usual (insulating) ferroelectrics with finite dimensions, domains are formed to minimize the electric field energy $\sim \int d^3x \frac{\vec{E}^2}{8\pi}$, coming from effective surface charges $\sigma(\vec{x}) \sim \hat{n}.\vec{P}(\vec{x})$, where $\hat{n}$ is a surface unit vector. In this section the criteria of domain formation in the presence of free charges is studied. For simplicity we shall consider a ferroelectric with a finite width $2L$ in $z$-direction, and with infinite extent in $x$ – $y$ plane. We shall assume a transverse polarization field $\vec{P}_T$ with $\vec{P}_T$ pointing in $z$-direction, and with magnitude function of $x$– and $y$– coordinates, i.e. $\vec{P} = \hat{z}P(x,y)$ for $-L < z < L$. For a finite $L$ surface charges $\sigma(x,y) = (\delta(z - L) - \delta(z + L))P(x,y)$ will be set up, and the total energy of the system is given in momentum space by

$$F = \sum \vec{q} \left[ \frac{1}{2} (\chi(q) - \chi_L) |\phi(\vec{q})|^2 - \sigma(\vec{q}) \phi(-\vec{q}) + \frac{1}{2\chi} (\omega_0^2 + \gamma^2 q^2) |\vec{P}(\vec{q})|^2 \right]$$

$$+ \frac{u}{4} \int_{-L}^{L} dz \int \int dx dy \vec{P}^4,$$ (9)

where $\sigma(q) = (2i)sin(qz)L)P(q_x, q_y)$ is the fourier transform of the surface charge density. Notice that $\vec{q}.\vec{P}_T(\vec{q}) = 0$ in the sample. Minimizing the energy with respect to $\phi$ we obtain

$$F = \sum \vec{q} \left[ \frac{1}{2} \frac{(2sin(qz)L)}{v(q) - \chi_L} |P(q_x, q_y)|^2 \right]$$

$$+ \frac{u}{4} \int_{-L}^{L} dx \int \int dx dy \vec{P}^4.$$ (10)

Summing over $q_z$, and using the results that

$$\int_{-\infty}^{\infty} dq_z \frac{\sin^2(qzL)}{q_z^2 + Q^2} \sim \int_{-\infty}^{\infty} dq_z \frac{1}{2(q_z^2 + Q^2)} = \frac{\pi}{2Q},$$

when $L \to \infty$, where $Q^2$ is a positive number, we obtain
\[ F \to (L) \sum_{q_x,q_y} \left[ \frac{\pi}{L} \frac{\overline{P}(\vec{q})^2}{\sqrt{q^2 + q_z^2}} + \frac{1}{\chi} (\omega_i^2 + \gamma^2 q^2) \overline{P}(\vec{q})^2 \right] \]
\[+ \int \int dx dy \, u \frac{L}{2} \frac{\vec{P}(\vec{q})^4}{\phi} \]

(11)

where \( \vec{q} = (q_x, q_y) \) in Eq. (11). Minimizing the free energy with respect to \( P(\vec{q}) \) and \( \vec{q} \) we see that the system has now an instability at finite \( q \) which indicates the instability of the system to domain formation. Expanding the quadratic terms in \( \overline{P} \) in Eq. (11) in powers of \( q^2 \) at small \( q \), we find that the system has an instability towards domain formation when

\[ \frac{\gamma^2}{\chi} < \frac{2\pi}{q_z^2 L} \]

or when \( q_{sc} \leq L_D^{-1} = \left( \frac{\pi}{2\gamma L} \right)^{\frac{3}{2}} \). It is easy to show from Eq. (11) that in the absence of free electrons \( (q_{sc} = 0) \) \( L_D^{-1} \) gives the characteristic size of the domains. The criteria for formation of domains (12) can thus be interpreted as simply saying that the screening length of free electrons should be longer than the natural domain size in order for domains to be formed when free electrons are present.

The presence of a finite charge density has important consequences for the switching and hysteresis properties of domains by reversing external-fields. Domain reversal must be accompanied now by motion of charges. The time scale for this is now limited by the time for the charges to diffuse over the characteristic size of the domains.

V. DIELECTRIC FUNCTIONS

To obtain the dielectric function at \( T > T_c \), we neglect the \( L_u \) term and integrate out the \( \overline{P} \) fields first in the Lagrangian (2). As a result, we obtain two effective Lagrangian \( L_{\text{eff}}(\phi) \) and \( L_{\text{eff}}(\vec{A}) \) for the electromagnetic potentials. The dielectric functions can be obtained by identifying

\[ L_{\text{eff}}(\phi) = \frac{\epsilon L(q, i\omega)}{2v(q)} \phi^2, \]
\[ L_{\text{eff}}(\vec{A}) = \frac{\epsilon T(q, i\omega) [(i\omega)^2 - c^2 q^2]}{8\pi} A_\mu^2, \]

where we have again considered the Coulomb gauge \( \nabla \cdot \vec{A} = 0 \). After some algebra we obtain

\[ \epsilon_L(q, i\omega) = 1 - v(q) \chi_L(q, i\omega) - \frac{4\pi \chi}{(i\omega)^2 - \omega_i^2(q)}, \]

(14a)

and

\[ \epsilon_T(q, i\omega) = 1 - \frac{4\pi \chi T(q, i\omega)}{(i\omega)^2} - \frac{4\pi \chi}{(i\omega)^2 - \omega_o(q)^2}, \]

(14b)
where $\omega_o(q)^2 = \omega_o^2 + \gamma^2 q^2$. A similar expression can also be derived for $T < T_c$. The only difference is that $\omega_o^2$ is replaced by $-2\omega_o^2$ when $T < T_c$. Notice that $\omega_o(q)^2$ is positive definite at all temperatures $T \neq T_c$.

The longitudinal electromagnetic collective mode dispersions in the system can be obtained by solving the equation $\epsilon_L(q, \omega(q)) = 0$. In the small $q$ limit and with $\omega \gg q$, $v(q)\chi_L(q, \omega) \to \frac{\omega^2}{\omega_p^2}$, where $\omega_p$ is the electronic plasma frequency, and we obtain the secular equation,

$$1 - \frac{\omega_p^2}{\omega^2} - \frac{4\pi \chi}{\omega^2 - \omega_o(q)^2} = 0.$$  

(This equation is not modified in the classical limit for long-wavelengths.) Solving the equation we find that there are in general two solutions $\omega_1$ and $\omega_2$ in the equation. At small $q$ and for $\omega_o(q)^2 << \omega_p^2$, we obtain

$$\omega_1^2 \to \omega_p^2 + 4\pi \chi \quad \omega_2^2 \to \left(\frac{\omega_p^2}{\omega_p^2 + 4\pi \chi}\right) \omega_o(q)^2.$$  

The transverse electromagnetic collective mode dispersions are obtained by solving $\omega^2\epsilon_T(q, \omega) - c^2 q^2 = 0$. We obtain after some simple algebra a secular equation very similar to Eq. (15), except that $\omega_p^2$ is replaced by $\omega_p^2 + c^2 q^2$, with similar solutions

$$\omega_1^2 \to \omega_p^2 + 4\pi \chi + c^2 q^2 \quad \omega_2^2 \to \left(\frac{\omega_p^2 + c^2 q^2}{\omega_p^2 + c^2 q^2 + 4\pi \chi}\right) \omega_o(q)^2.$$  

Notice that $\omega_1$ gives the usual plasmon and polariton modes, respectively for longitudinal and transverse EM fields in metals, with modifications coming from polarization field, whereas $\omega_2$ gives the collective modes in longitudinal and transverse polarization fields $\vec{F}_L$ and $\vec{F}_T$, respectively, with modifications coming from metallic behaviour. Notice that at small $q$ and when $\omega_o^2 \to 0$, $\omega_2$ becomes very small and will be in the hydrodynamic regime where $\chi_L$ would have a diffusive form

$$\chi_L(q, \omega) = \frac{dn}{d\mu} \left(\frac{D q^2}{i\omega - D q^2}\right).$$  

In this regime, the dispersion $\omega_2$ will be modified. In particular, a finite damping of the collective mode will occur because of coupling to the electronic degrees of freedom.

VI. FERROELECTRICS WITH LOCALIZED ELECTRONS

We shall consider here ferroelectrics in the presence of strongly localized electrons in the Coulomb glass phase. In the dilute particle-hole pairs approximation (see Appendix), the localized electrons have only longitudinal response to external electric fields, and with response functions $\chi_{CG}(q, \omega)$ given in the Appendix. Their effects on the ferroelectrics can be studied by replacing $\chi_L$ for free electrons by $\chi_{CG}$. First we consider $\omega = 0$ and study ferroelectric instability and domain formation at different temperature ranges.
A. ferroelectric instability and domain formation

As a function of temperature, the response function $\chi_{CG}(q, 0)$ has three different regimes. First we consider high temperature $k_B T >> \Delta$ where the Coulomb glass effect is unimportant and the response of the electrons are dominated by phonon-assisted hopping. This is probably the regime of experimental interests in ferroelectrics. Using Eq. (A11) for $\text{Re}\chi_{CG}(q, 0)$ in Eq.(10) and repeating the analysis afterward we find that the free energy is given by Eq.(11) with $\sqrt{q^2 + q_{sc}^2}$ replaced by $q\sqrt{\epsilon}$ in first term of Eq.(11), where $\epsilon \sim \epsilon_o + \left(\frac{4\pi^4g^2Aa_o^5}{1440}\right)\left(\frac{A}{k_BT}\right)^\frac{1}{4}$, where $\epsilon_o$ includes all the non-singular contributions to $\epsilon$. The characteristic domain size $L_D$ is given by

$$L_D \sim \left(\frac{2\gamma^2 L\sqrt{\epsilon}}{\pi\chi}\right)^\frac{1}{3},$$

which differs from the pure ferroelectric case only by the factor $\epsilon$. Notice that $\epsilon$ is expected to be large in the Coulomb or fermi glass regime and we expect that the effect of introducing localized electrons in the system is to enlarge the domain size. Notice that for small enough $L$, we may enter a regime where $L_D/a_o << (r_T/a_o)^\frac{3}{2}$. In this regime, we should use Eq. (A10) for $\text{Re}\chi_{CG}(q, 0)$. In this regime, we find that the enhancement in domain size by the factor $\epsilon$ is lost, and the analysis is similar to the case of metals except that the screening length $q_{sc}^{-1}$ is given by

$$q_{sc}^2 \sim \frac{4\pi^4e^2g^2}{144}a_o^3(k_BT).$$

Notice that in contrast to metals, the screening length increases as temperature is lowered.

As temperature is lowered we find that for large enough $L$ the domain size is still given by Eq. (18) except that the value of $\epsilon$ goes thought two more regimes. At temperature $\Delta > k_B T$ but $\omega_T > I(r_o)$, we find

$$\epsilon \sim \epsilon_o + \frac{\pi g^2 e^4 a_o^4}{6} \left(\frac{T_o}{T}\right)^2,$$

whereas at $\omega_T < I(r_o)$, we find

$$\epsilon \sim \epsilon_o + \frac{n^2}{10\pi} ln\left(\frac{T_o}{T}\right).$$

Notice that our theoretical prediction of domain size variation as a function of temperature can be tested experimentally. Note that for small enough $L$, the effect of screening will become stronger as in the high temperature case $k_B T > \Delta$, and the enhancement factor $\epsilon$ in domain wall size is lost.

It should also be kept in mind that the Coulomb glass has hysteretic low frequency response. One should therefore expect a slow and sluggish transition over a wide temperature range starting from about the $T_c$ to roughly when $\omega_0^2 + 4\pi \chi \approx 0$. 

8
B. (longitudinal) collective modes

At \( T > T_c \), the longitudinal collective modes of the system can be obtained by solving

\[
1 - v(q)\chi_{CG} - \frac{4\pi\chi}{\omega^2 - \omega_o(q)^2} = 0.
\]  

(19)

In the \( \omega \gg q \rightarrow 0 \) limit, we obtain the secular equation

\[
\omega^2 = \omega_o(q)^2 + \frac{4\pi\chi}{1 - v(q)\chi_{CG}(q \rightarrow 0, \omega)}.
\]  

(20)

where \( \chi_{CG}(q \rightarrow 0, \omega) \) are given by Eqs.(A6a), (A6b), at temperature range \( k_B T < \Delta \) at \( \omega < I(r_o) \) and \( \omega > I(r_o) \), respectively. At temperatures \( k_B T >> \Delta, \chi_{CG}(q \rightarrow 0, 0) \) is given by Eq.(A9). Although the quantitative behaviours of the collective modes are different, logarithmic corrections appear in the pure dielectric collective mode frequency \( \omega_o(q) \) in all the above cases. The logarithmic correction vanishes in the ferroelectric instability limit \( \omega \sim \omega_o(0) \rightarrow 0 \), in agreement with the static instability analysis which indicates that the ferroelectric instability occurs exactly when \( \omega_o(0) \rightarrow 0 \). Notice, however that a collective mode solution with \( \omega^2 \sim \omega_o(q)^2 + \frac{4\pi\chi}{\epsilon} \) exists even up to the instability limit \( \omega_o(0) \rightarrow 0 \). The polarization collective modes are in general much broadened by the Coulomb glass particle-hole excitation spectrum because of the very slow vanishing of \( Im\chi_{CG}(q, \omega) \) at small \( \omega \). Notice that at \( T < T_c \), we may obtain the collective modes by replacing \( \omega_o^2 \) by \( -2\omega_o^2 \) in Eq. (19). This is valid as long as we are interested at responses of the system at wave vectors \( q < L_D^{-1} \).

APPENDIX A: ELECTROMAGNETIC RESPONSE OF COULOMB GLASS

In this appendix we summarize our theoretical understanding for response functions of Coulomb glass systems. (Notice that we have set \( e^2 = 1 \) in the main text. Here \( e^2 \) is kept to make the equations more clear). The electromagnetic responses of Coulomb glass systems are rather complicated, and can be divided into many different regimes, depending on temperature, frequency and wavevector. A detailed discussion of these can be found in ref[8].

The starting model for responses of Coulomb glass systems is the effective two-site Hamiltonian by Shklovskii and Efros[7]. The Hamiltonian is derived under the assumption that the system is in the strongly disordered regime where the electrons are strongly localized. In this regime tunneling events of electrons from one site to another is rare and can be treated in a dilute particle-hole pairs approximation where interaction between different tunneling events are neglected and the tunneling of electron between two sites (particle-hole pair) is described by a two-site Hamiltonian

\[
H_{ij} = E_i n_i + E_j n_j + \frac{e^2}{r_{ij}} n_i n_j + I(r_{ij})(a_i^+ a_j + a_j^+ a_i),
\]  

(A1a)

where \( n_i \) is the electron occupation number \( (= 0, 1) \) at site \( i \), \( r_{ij} \) is the distance between the two sites, \( I(r) \sim I_0 e^{-r/a_o} \) is the effective tunneling matrix element between the two sites.
where $a_o \sim$ lattice spacing and $a(a^+)$ are electron annihilation and creation operators. the on-site energy $E_i$ is given by

$$E_i = \epsilon_i + \sum_{l \neq i,j} \frac{n_l e^2}{|r_l - r_i|}, \quad (A1b)$$

where $-A < \epsilon_i < A$ is the random on-site energy with bandwidth $2A$ and the second term comes from Coulomb interaction. Notice that electron spins are ignored in the theory. $H_{ij}$ can be diagonalized easily to obtain the following energy spectrum,

$$E_1^\pm = \frac{1}{2}(E_i + E_j) \pm \frac{\Gamma}{2},$$

$$E_2 = E_i + E_j + \frac{e^2}{r_{ij}}$$

where $E_1^+$ and $E_1^-$ are the two possible energy states when the two-site system is occupied by a single electron, and $E_2$ is the energy when both sites are occupied, $\Gamma = \sqrt{(E_i - E_j)^2 + 4I(r_{ij})^2}$. Notice that for the pair of sites to be occupied by a single electron and participate in the electromagnetic response, we must have $E_1^- < \mu < E_2 - E_1^-$, where $\mu$ is the chemical potential. The whole system is described as a diluted gas of independent (i.e. non-interacting), randomly distributed particle-hole pairs and the total response of the system to external electromagnetic fields is given by by sum of the response of individual pairs. For example, the density-density response function of a pair in the two-site Hamiltonian approximation is found to be (at temperature $T = 0$)

$$\chi_p(\vec{q}, i\omega) = 2 \frac{I(r_{ij})^2}{\Gamma(r_{ij})^2} (1 - \cos(\vec{q}.\vec{r}_{ij})) \left[ \frac{1}{i\omega - \Gamma(r_{ij})} - \frac{1}{i\omega + \Gamma(r_{ij})} \right], \quad (A3a)$$

and the average density-density response function of the whole system is

$$\chi_{CG}(\vec{q}, i\omega) = < \sum_p \chi_p(\vec{q}, i\omega) >$$

$$\sim 2 \int_{-A}^A dE_1 \int_{E_1}^A dE_2 \int d^3 r \frac{I(r)^2}{\Gamma(r)^2} (1 - \cos(\vec{q}.\vec{r})) F(E_1, E_2, r) \frac{2\Gamma(r)}{(i\omega)^2 - \Gamma(r)^2},$$

where $F(E_1, E_2, r)$ is the probability that a particle-hole pair with on-site energies $E_1$ and $E_2$ is found separated by distance $r$. For $E_1, E_2$ larger than the Coulomb gap energy $\Delta \sim (e^2/a_o)^{3/2}/A^{1/2}$, $F \sim g^2$ where $g = n/Aa_o^3$ is the density of states above the Coulomb gap, $n$ is the average number of electrons per site. For $E_1, E_2$ much smaller than $\Delta$, $F \sim \rho(E_1) \rho(E_2)$, where

$$\rho(E) = \frac{3n}{\pi e^6} E^2.$$ 

Notice that a two-site system behaves as a electric dipole and has only longitudinal response to external electric fields. Evaluating the integrals, we find for $I(r_o) \ll \omega \ll A$,

$$Im \chi_{CG}(q, \omega) \sim a_o \pi g^2 e^2 r_o (1 - \frac{\sin(qr_\omega)}{qr_\omega}), \quad (A4a)$$
where \( r_\omega = a_o \ln(\frac{2I_o}{\omega}) \), \( r_o = e^2/\Delta \). For \( \omega << I(r_o) \), we obtain

\[
Im \chi_{CG}(q, \omega) \sim \frac{3n^2 a_o}{10\pi e^2 r_\omega^3} \left( 1 - \frac{\sin(q r_\omega)}{q r_\omega} \right).
\]

(A4b)

The real part of the response function can be obtained using the Kramers-Kronig relation, we obtain for \( qr_o << 1 \),

\[
Re \chi_{CG}(q, 0) \sim \frac{n^2}{20\pi^2 e^2} q^2 \ln(qr_o),
\]

(A5a)

and for \( qr_o >> 1 \),

\[
Re \chi_{CG}(q, 0) \sim -\frac{g^2}{2} e^2 r_o^2 = -\frac{g^2}{2} r_o^3 \Delta.
\]

(A5b)

For \( I(r_o) > \omega \) and \( qr_\omega << 1 \), we obtain

\[
Re \chi_{CG}(q, \omega) \sim \frac{n^2}{20\pi^2 e^2} q^2 \ln(\frac{\omega}{2I_o})),
\]

(A6a)

and for \( \omega > I(r_o) \),

\[
Re \chi_{CG}(q, \omega) \sim -\frac{g^2 e^2}{24} q^2 r_\omega^4.
\]

(A6b)

At finite temperatures \( T < \Delta \), eq. (A4b) for \( Im \chi_{CG}(0, \omega) \) is cutoff at a low frequency \( \omega_T \sim e^{-(T_o/T)^{1/4}} \) by the thermal mechanism of Mott-variable range hopping \([8]\) (in the presence of Coulomb gap) where \( T_o \sim e^2/a_o \). Correspondingly, at temperature \( \omega_T < I(r_o) \), \( Re \chi_{CG}(q, 0) \) is replaced by \([8]\)

\[
Re \chi_{CG}(q, 0) \sim \frac{n^2}{20\pi^2 e^2} q^2 \ln(\frac{a_o}{r_\omega_T}) \sim \frac{n^2}{40\pi^2 e^2} q^2 \ln(\frac{T}{T_o}),
\]

(A7)

at \( \omega < \omega_T \), \((q = 0)\) and at \( qr_o < r_o/r_\omega_T \), \((\omega = 0)\). At temperature \( \omega_T > I(r_o) \), a corresponding analysis gives

\[
Re \chi_{CG}(0, 0) \sim -\frac{g^2 e^2}{24} q^2 r_\omega^4 \sim -\frac{g^2 e^2 a_o^4}{24} q^2 (\frac{T_o}{T})^2,
\]

(A8)

for the same low frequency range and at small wavevector range \( qr_o < (r_o/r_\omega_T)^2 \).

At still higher temperatures \( k_B T >> \Delta \) where the Coulomb gap becomes unimportant and phonon-assisted hopping becomes dominant, we enter another regime where \( \chi_{CG} \) become different again \([8]\). At frequencies \( qr_\omega << 1 \) and \( \omega > \omega_T \), where \( \omega_T \sim \omega_p e^{-(A/k_B T)^{1/4}} \), where \( \omega_p \) is a characteristic phonon frequency, we obtain

\[
Re \chi_{CG}(q, \omega) \sim \frac{\pi^3 g^2 k_B T}{1440} q^2 r_\omega^5,
\]

(A9)

and for \( \omega = 0 \),
\[ \text{Re}\chi_{CG}(q, 0) \sim -\frac{\pi^3 g^2}{144} a_o^3(k_B T). \] (A10)

For frequencies \( \omega < \bar{\omega}_T \) and for wavevectors \( qa_o << (a_o/r_T)^\frac{5}{2} \), where \( r_T \sim (\frac{A}{k_B T})^\frac{1}{4}\) is the characteristic thermal hopping distance, \( \text{Re}\chi_{CG} \) saturates at a value \[ \text{Re}\chi_{CG}(q, 0) \sim -\frac{\pi^3 g^2 k_B T}{1440} q^2 a_o^5(k_B T)^\frac{5}{2}. \] (A11)

Notice that the Mott variable range hopping introduce characteristic cutoff length scales \( r_{\omega_T} \) and \( r_T \) at different temperature regimes. As a result the dielectric constant \( \epsilon(q \to 0, 0) = 1 - \nu(q)\chi_{CG}(q \to 0, 0) \) becomes finite but large at low temperatures although the temperature dependence of its value goes through several different regimes \[ \text{[8].} \]
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