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Fluctuations and criticality in quantum paraelectrics

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Abstract
The temperature dependence of the static dielectric susceptibility of a system with strongly coupled fluctuating dipoles is calculated within a self-consistent mean fluctuation field approximation. Results are qualitatively in good agreement with a quantum paraelectric $SrTiO_3$ in the low temperature regime. We identify this system as a *gapped quantum paraelectric* and suggest a possible experimental realization of a *quantum critical paraelectric* through the application of hydrostatic pressure or doping by impurity.

1. Introduction and summary

Phase transitions in displacive systems cannot be described by an Ising type Hamiltonian, which is usually invoked for a system going through an order–disorder transition. The behavior of these systems is essentially governed by collective oscillations of coupled dipoles and the phase transition is described by a softening of the corresponding optical mode due to thermal fluctuation [1, 2]. There are materials like $SrTiO_3$ and $KTaO_3$ which are supposed to show a displacive transition similar to that which occurs in $BaTiO_3$, but fail to do so. In fact, there is a softening of optical phonon modes in these materials also, but that does not lead to a transition even at very low temperature [3, 4]. Instead, there is a strong enhancement of the low temperature dielectric constant. For example, in $SrTiO_3$ the static dielectric susceptibility has a very high saturated value ($\mathcal{O}(10^4)$) at low temperature ($\sim$10 K) followed by a Curie regime (10–100 K) and a long tail thereafter. It seems that the classical soft mode concept is insufficient to describe various aspects of low temperature behavior. An explanation of the unusual behavior of dielectric susceptibility and the stability in the low temperature paraelectric phase has been a long-standing puzzle. Long ago Barrett [5] gave a semi-phenomenological theory, which essentially recasts the Curie–Weiss formula with a replacement of temperature T there by average energy; thereby the inverse of dielectric susceptibility could be written as $\chi^{-1} \propto T_1 \coth(T_1/T) - T_c$, where T_c is a classically calculated critical temperature and T_1 is a quantum scale $\mathcal{O}(\hbar/\text{mass})$. This theory, in the high temperature limit, reproduces the Curie–Weiss law. To match experimental data in $SrTiO_3$ Barrett's formula has been found inadequate as one single constant quantum scale T_1 cannot trace the full curve. The formula has since been modified in various ways, for example, by introducing an extra exponent [6], that is, by writing χ^{-1} as $(T_1 \coth(T_1/T) - T_c)^{-\nu}$, and by making T_1 temperature-dependent with an extra scale [7], to take care of various 'anomalies', for example the one near 40 K. There has been a proposal to attribute this extra energy scale to the structural transition which occurs at 110 K [8]. These proposals either follow an order parameter expansion similar to the Landau expansion or some modifications thereof, hence they do not introduce any new microscopic description. In $SrTiO_3$ and $KTaO_3$ there is no ordering, therefore in the low temperature regime where the dielectric constant is enhanced, the physics is dominated by fluctuations of relevant microscopic degrees of freedom rather than their averages. In this paper we analyze the fluctuation in such systems within a self-consistent mean fluctuation field approximation. There are mainly two parameters, namely the anharmonicity parameter and the effective stiffness. The zero-point or quantum fluctuation will be dominant when the stiffness is small. The qualitative behavior of susceptibility is reproduced as well as a new insight gained into the quantum critical behavior of such systems. A mismatch in theory and experimental curves for the dielectric constant at high temperature can be attributed to the effect of a structural transition which occurs at higher temperature (i.e. at 110 K in $SrTiO_3$). Such a discrepancy is irrelevant for the following discussion which refers mainly to the low temperature regime.

2. Mean-field analysis

The low temperature physics of $SrTiO_3$ is dominated by fluctuations of Ti ions [9]. The Hamiltonian for such ions is

modeled in terms of local quartic oscillators coupled with a nearest-neighbor harmonic interaction [10]:

$$H = \sum_l \left\{ \frac{p_l^2}{2} + \frac{1}{2}\omega_0^2 u_l^2 + \frac{1}{4}\lambda u_l^4 \right\} - \frac{1}{2}\sum_{ll'} v u_l u_{l'}. \quad (1)$$

The constants λ and v are assumed to be positive and mass taken as unity. This Hamiltonian describes two local minima with a nearest-neighbor coupling v. For $|v| \ll |\omega_0^2|$ and $\omega_0^2 \ll 0$, it mimics a two-state Ising system with Gaussian fluctuations around one of the local minima. When $|v| \sim |\omega_0^2|$, there is a possibility of large tunneling between these minima. In this regime the system has to be described in terms of its collective behavior. Such a system is called a displacive system and the limit $|v| \to |\omega_0^2|$ is called the displacive limit. In momentum space

$$H = \sum_q \tfrac{1}{2}p_q^2 + \tfrac{1}{2}\sum_q (\omega_0^2 - v\delta\cos qa) u_q u_{-q} + \tfrac{1}{4}\lambda \times \sum_{q_1,q_2,q_3} u_{q_1} u_{q_2} u_{q_3} u_{-q_1-q_2-q_3}. \quad (2)$$

Here δ is the coordination number and a is the lattice spacing. Now with $p_q = \dot{u_q} = -\imath\omega u_q$ in the kinetic energy term, finally the Hamiltonian within the quasi-harmonic approximation, i.e.

$$\sum_l u_l^4 \approx 6N(\sigma + \langle u\rangle^2) \sum_{q_1} u_{q_1} u_{-q_1} \quad (3)$$

where

$$\sigma = \sum_q \langle T u_q(0) u_{-q}(0^+)\rangle \quad (4)$$

is given by

$$H = \tfrac{1}{2}\sum_q (\omega_q^2 - \omega^2) u_q u_{-q} \quad (5)$$

where

$$\omega_q^2 = \omega_0^2 - v\delta\cos qa + 3\lambda\sigma \simeq \omega_0^2 - v + v\delta a^2 q^2 + 3\lambda\sigma \quad (6)$$

is the renormalized frequency for small q (such a truncation is quite justified for low temperature properties of a near-critical system). We are interested in the paraelectric phase of the system, that is, where $\langle u\rangle = 0$. Since the system is at low temperature and the dielectric constant has an enhanced value, $\langle u^2\rangle$ need not vanish, however. The purpose of the present work is to present a self-consistent calculation of $\langle u^2\rangle$ in the classical as well as in the quantum regime. The susceptibility, which is related to $\langle u^2\rangle$, is essentially the phonon propagator:

$$\chi(q,n) = -\frac{1}{(\imath\omega_n)^2 - \omega_q^2}, \qquad \omega_n = 2n\pi T. \quad (7)$$

With ω_q given by equation (6) we have a self-consistent equation:

$$\sigma = \sum_q \langle T u_q(0) u_{-q}(0^+)\rangle = \frac{1}{\beta}\sum_{q,n} \chi_{qn} \mathrm{e}^{\imath\omega_m 0^+} = \frac{1}{\beta}\sum_{q,n} \frac{1}{\omega_n^2 + \omega_q^2} = \sum_q \frac{1}{2\omega_q}\coth\left(\frac{\omega_q}{2T}\right). \quad (8)$$

The solution of this equation will give $\sigma(T)$ which in its asymptotic forms reduces to

$$\sigma = \sum_q \frac{T}{\omega_q^2} \sim \int \mathrm{d}q\, q^2 \frac{T}{\omega_0^2 - v + v\delta q^2 + 3\lambda\sigma} \quad \text{(Classical)} \quad (9)$$

$$= \sum_q \frac{1}{\omega_q} \sim \int \mathrm{d}q\, q^2 \frac{1}{\sqrt{\omega_0^2 - v + v\delta q^2 + 3\lambda\sigma}} \quad \text{(Quantum)}. \quad (10)$$

To go into details of the temperature dependence of susceptibility, we need to define some physically interesting dimensionless parameters as $\Delta = -(\omega_0^2 - v)/\omega_0^2$, $\sigma_c = -(\omega_0^2 - v)/3\lambda$ and $\eta = \hbar/(2\omega_0\sigma_c)$ ($\hbar$ is taken as unity in this paper), so that $\Delta \sim \sigma_c \sim \eta^{-1}$. The parameter Δ describes the effective stiffness for collective modes at the harmonic level. The strength of coupling between various modes near $q = 0$ is determined by σ_c^{-1} while the parameter η tells us about the vicinity to the quantum limit in the system. Introducing normalized temperature $x = T/m\omega_0^2\sigma_c$ and using the previously defined parameters, we rearrange equation (6) as follows:

$$\frac{\omega_q^2}{\omega_0^2} = \frac{v\delta a^2 q^2}{m\omega_0^2} + \Delta\left(\frac{\sigma}{\sigma_c} - 1\right) \quad (11)$$

and

$$\frac{\sigma}{\sigma_c} = \sum_q \frac{\eta\omega_0}{\omega_q}\coth\left(\frac{\eta\omega_q}{\omega_0 x}\right). \quad (12)$$

A self-consistent solution of these equations will give

$$\chi(0,0)^{-1} \propto \Delta\left(\frac{\sigma}{\sigma_c} - 1\right). \quad (13)$$

For large enough Δ the system shows classical behavior, that is, $\sigma \sim T$ from equation (9). The mode coupling would give corrections higher order in temperature and T_c would be proportional to Δ. On the other hand, as Δ become smaller and η becomes larger the system moves towards the quantum domain. When Δ or T_c becomes identically zero we have a quantum critical point. At this point the zero temperature static long wavelength susceptibility also diverges. Interestingly the $\Delta = 0$ or $\omega_0^2 = v$ limit is the *displacive limit*, well known in the structural transition literature. A non-self-consistent estimate, with a temperature-dependent momentum cutoff ($q_{\max} \sim T$), tells us that σ starts from a constant value in the low temperature side and then follows a T^2 behavior in the high temperature (up to Debye temperature) side. Such a non-self-consistent estimate gives quite correct results when the system is far away from the quantum critical point, i.e. $|(\omega_0^2 - v)/3\lambda\sigma| \ll 1$. At the quantum critical point, an estimation of the self-consistent correction is also $\sim T^2$. The Barret formula cannot reproduce this result. That formula is essentially the outcome of quantum fluctuations in a single-mode theory, which would fail near the quantum critical point as many modes and their coupling would dominate the behavior of the system there. This necessitates a self-consistent calculation for quantum paraelectrics near their quantum critical point. From figure 1, we learn that the high value of the static dielectric susceptibility of $SrTiO_3$

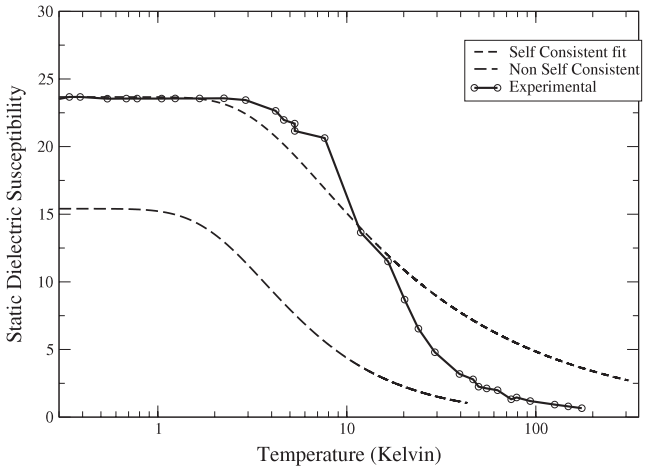

Figure 1. Numerical solution shows saturation in static susceptibility (in units of 10^4) versus temperature curve. This curve is in good agreement with Muller's experiment on the low temperature side, with $\frac{\upsilon\delta a^2}{\omega_0^2} = 1$, $\Delta = 0.003$, $\eta = 1/\Delta$, $q_{\max} = 0.1$ and at the end χ and T are rescaled with $0.4/\Delta$ and 30Δ, respectively. The lower curve is the non-self-consistent fit with the same parameters as the upper one but with rescaling of χ and T by 9.5 and 100, respectively.

is attributed to the smallness of the parameter $\Delta(=0.003)$. This motivates us to treat this system to be near the quantum critical point. The static dielectric susceptibility data of $SrTiO_3$ remind us of the behavior of itinerant fermionic systems near the quantum phase transition point and the fluctuation regime around that. There the (staggered) magnetic susceptibility diverges for the (anti-)ferromagnetic transition as the coupling constant crosses a critical value [11]. The case of $SrTiO_3$ is similar to that of liquid helium-3 [12], where the magnetic susceptibility gets enhanced, as large as ten times, depending upon pressure, from its free fermionic value.

3. Quantum criticality and hydrostatic pressure at QCP

After the above identification we now focus on theoretical aspects of quantum criticality in ferroelectric systems. At zero temperature the zero-mode fluctuation is the most dominant. From equation (12) it is clear that the zero-temperature fluctuation σ_s is given by

$$\sigma_s/\sigma_c = \eta\frac{\omega_0}{\omega_q} = \frac{\eta}{\sqrt{\Delta(\sigma_s/\sigma_c - 1)}}. \qquad (14)$$

Writing σ_s/σ_c as y we get

$$y^3 - y^2 - a = 0, \qquad a = \frac{\eta^2}{\Delta}. \qquad (15)$$

This tells us if $a = 0$ then $\sigma_s = 0$ is a solution, which is the classical limit. For $a \neq 0$ all solutions become non-zero and since $y^3 - y^2 = a \geqslant 0$ that means $y \geqslant 1$. Thus $\sigma_s \geqslant \sigma_0$; moreover the σ_s increases as a increases. The meaning of quantum criticality, in terms of y, is $y \to 1$. In that limit the zero-temperature properties will show a scaling behavior

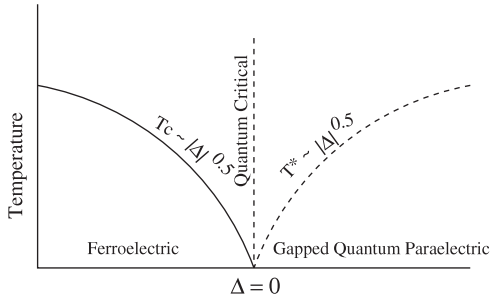

Figure 2. Schematic phase diagram of a typical quantum paraelectric system.

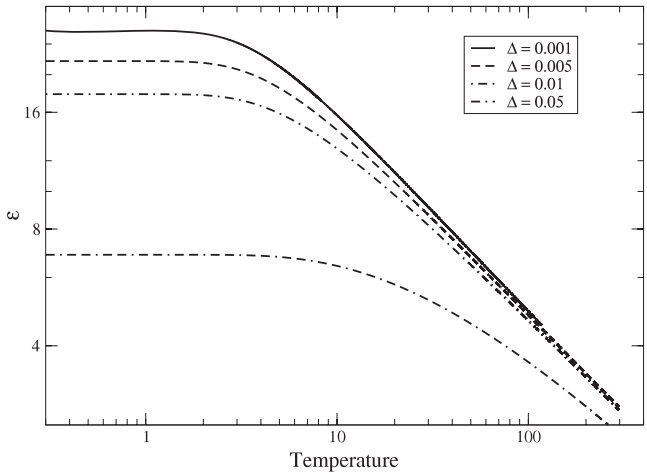

Figure 3. Temperature variation of susceptibility at different values of Δ and the log–log plot of the same.

with (the inverse of correlation length) $\chi^{-1} \sim \Delta(y-1) \sim \eta^2 \sim (1 - \upsilon/\omega_0^2)^2$. If we define a *quantum scale* $\xi_Q = (1 - \upsilon/\omega_0^2)^{-\frac{1}{2}}$, then $\chi \sim \xi_Q^{-4}$. The point $y = 1$ is essentially the point where effective stiffness (Δ) changes sign. In the regime $\Delta \geqslant 0$ self-consistency in fluctuation breaks down, the system seeks ordering and hence an expansion about the non-zero $\langle u \rangle$ is required. In this case the transition temperature $T_c \sim \Delta^{\frac{1}{2}}$. On the other hand, in the $\Delta \leqslant 0$ regime the system cannot have any ordering and its behavior has to described by self-consistent fluctuations. There is a characteristic temperature (crossover temperature in modern parlance [13]) $T^* \sim \Delta^{\frac{1}{2}}$ which demarcates the boundary between the low temperature *gapped quantum paraelectric* behavior and the classical behavior (figure 2). In the case of $SrTiO_3$, the plateau in the susceptibility versus temperature curve is the signature of gapped quantum paraelectric behavior. There is no transition in this system. But there is a crossover from low temperature quantum to high temperature classical behavior at the crossover temperature T^* (~10 K). This is exactly the temperature where the plateau ends and the susceptibility curve starts following a Curie behavior (figures 1 and 3). One can now hope to reach $\Delta = 0$ through tuning some parameters like pressure, impurity, etc. The width of this plateau regime vanishes at this point and the system becomes *quantum critical*. At this point thermodynamics will be described by power laws in temperature (e.g. $\chi(0,0)^{-1} \sim T^{-2}$) and the system will show

some non-trivial dynamics. The latter is beyond the scope of the present work. It is quite evident here that the controlling factor $v/m\omega_0^2$ strongly depends upon structural aspects and hence this quantumness in $SrTiO_3$ can be properly understood through some intrinsic mechanism which gives rise to such large tunneling.

A good possibility for exploring the physics near such a quantum critical point is through application of hydrostatic pressure. Such a technique has already been used in the case of ferroelectrics and quantum paraelectrics for some time [14] and more recently [15] in different contexts. We found that those experimental results can be discussed more interestingly as is done in the context recently of an itinerant magnetic system [16]. Application of hydrostatic pressure will couple to the optical mode via its coupling to the acoustic mode. In this case the starting Hamiltonian takes the form

$$H = \frac{1}{2}\int \mathrm{d}q[p_q^2 + (\omega_0^2 - v\delta\cos qa)u_q u_{-q}] + \frac{\lambda}{4} \times \int \Pi_{i=1}^4 (\mathrm{d}q_i\, u_{q_i})\delta\left(\sum_i q_i\right) + g\int \mathrm{d}k\,\mathrm{d}q\,\epsilon(k)\,u_q u_{k-q} + \frac{K}{2}\int \mathrm{d}q\,\epsilon^2(q) - p\epsilon(0). \tag{16}$$

Here the last three terms are the results of applications of pressure, in the lowest possible order. The parameter g couples strain fields to unit cell displacement related to the optical mode, K is the force constant for harmonic acoustic phonons and the last term shows the coupling of the hydrostatic pressure p to the static strain with some unit strength. Now if the pressure is strong enough ϵ has a minima at $\epsilon = \epsilon(0)$ and is given by

$$\epsilon(0) = p/K. \tag{17}$$

Integrating out the strain field, we get an effective Hamiltonian:

$$H = \int \mathrm{d}q\left[\tfrac{1}{2}p_q^2 + \tfrac{1}{2}(\omega_0^2 + gp - v\delta\cos qa)u_q u_{-q}\right] + \tfrac{1}{4}\lambda_\mathrm{R}\int \Pi_i \mathrm{d}q_i\, u_{q_1}u_{q_2}u_{q_3}u_{-q_1-q_2-q_3} \tag{18}$$

with a renormalized coupling constant of quartic term

$$\lambda_\mathrm{R} = \left(\lambda - \frac{2g^2}{K}\right). \tag{19}$$

Again we write a self-consistent equation for paraelectric fluctuations as

$$\sigma = \int \mathrm{d}^d q \frac{1}{\omega_q}\coth\left(\frac{\omega_q}{T}\right) \tag{20}$$

where

$$\omega^2(q) = 3\Delta\lambda(1 + p/p_0) + v\delta q^2 a^2/2 + 3\lambda_\mathrm{R}\sigma \quad \text{and} \quad p_0 = \frac{3K\Delta\lambda}{g}. \tag{21}$$

Up to this point the result is just a renormalization of the factor Δ as $\Delta(1 + p/p_0)$ and it becomes an experimentally controllable parameter. Also the behavior of susceptibility at different values of Δ is shown in the figure. In this proposal we assume the positivity of λ_R. Otherwise the transition will be first order and the scaling behavior will not be valid. In real life one can try to induce the effect of negative pressure required in these systems to achieve QCP through some homogeneous effects of non-polar impurity. But in either case the nature of the transition can be modified because of strain coupling or disorder, respectively. Analysis of such a transition in these materials will be discussed in an upcoming paper [17].

4. Discussion

We have shown that a mean fluctuation field theory within a quasi-harmonic approximation reproduces the low temperature behavior of susceptibility of a quantum paraelectric quite well. The short range model studied here is justified since only transverse optical modes are involved in the ferroelectric fluctuations. In the presence of a long range force the longitudinal mode becomes stiff and only transverse modes can get soft. The presence of long range dipolar forces can induce a certain amount of anisotropy in the transverse modes, which can certainly change the critical behavior, however, only with a fairly large value of dipolar contribution to anisotropy in the quadratic term [18]. We are not aware of first-principles results for anisotropy parameters in the case of $SrTiO_3$ or $KTaO_3$. However, first-principles calculations support our choice of parameter for the effective stiffness. Compared to $BaTiO_3$ it is about 20 times smaller (table V in [19]) for $SrTiO_3$, which makes it more near the quantum domain. On the other hand, the lattice-induced anisotropy in the quartic term is of the same order of magnitude and it would not play a key role in distinguishing the low temperature behavior in these systems. We leave discussions on anisotropy dependence for future work and stick to the isotropic short range model. It is also clear that there is no need to introduce an 'anomalous' regime as proposed earlier. That proposal might be due to the insistence on comparing experimental results with Barrett's formula and its extensions. The experimental behavior is well accounted for in the quantum region and at high temperature the susceptibility smoothly crosses over to the classical behavior. Here we have focused more on the physics of low temperature behavior than the exact calculation of various properties. Thus the structural aspects and anisotropy effects are not attempted here.

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