

PHONON ANOMALIES IN HIGH TEMPERATURE
SUPERCONDUCTORS

A THESIS
SUBMITTED TO THE DEPARTMENT OF PHYSICS
AND THE INSTITUTE OF ENGINEERING AND SCIENCE
OF SIKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

By
E. Hakan Türeci
August 1996

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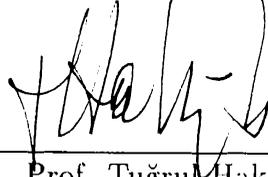
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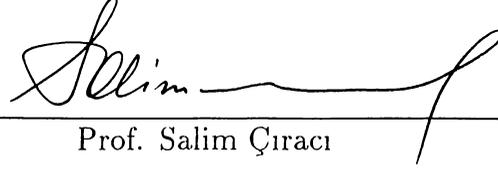
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Abstract

PHONON ANOMALIES IN HIGH TEMPERATURE SUPERCONDUCTORS

E. Hakan Türeci

M. S. in Physics

Supervisor: Assist. Prof. Tuğrul Hakioglu

August 1996

Anomalously large low temperature phonon anharmonicities can lead to static as well as dynamical changes in the low temperature properties of the vibrational system. In this work, we focus our attention on the low temperature lattice anharmonicity and its effect on the electron-phonon ground state. We are, in particular, motivated by certain high temperature superconductors. The third and fourth order anharmonic coupling constants for YBCO, LBCO and several other superconducting compounds are extracted from their measured elastic constants using the anharmonic elastic continuum model. The coupling constants are then used to extract the average anharmonic potential energy for the transverse and longitudinal modes in the Cu-O planes. We find that, anharmonic contribution to the lattice potential relative to the harmonic one is unusually high for all examined high T_c compounds.

The presence of anharmonic phonons elicits non-perturbative dynamical effects in the ground state of the electron-phonon system. Phonon correlations induced by anharmonic effects enhance the electron-phonon interaction which then create a self-consistent mechanism to act back on the ground state of

the electron-phonon system. In result, strong momentum correlations are created and the ground state comprises fluctuating polarons. The zero point fluctuations and other ground state properties are obtained by self-consistent numerical calculations. The influence of low temperature phonon anharmonicity on the superconducting properties in the intermediate coupling range is also investigated. It is shown that, the otherwise bare electron-phonon coupling is strengthened in the presence of correlated polarons and the zero point fluctuations are enhanced. Within this frame, it is plausible to achieve superconducting transition temperatures as high as %20 of the characteristic vibrational energy scale. The non-perturbative, self-consistent formalism thus introduced also offers an account for the recently observed temperature anomalies near T_c in the Debye-Waller factor and dynamical pair correlations of certain high temperature superconductors.

Keywords:

Phonon anharmonicity, electron-phonon interaction, Fröhlich Hamiltonian, squeezed states, polarons, high temperature superconductors, elastic continuum theory.

Özet

YÜKSEK SICAKLIK SÜPERİLETKENLERİNDE FONON ANORMALLIKLARI

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Fizik Yüksek Lisans

Tez Yöneticisi: Yard. Doç. Dr. Tuğrul Hakioglu

Ağustos 1996

Düşük sıcaklıklardaki anormal fonon anharmonikliklerinin, fonon sisteminin düşük sıcaklık özelliklerinde statik olabildiği gibi dinamik değişimlere neden olabileceği bilinmektedir. Bu çalışmada, düşük sıcaklık fonon anharmonikliği ve bunun elektron-fonon taban seviyesine olan katkısı incelendi. Bizi bu konuda motive eden etkenlerden biri, bazı yüksek sıcaklık süperiletkenlerinin gösterdiği özelliklerdir. Bu doğrultuda, YBCO, LBCO ve diğer birtakım süperiletken bileşiklerin üçüncü ve dördüncü derece anharmonik sabitleri hesaplandı. Ardından, bu sabitler kullanılarak $Cu - O$ düzlemlerinde hareket eden boylamsal ve enlemsel fonon modlarının ortalama anharmonik potansiyel enerjileri hesaplandı. İncelenen bütün yüksek sıcaklık süperiletken bileşiklerde, potansiyel enerjiye olan anharmonik katkının, harmonik enerjiye nazaran oldukça yüksek olduğu gözlemlendi.

Anharmonik fononların varlığı, elektron-fonon sisteminde pertürbatif olmayan etkiler yaratabilir. Anharmonik etkilerin sebep olduğu fonon korelasyonları, elektron-fonon etkileşimini güçlendirdiği gibi, ayrıca kendinden tutarlı bir şekilde elektron-fonon sisteminin taban seviyesine de geri-etki yaratır. Sonuçta, sistemde

güçlü momentum korelasyonları oluşur ve taban seviyesi titreşen polaronları ihtiva eder. Bu doğrultuda, sıfır noktası titreşimleri ve diğer bazı taban seviyesi özellikleri kendinden-tutarlı nümerik metodlarla hesaplandı. Ayrıca, düşük sıcaklık fonon anharmonikliğinin, süperiletken parametreler üzerine olan etkisi de gösterildi. Çıplak elektron-fonon etkileşim sabitinin, korele polaronların varlığında güçlendiği gözlemlendi. Bu çerçevedeki bulgularımız, karakteristik titreşim enerjisinin % 20'sine varan süperiletkenliğe geçiş sıcaklıklarının (T_c) elde edilebileceğini ortaya koymaktadır. Çalışmada kullanılan pertürbatif olmayan, kendinden tutarlı yapı, bazı süperiletken bileşiklerin Debye-Waller faktörlerinde ve dinamik çift korelasyonlarında, T_c civarında gözlenen anormallikleri de açıklamayı mümkün kılmakta.

Anahtar

sözcükler: fonon anharmonikliği, elektron-fonon etkileşimi, fröhlich hamiltonian, sıkıştırılmış fononlar, polaron, yüksek sıcaklık süperiletkenliği, elastik teori

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"nanamuşi mundi içinami?.."

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Chapter 1

INTRODUCTION

After more than ten years of intense study, since the discovery of high temperature superconductivity of the layered copper-oxide compounds by Bednorz and Müller,¹ there is no clear evidence which mechanism(s) is(are) responsible for pairing leading to high superconducting transition temperature T_c . Many different theoretical explanations have been proposed, but by now none of these could be either proved or rejected on firm grounds.

Among these proposals, conventional electron-phonon mechanism is still under discussion. Although experiments^{2,3} show that the isotope effect on T_c is small and the results of Weber⁴ and, Weber and Mattheiss⁵ from band structure calculations indicate that T_c much above 40K is unlikely to be explained by a pure electron-phonon mechanism, recent experiments have proven that for the oxide superconductors, electronic and lattice degrees of freedom are strongly coupled at least in some portions of the phase space.⁶ This is reflected in the strong low temperature anomalies of certain vibrational modes⁷⁻¹² which are commonly observed in most high temperature superconductors(HTS).

An essential part of the contribution to the evidence comes from neutron scattering and optical (Raman,infrared) experiments yielding information about the static as well as dynamic state of the crystal lattice. Phonon spectrum was of significance in developing the microscopic theory of pairing in conventional superconductors.¹³ Therefore, much attention has been paid to the investigation

of phonon spectrum in HTS, aimed at finding a certain phonon contribution to the formation of the Cooper pair condensate.

The methodology as applied to phonon spectra rests on the fact that electron-phonon interaction leads to the renormalization of ionic frequencies $\omega_{\mathbf{q}s}$ (\mathbf{q} is a wavevector, s is a polarization index) according to the following relation

$$\Omega_{\mathbf{q}s}^2 = \omega_{\mathbf{q}s}^2 + 2\omega_{\mathbf{q}s} \text{Re}\Sigma_{\mathbf{q}s}(\Omega = \Omega_{\mathbf{q}s}). \quad (1.1)$$

Here $\Omega_{\mathbf{q}s}$ is a renormalized phonon frequency, $\Sigma_{\mathbf{q}s}$ is the phonon polarization. Including second order effects in electron-phonon interaction, the latter may be written as

$$\Sigma_{\mathbf{q}s}(\omega) = \sum_{\mathbf{p}, m, n} |g_s(\mathbf{p}, m; \mathbf{p} + \mathbf{q}, n)|^2 \frac{f_m(\mathbf{p}) - f_n(\mathbf{p} + \mathbf{q})}{\epsilon_m(\mathbf{p}) - \epsilon_n(\mathbf{p} + \mathbf{q}) + \omega} \quad (1.2)$$

where $g_s(\mathbf{p}, m; \mathbf{p}', n)$ is the electron-phonon interaction matrix element on the Fermi surface between single electrons, $f_m(\mathbf{p})$ is the Fermi distribution function for electrons with energy $\epsilon_m(\mathbf{p})$ and wave number \mathbf{p} , and, m is the band index. The real part of the polarization (1.2) determines a frequency renormalization of the new quasi-particles

$$\delta\omega_{\mathbf{q}s} = \Omega_{\mathbf{q}s} - \omega_{\mathbf{q}s} = \text{Re}\Sigma_{\mathbf{q}s}(\Omega_{\mathbf{q}s}) < 0, \quad (1.3)$$

and its imaginary part gives rise to finite lifetime $1/\gamma_{\mathbf{q}s}$ as

$$\gamma_{\mathbf{q}s} = -\text{Im}\Sigma_{\mathbf{q}s}(\Omega_{\mathbf{q}s} + i\delta). \quad (1.4)$$

The latter is directly related to the Eliashberg function

$$\alpha^2 F(\omega) = \frac{1}{\pi\hbar N(0)} \sum_{\mathbf{q}} \frac{\gamma_{\mathbf{q}s}}{\Omega_{\mathbf{q}s}} \delta(\omega - \Omega_{\mathbf{q}s}), \quad (1.5)$$

where $N(0)$ is the density of electronic states on the Fermi surface. This relation allows one to compute the dimensionless coupling constant λ

$$\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega} = \frac{2}{\pi\hbar N(0)} \sum_{\mathbf{q}s} \frac{\gamma_{\mathbf{q}s}}{\Omega_{\mathbf{q}s}^2}, \quad (1.6)$$

in the conventional perturbative approach.

The phonon density of states (PDOS) $F(\omega)$ is usually extracted from the inelastic neutron scattering data. Phonon frequency shift $\delta\omega_{\mathbf{q}_s}$ can be obtained efficiently from the resonance Raman scattering experiments. Thus an estimate for electron-phonon coupling can in principle be obtained which works at best for materials with simple structures and symmetries.

After synthesizing sufficiently large single crystals, it became possible to measure the phonon dispersion curves throughout the Brillouin zone for typical HTS crystals such as $NdCuO_4$, La_2CuO_4 and $YBa_2Cu_3O_{7-x}$.^{14,15}

Early investigations of the inelastic neutron scattering data on $YBa_2Cu_3O_{7-x}$ revealed strong changes in the phonon spectrum in transition from insulating to metallic state as the oxygen concentration was varied from non-superconducting $x = 1$ limit to superconducting fully doped $x = 0$ limit.¹⁶⁻¹⁸

The locations where strong changes in PDOS are observed can be separated into three distinct regions ($\hbar\omega \leq 15$ meV, $\hbar\omega \sim 20$ meV, $\hbar\omega \geq 35$ meV). Model calculations for the lattice dynamics of this material¹⁶ show that in the low energy regime (≤ 15 meV) the essential part of PDOS is due to $Cu1$ modes. In the process of continuous doping with oxygen from $x = 1$ to the superconducting $x = 0$ limit, a filling of $O1$ positions along the chains occurs, which changes the number of bonds for $Cu1 - O1$ and $O1 - O4$ atoms. This structural changes can account properly for the differences in the low temperature part of PDOS. However, the increase in PDOS in the high energy (≥ 35 meV) regime, which from model calculations is found to correspond mainly to $Cu2 - O2, O3$ bond bending vibrations in the planes, cannot be explained by structural changes alone. Investigations of $F(\omega)$ at a continuous adding of oxygen from $x = 1$ to $x = 0$ have made the authors¹⁶ thus to conclude that in this frequency range, for the vibration modes related to stretching and bending of bonds $Cu2 - O2, O3$ in the planes, the effects of strong electron-phonon interaction display themselves: at an increase of the in-plane carrier density occurs an essential softening of the corresponding force-constants due to enhanced Coulomb screening.

Low temperature anomalies have been observed also for $La_{2-x}Sr_xCuO_4$ based

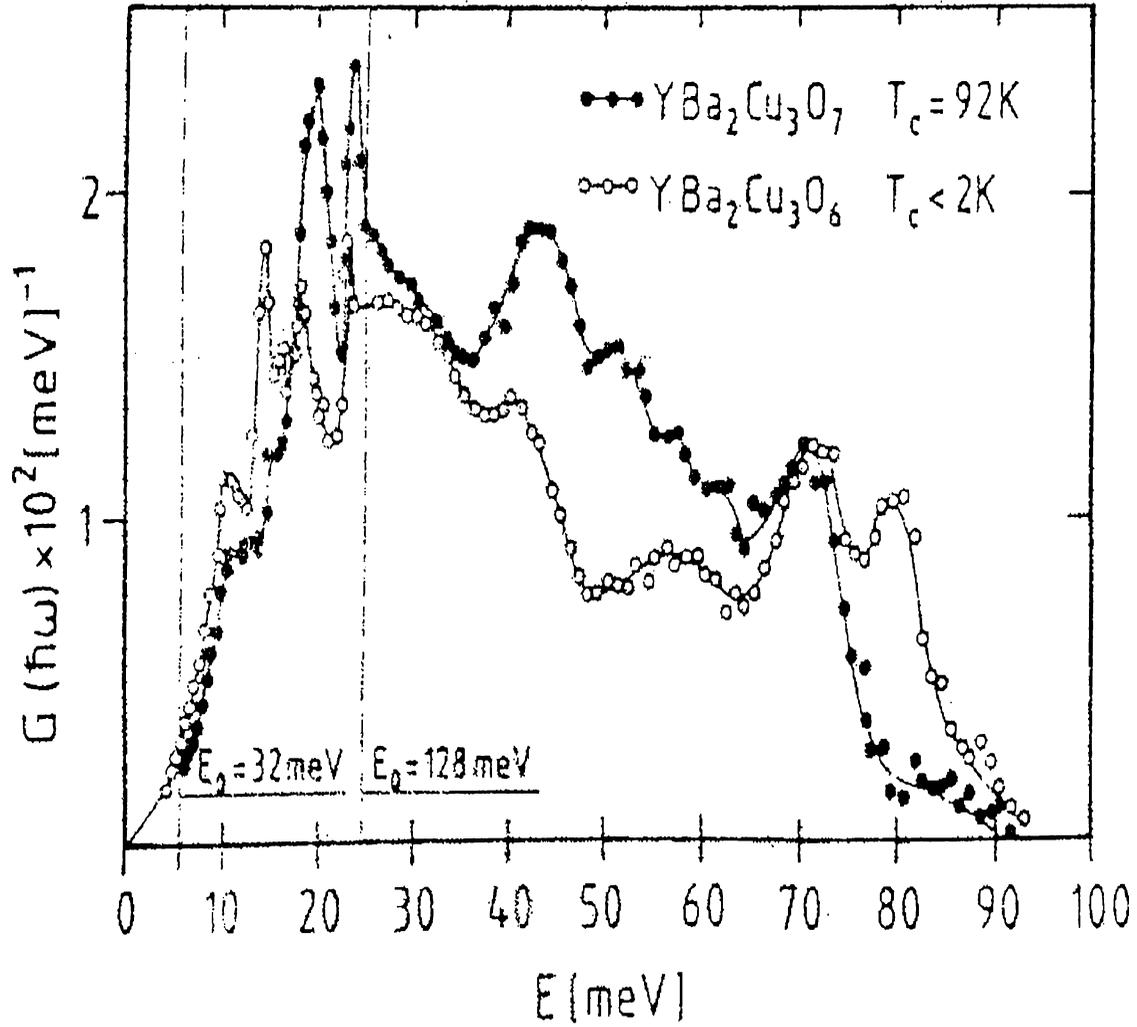


Figure 1.1: Neutron Scattering Results for YBCO
 Comparison of PDOS for $YBa_2Cu_3O_7$ ($T_c = 92K$, dots) and $YBa_2Cu_3O_6$ ($T_c < 2K$, circles). Measurements performed at 6 K with $E_0 = 32 meV$ and $128 meV$

compounds in the form of softening of the $Cu - O$ optical tilting mode along the (110) and $(\bar{1}10)$ crystallographic axes¹² as the crystal symmetry in the planes changes from high temperature tetragonal (HTT) to low temperature orthorhombic (LTO). Although doping by Ba, Sr, Ca can induce slight changes

in the phonon density of states,¹⁰ no evidence has been found in this compound between the onsets of superconducting and the structural phase transitions^{19,20} (SPT). The SPT resulting from the tilting of the $Cu-O$ octahedra in LSCO is now strongly believed to originate from the coupling of the z-polarized anharmonic longitudinal soft mode of the apical oxygen moving in a double well potential¹² to low energy acoustic vibrations in the planes.

Raman scattering and infrared absorption have played an important role in the assignment of certain modes in copper-oxide superconductors. Several Raman scattering studies have noted a rapid change of certain vibrational frequencies beginning at T_c and completing within 10 – 20K below; with YBCO being a prominent example displaying strong softening of the z-polarized planar $\omega = 333cm^{-1}$ mode (B_{1g}) and hardening of the $\omega = 437cm^{-1}$ mode (A_{1g}) up to few percent^{7,8} as the temperature is lowered below T_c .

It has been shown for the Raman active phonon at $333cm^{-1}$ that, the phonon softening in the superconducting state vanishes if superconductivity is destroyed by a magnetic field just below T_c at a constant temperature.²¹ This, together with the fact that four of the five Raman lines do not show any softening below T_c strongly suggests that the phonon softenings below T_c reflect directly the coupling between these particular phonons with electronic states which take part in the formation of Cooper pairs.

It was subsequently shown by Zeyher *et al.*²² remaining within the conventional strong electron-phonon coupling scheme (Eliashberg formalism) that, practically all the experimental data concerning phonon frequency shifts at the onset of superconductivity could be explained by using strong coupling theory with an average Eliashberg coupling $\lambda \sim 2.9$ corresponding to $2\Delta/kT_c \sim 5.2$. Nevertheless, electron-phonon interaction constant for the above optical modes obtained from ab initio calculations ($\lambda_o \leq 0.02$) is too small to explain the high T_c in YBCO compound and clearly in contradiction with Zeyher's results.

The motivation of this study actually derives from a further class of experiments on the dynamical structure factor as the temperature is varied across T_c . In those experiments by Arai *et al.*²³, a marked enhancement of the structure

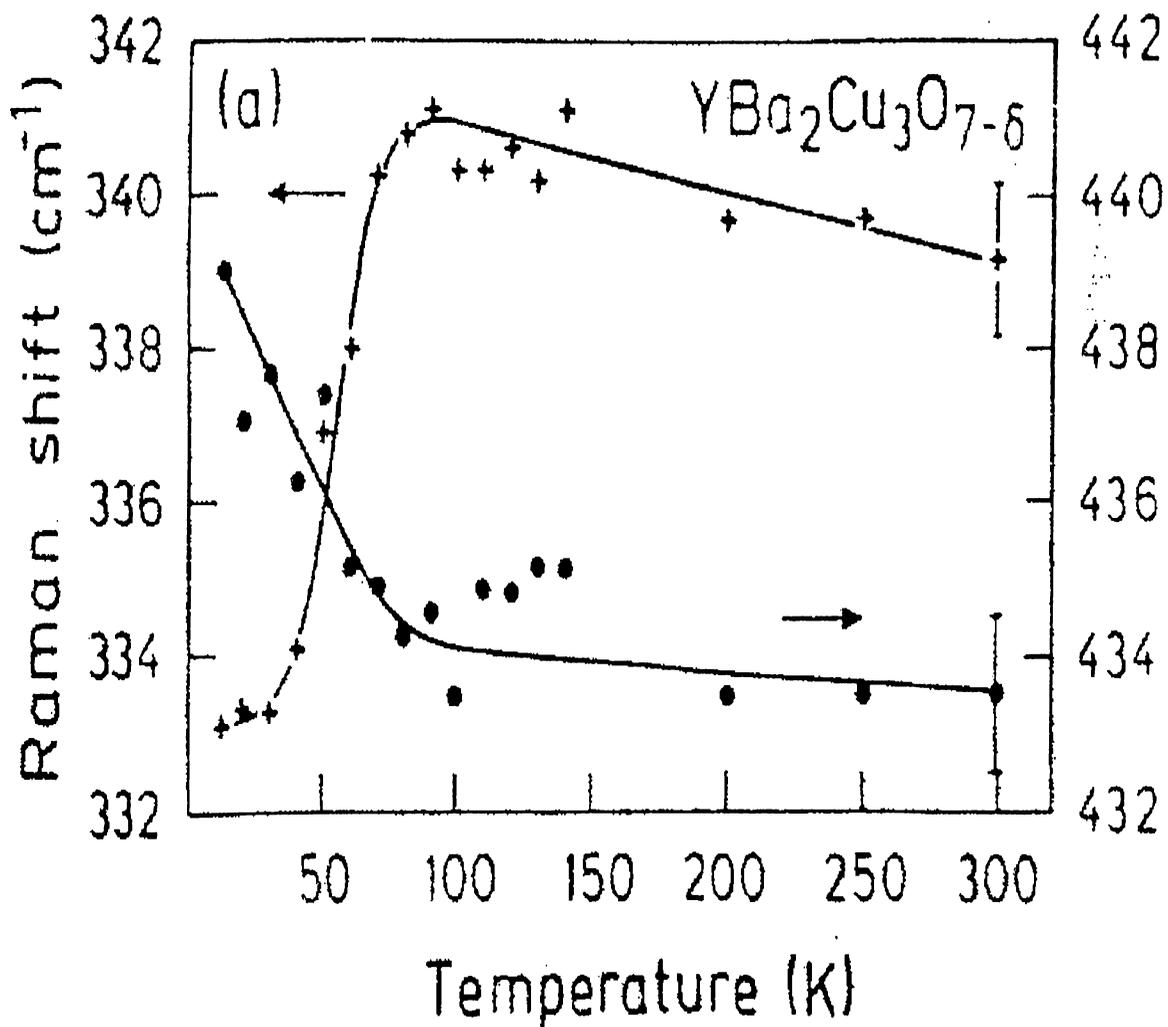


Figure 1.2: Results of Raman scattering experiments for YBCO. Anomalous phonon frequency shifts of the A_{1g} and B_{1g} phonon modes near $T_c = 90\text{K}$ in YBCO.

factor is observed as the temperature is varied across T_c at the Brillouin zone boundary.

We argue at this point that, anharmonicity and phonon softening which

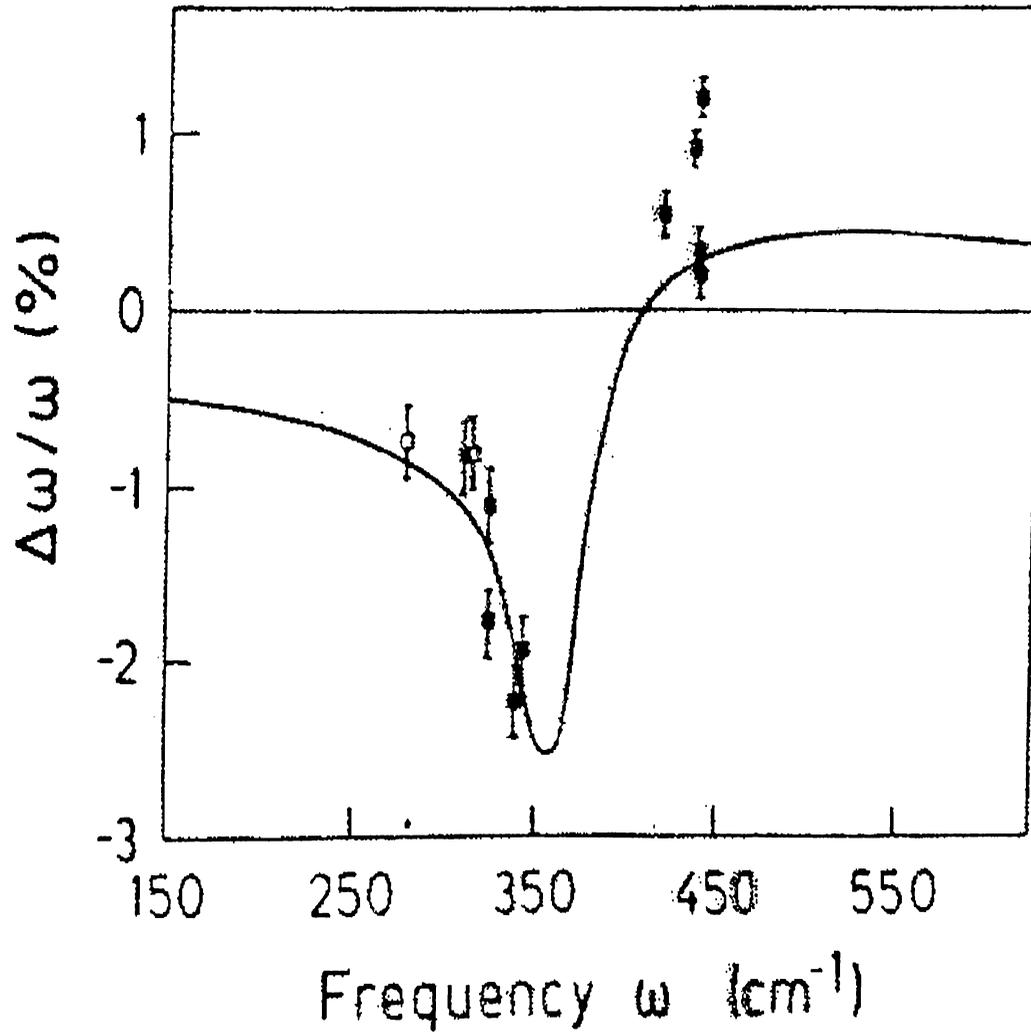


Figure 1.3: Results of Raman scattering experiments for YBCO. Experimental (squares) and theoretical (curve) phonon self energies (real part) in YBCO. Plotted is the relative shifts $\Delta\omega_\nu/\omega_\nu$ in percent vs. the phonon frequency ω at T_c . The theoretical curve is obtained from Zeyher²² with parameters $2\Delta = 333\text{cm}^{-1}$ and electron-phonon coupling $\lambda = 0.02$.

is commonly observed in aforementioned experiments play a dual role: Anharmonicity is unavoidable when a phonon frequency is abnormally softened, resulting in large amplitude vibrations of the corresponding mode. Large

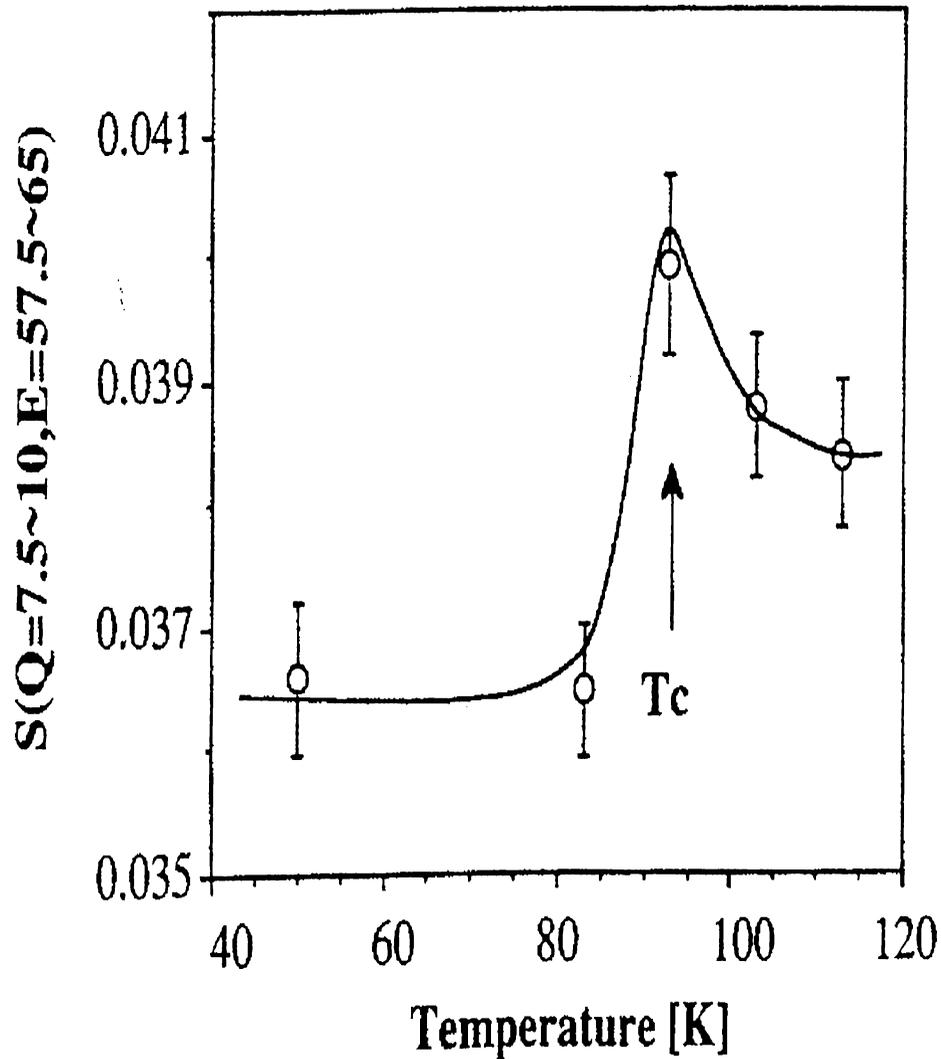


Figure 1.4: Anomaly in the structure factor
 Temperature dependence of the structure factor $S(Q, E)$ for $Q = 7.5 \sim 10 \text{ \AA}^{-1}$ and $E = 57.5 \sim 65 \text{ meV}$. Note the enhancement of $\sim 10\%$ at about T_c

amplitude vibrations broaden the real space phonon wave function. Conversely, the phonon frequency softening can be observed as a result of low temperature anharmonicity.²⁴ In this context, one can mention recent second order resonance Raman scattering experiments displaying strong evidence for the low temperature

phonon anharmonicity, principally for the buckling and tilting modes in the Cu-O planes²⁵ of some HTS. Another hint comes from neutron scattering experiments, measuring resonant frequency dispersions of LSCO and YBCO compounds. In those experiments more peaks are observed in the PDOS than that corresponding to the total degrees of freedom of the harmonic crystal.⁹ The second order nature of these additional peaks corresponding to the overtones of the combinations of single phonon resonances have been recently shown by Yoshida *et al.*²⁵

In summary, the observation of strong electron-phonon coupling and low temperature anharmonic effects are likely to be the major source of the phonon anomalies observed in the HTS. In this thesis, I follow up this direction to derive the self-consistent system of equations for the electron-phonon system. The solution of these equations yield the low temperature properties of the coupled electron-phonon system. We do this for the metallic layers in the presence of superconductivity and explicitly show the dual nature of the low temperature phonon anharmonicity and the strong electron-phonon interaction. Our results naturally lead to non-perturbative dynamical low-temperature states of the coupled electron-phonon system which are shown to dominate the low temperature regime. The temperature anomalies observed in the dynamical structure factors as well as zero point oscillations are shown to be compatible with the predictions of our model.

In the first chapter, we determine the third and fourth order polarization and momentum dependent anharmonic coupling constants of a number of copper-oxide superconductors, by using the anharmonic elastic continuum model. Their contribution to the lattice potential energy is found to be unusually high for all examined compounds, thus pointing unequivocally to the relevance of anharmonicity for them.

Based on our anharmonic coupling constants found in the first chapter, in the second chapter, we devise a microscopic low temperature anharmonic model for the bare phonon subsystem and explicitly present its self-consistent low temperature solution.

The last chapter employs the results of the first two chapters where we

additionally introduce superconducting electron-phonon interaction into the picture and derive the parameters of the superconducting ground state. We finally calculate the structure factor and elaborate on the related anomalies in the context of this model.

Chapter 2

THE ANHARMONIC ELASTIC CONTINUUM MODEL

2.1 Introduction

Although the formal expression for anharmonic terms in the crystal potential is known as given by Eq.(A.1.8), it is a formidable task to draw general conclusions about the lattice dynamics even if the crystal potential \mathcal{V} were given. It is desirable to have some simplified description of lattice modes, governed by a few parameters, in which the essential properties are preserved, at the cost of some loss of absolute accuracy. The basis of such a description is the study of the dynamics of an elastic continuum.

It is well known that the long wavelength acoustic modes tend to be simple elastic waves and that in this limit all the structure of the crystal can be smeared out to an elastic continuum. The dynamics is then controlled, as promised, by a few macroscopic, experimentally observable parameters, the so called elastic constants and the density of the crystal. The knowledge of these will enable us to set up a microscopic model for the anharmonic potential.

2.2 Elasticity Theory and Lattice Dynamics

The classical theory of elasticity ignores the microscopic atomic structure of a solid and treats it as a continuum. A general deformation of the solid is described in terms of a continuous displacement field $\mathbf{u}(\mathbf{r})$, specifying the vector displacement of the part of the solid that in equilibrium occupies position \mathbf{r} .

We can derive the continuum theory of elasticity^{26,27} from the theory of lattice vibrations by considering only lattice deformations that vary slowly on a scale determined by the range of interionic forces. For the case of *acoustic modes*, in this limit, the long wavelength limit, the atoms in a unit cell move together, having vanishingly small frequencies, which are determined by the macroscopic elastic constants and the density of the crystal. On the other hand, the frequencies of all the modes are determined by the atomic force constants $\Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}')$ (Eq.A.1.4) and the masses of the atoms. Therefore, relations between the macroscopic elastic constants and the microscopic atomic force constants, or in the case of anharmonicity, anharmonic couplings can be established.

In order to avoid lengthy calculations, I shall discuss the case of crystal with only one atom per unit cell. The classical equation of motion for the atom in $\mathbf{R} = 0$ cell is

$$m\ddot{u}_\alpha(0) = - \sum_{\mathbf{R},\beta} \Phi_{\alpha\beta}(0, \mathbf{R}) u_\beta(\mathbf{R}) \quad (2.1)$$

here $u_\alpha(\mathbf{R})$ is the α th Cartesian component of the displacement vector $\mathbf{u}(\mathbf{R} \equiv \mathbf{lb})$ as defined in Appendix.1.

Since the wavelengths are very large compared with the lattice constant, the variation of the displacement $\mathbf{u}(\mathbf{R})$ are very slight from cell to cell. We therefore define a spatially slowly-changing displacement field $\mathbf{u}(\mathbf{r})$ which is equal to $\mathbf{u}(\mathbf{R})$ at lattice sites \mathbf{R}

$$\mathbf{u}(\mathbf{r} = \mathbf{R}) = \mathbf{u}(\mathbf{R}).$$

Expanding the field $\mathbf{u}(\mathbf{r})$ at the site \mathbf{R} about \mathbf{R}' ,

$$u_\alpha(\mathbf{R}) = u_\alpha(\mathbf{R}') + \sum_{\beta} u_{\alpha\beta}(\mathbf{R} - \mathbf{R}')_\beta + \frac{1}{2!} \sum_{\beta\gamma} u_{\alpha\beta\gamma}(\mathbf{R} - \mathbf{R}')_\beta (\mathbf{R} - \mathbf{R}')_\gamma \quad (2.2)$$

where

$$u_{\alpha\beta} = \left. \frac{\partial u_\alpha}{\partial r_\beta} \right|_{\mathbf{R}=\mathbf{R}'}, \quad u_{\alpha\beta\gamma} = \left. \frac{\partial^2 u_\alpha}{\partial r_\beta \partial r_\gamma} \right|_{\mathbf{R}=\mathbf{R}'} \quad (2.3)$$

Consider now the expansion of crystal potential in Eq.(A.1.3). The harmonic term \mathcal{V}_2 can be written as

$$\mathcal{V}_2 = -\frac{1}{4} \sum_{\mathbf{R}, \mathbf{R}'} [\mathbf{u}(\mathbf{R}') - \mathbf{u}(\mathbf{R})]_\alpha \Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') [\mathbf{u}(\mathbf{R}') - \mathbf{u}(\mathbf{R})]_\beta \quad (2.4)$$

where we exploited the relation

$$\Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = \Phi_{\beta\alpha}(\mathbf{R}, \mathbf{R}') = \Phi_{\beta\alpha}(\mathbf{R}', \mathbf{R}) \quad (2.5)$$

If now $\mathbf{u}(\mathbf{R})$ varies very little over the range of $\Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}')$ we can make use of the expansion Eq.(2.2) to write \mathcal{V}_2 in the form

$$\mathcal{V}_2 = \frac{1}{2!} \sum_{\mathbf{R}, \alpha, \beta, \gamma, \delta} \frac{\partial u_\alpha(\mathbf{R})}{\partial r_\beta} \frac{\partial u_\gamma(\mathbf{R})}{\partial r_\delta} E_{\alpha\beta\gamma\delta} \quad (2.6)$$

The quantity $E_{\alpha\beta\gamma\delta}$ which constitutes a tensor of fourth rank, are given in terms of the harmonic force constants $\Phi_{\alpha\beta}(\mathbf{R})$ by

$$E_{\alpha\beta\gamma\delta} = -\frac{1}{2} \sum_{\mathbf{R}} R_\alpha \Phi_{\beta\delta}(\mathbf{R}) R_\gamma \quad (2.7)$$

Since $\mathbf{u}(\mathbf{r})$ are slowly varying, we can convert the sum into an integral

$$\mathcal{V}_2 = \frac{1}{2!} \int d^3r \sum_{\substack{\alpha, \beta \\ \gamma, \delta}} J_{\alpha\beta\gamma\delta} \frac{\partial u_\alpha}{\partial u_\beta} \frac{\partial u_\gamma}{\partial u_\delta} \quad (2.8)$$

where

$$J_{\alpha\beta\gamma\delta} = \frac{1}{v} E_{\alpha\beta\gamma\delta} \quad (2.9)$$

v is the volume of the primitive cell.

At this point we go one step further and find the long wavelength elastic continuum limit of anharmonic potential terms in Eq's.(A.1.3). We can proceed

in the same way as we did for the harmonic term and find²⁸

$$\mathcal{V}_3 = \frac{1}{3!} \int d^3r \sum_{\substack{\text{lmn} \\ \text{hij}}} A_{hij}^{lmn} u_{hl} u_{mi} u_{nj} \quad (2.10)$$

$$\mathcal{V}_4 = \frac{1}{4!} \int d^3r \sum_{\substack{\text{lmnp} \\ \text{hijk}}} A_{hijk}^{lmnp} u_{hl} u_{mi} u_{nj} u_{pk} \quad (2.11)$$

Equations (2.14),(2.10) and (2.11) constitute the starting point in the analysis of classical elasticity theory. The subject may be pursued further to extract the symmetries of the tensor $J_{\alpha\beta\gamma\delta}$ that the theory exploits.

2.3 Symmetries, Elastic Constants and a new Notation

First note that it follows directly from (2.7) and (2.5) that $J_{\alpha\beta\gamma\delta}$ is unaltered by the interchange ($\beta \leftrightarrow \delta$) or ($\alpha \leftrightarrow \gamma$). Thus it is enough to specify $J_{\alpha\beta\gamma\delta}$ for the six values

$$xx, yy, zz, yz, zx, xy$$

of the pair $\beta\delta$, and the same six values of the pair $\alpha\gamma$. This indicates that $6 \times 6 = 36$ independent numbers are required to specify the harmonic energy of a given deformation.

A further reduction in the number of elastic constants is achieved by noting that the energy of the crystal is unaffected by a rigid rotation. However, under a rotation through an infinitesimal angle $\delta\omega$ about an axis \hat{n} passing through the origin, each Bravais lattice vector will be shifted by

$$\mathbf{u}(\mathbf{R}) = \delta\omega \times \mathbf{R}, \quad \delta\omega = \delta\omega \hat{n} \quad (2.12)$$

If we substitute (2.12) into (2.14), we must find that $\mathcal{V}_2 = 0$ for arbitrary $\delta\omega$. It is not difficult to show that this implies that \mathcal{V}_2 can depend on the derivatives

$\frac{\partial u_\alpha}{\partial u_\beta}$ only in the symmetrical combination (the *strain tensor*):

$$\varepsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial u_\beta} + \frac{\partial u_\beta}{\partial u_\alpha} \right). \quad (2.13)$$

Consequently we can write (2.14) as

$$\mathcal{V}_2 = \frac{1}{2!} \int d^3r \sum_{\substack{\alpha, \beta \\ \gamma, \delta}} c_{\alpha\beta\gamma\delta} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\delta} \quad (2.14)$$

where

$$c_{\alpha\beta\gamma\delta} = \frac{1}{4} [J_{\alpha\beta\gamma\delta} + J_{\beta\alpha\gamma\delta} + J_{\alpha\beta\delta\gamma} + J_{\beta\alpha\delta\gamma}] \quad (2.15)$$

Here $c_{\alpha\beta\gamma\delta}$ is invariant under $\alpha\beta \leftrightarrow \gamma\delta$ and under the transpositions $\alpha \leftrightarrow \beta$ and $\gamma \leftrightarrow \delta$. As a result, the number of independent components of $c_{\alpha\beta\gamma\delta}$ is reduced to 21.

Depending on the crystal system one can further reduce the number of independent elastic constants. For example, the crystal structure of $YBa_2Cu_3O_{7-x}$ and $La_{2-x}Sr_xCuO_4$, the cases to be treated in this chapter, is approximately tetragonal (D_{4h}^{17}) and hence its elastic properties can be described by six independent elastic constants. These are

$$\begin{aligned} C_{11} &= c_{xxxx} = c_{yyyy} \\ C_{33} &= c_{zzzz} \\ C_{44} &= c_{yzyz} = c_{zxzx} \\ C_{66} &= c_{xyxy} \\ C_{13} &= c_{xxzz} = c_{yyzz} \\ C_{12} &= c_{txxy} \end{aligned} \quad (2.16)$$

The constants in the first column appear in contracted notation. It is usual to contract the indices as follows³⁰:

$$\begin{aligned} 11 \rightarrow 1 & \quad 22 \rightarrow 2 & \quad 33 \rightarrow 3 \\ 23, 32 \rightarrow 4 & \quad 31, 13 \rightarrow 5 & \quad 12, 21 \rightarrow 6 \end{aligned} \quad (2.17)$$

The elastic potential energy, including anharmonic terms upto fourth order \mathcal{V}_4 can conveniently be written in contracted notation through the usage of *Lagrangian strain components*³¹ η_{ij} defined by

$$\eta_{ij} = u_{ij} + \frac{1}{2} \sum_p u_{pi} u_{pj} \quad (2.18)$$

and

$$\begin{aligned} \eta_1 &= \eta_{11} & \eta_2 &= \eta_{22} & \eta_3 &= \eta_{33} \\ \eta_4 &= \eta_{23} + \eta_{32} & \eta_5 &= \eta_{31} + \eta_{13} , & \eta_6 &= \eta_{12} + \eta_{21} \end{aligned} \quad (2.19)$$

and the form of the potential^{28,29} is

$$\begin{aligned} \mathcal{V} &= \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 \\ &= \int d^3r \left[\frac{1}{2} \sum_{PQ} C_{PQ} \eta_P \eta_Q + \frac{1}{3!} \sum_{PQR} C_{PQR} \eta_P \eta_Q \eta_R \right. \\ &\quad \left. + \frac{1}{4!} \sum_{PQRS} C_{PQRS} \eta_P \eta_Q \eta_R \eta_S \right] \end{aligned} \quad (2.20)$$

If we expand the expression for potential energy (2.20) in terms of strains u_{ij} using relation (2.18), with an hindsight on the tetragonal symmetry, the third and fourth order anharmonic contributions to the elastic potential energy in the elastic continuum are given by

$$\begin{aligned} \mathcal{V}_3 &= \int d^3r \frac{1}{2} \left\{ C_{11} (u_{11} \sum_p u_{p1}^2 + u_{22} \sum_p u_{p2}^2) + C_{33} u_{33} \sum_p u_{p3}^2 \right. \\ &\quad + C_{13} (u_{22} \sum_p u_{p3}^2 + u_{33} \sum_p u_{p2}^2 + u_{11} \sum_p u_{p3}^2 + u_{33} \sum_p u_{p1}^2) \\ &\quad + C_{12} (u_{11} \sum_p u_{p2}^2 + u_{22} \sum_p u_{p1}^2) + 4 C_{66} u_{12} \sum_p u_{p1} u_{p2} \\ &\quad \left. + 4 C_{44} (u_{23} \sum_p u_{p2} u_{p3} + u_{13} \sum_p u_{p1} u_{p3}) \right\} \end{aligned} \quad (2.21)$$

$$\begin{aligned} \mathcal{V}_4 &= \int d^3r \frac{1}{2} \left\{ \frac{1}{4} C_{11} \sum_p (u_{p1}^4 + u_{p2}^4) + C_{33} \sum_p u_{p3}^4 \right. \\ &\quad + \frac{1}{2} C_{13} \sum_{p,q} (u_{p1}^2 + u_{p2}^2) u_{q3}^2 + \frac{1}{2} C_{12} \sum_p u_{p1}^2 u_{p2}^2 \\ &\quad + C_{44} \sum_{p,q} (u_{p2} u_{p3} u_{q2} u_{q3} + u_{p1} u_{p3} u_{q1} u_{q3}) \\ &\quad \left. + C_{66} \sum_{p,q} u_{p1} u_{p2} u_{q1} u_{q2} \right\} \end{aligned}$$

There are currently no experimental data available on third and fourth order elastic constants C_{PQR} and C_{PQRS} , so that in calculations I will not include the positive contributions of these, which will yield slightly underestimated values for anharmonic couplings.

2.4 Experimental Data

Miglioriet *al.*^{19,20} measured the second order elastic constants C_{PQ} of a single crystal sample of $La_{2-x}Sr_xCuO_4$ for $x = 0$ and $x = 0.14$ at $T = 297K$ using a resonant ultrasound technique.

The data for $YBa_2Cu_3O_{7-x}$ and *Bi* based compounds is obtained by Heet *al.*³² Note that *YBCO* compound is orthorhombic in superconducting ($x < 0.16$) and tetragonal in normal phases with slight changes in the *Cu – O* in-plane distance.³³ In transition to superconducting phase, elastic constants which are relevant for the c-axis tetragonality almost retain their symmetry.

The results are summarized in the first three rows of Table (2.1).

2.5 A Microscopic Model for Anharmonicity

A microscopic model necessarily must comprise quantization of observables. In this respect, we begin by writing the *continuum* displacement operator in second quantized form as

$$u_i(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}_s} \sqrt{\frac{\hbar}{2M\omega_{\mathbf{k}_s}}} e^i_{\mathbf{k}_s} (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^\dagger) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (2.22)$$

Here $e^i_{\mathbf{k}_s} \equiv e^i_{\mathbf{k}_s}(\mathbf{r})$ is the i^{th} component of the polarization vector at point \mathbf{r} for the phonon propagating in direction \mathbf{k} . Differentiating (2.22) with respect to \mathbf{r} we get the components of the elastic strain tensor u_{ij}

$$u_{ij} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}_s} \sqrt{\frac{\hbar}{2M\omega_{\mathbf{k}_s}}} q_j e^i_{\mathbf{k}_s} (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^\dagger) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (2.23)$$

Using (2.23) in expressions (2.10) and (2.11) one obtains for the third order term \mathcal{V}_3

$$\mathcal{V}_3 = \frac{1}{3!} \sum_{\mathbf{k}_s, \mathbf{k}'_{s'}, \mathbf{k}''_{s''}} \delta_{\mathbf{k} + \mathbf{k}' + \mathbf{k}''} (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^\dagger) (a_{\mathbf{k}'_{s'}} + a_{-\mathbf{k}'_{s'}}^\dagger) (a_{\mathbf{k}''_{s''}} + a_{-\mathbf{k}''_{s''}}^\dagger) \mathcal{V}_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{ss's''} \quad (2.24)$$

The expression of the anharmonic terms then takes the same form as (A.1.10) and (A.1.11) but now with

$$\begin{aligned} \nu_{\mathbf{k}, \mathbf{k}', \mathbf{k}''}^{ss's''} &= \frac{1}{\sqrt{N}} \sum_{\substack{\text{klm} \\ \text{hij}}} \left(\frac{\hbar}{2M} \right)^{\frac{3}{2}} A_{hij}^{klm} e_{\mathbf{k}_s}^k e_{\mathbf{k}'_{s'}}^l e_{\mathbf{k}''_{s''}}^m \frac{k_h k'_i k''_j}{\sqrt{\omega_{\mathbf{k}_s} \omega_{\mathbf{k}'_{s'}} \omega_{\mathbf{k}''_{s''}}}} \quad (2.25) \\ &= \frac{1}{\sqrt{N}} \left(\frac{\hbar}{2M} \right)^{\frac{3}{2}} \left(\frac{k k' k''}{\sqrt{\omega_{\mathbf{k}_s} \omega_{\mathbf{k}'_{s'}} \omega_{\mathbf{k}''_{s''}}}} \right) \mathcal{A}_{\mathbf{k} \mathbf{k}' \mathbf{k}''}^{ss's''} \quad (2.26) \end{aligned}$$

where

$$\mathcal{A}_{\mathbf{k} \mathbf{k}' \mathbf{k}''}^{ss's''} = \sum_{\substack{\text{klm} \\ \text{hij}}} e_{\mathbf{k}_s}^k e_{\mathbf{k}'_{s'}}^l e_{\mathbf{k}''_{s''}}^m n_h n'_i n''_j A_{hij}^{klm} \quad (2.27)$$

with \mathbf{n}, \mathbf{n}' and \mathbf{n}'' being the unit vectors along \mathbf{k}, \mathbf{k}' and \mathbf{k}'' respectively. The coefficients $\mathcal{A}_{\mathbf{k} \mathbf{k}' \mathbf{k}''}^{ss's''}$ which are components of the tensor A_{hij}^{klm} projected onto three polarizations $e_{\mathbf{k}}$ and directions of propagation \mathbf{k} , are called hereafter as the *anharmonic couplings*.

Similar arguments hold true for the fourth order coupling coefficients which are defined by

$$\nu_4 = \frac{1}{4!} \sum_{\substack{\mathbf{k}_s, \mathbf{k}'_{s'} \\ \mathbf{k}''_{s''}, \mathbf{k}'''_{s'''}}} \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'' + \mathbf{k}''') \nu_{\mathbf{k} \mathbf{k}' \mathbf{k}'' \mathbf{k}'''}^{ss's''s'''} Q_{\mathbf{k}_s} Q_{\mathbf{k}'_{s'}} Q_{\mathbf{k}''_{s''}} Q_{\mathbf{k}'''_{s'''}} \quad (2.28)$$

where $Q_{\mathbf{k}} = a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger$ and

$$\nu_{\mathbf{k} \mathbf{k}' \mathbf{k}'' \mathbf{k}'''}^{ss's''s'''} = \frac{1}{N} \left(\frac{\hbar}{2M} \right)^2 \left(\frac{k k' k'' k'''}{\sqrt{\omega_{\mathbf{k}_s} \omega_{\mathbf{k}'_{s'}} \omega_{\mathbf{k}''_{s''}} \omega_{\mathbf{k}'''_{s'''}}}} \right) \mathcal{A}_{\mathbf{k} \mathbf{k}' \mathbf{k}'' \mathbf{k}'''}^{ss's''s'''} \quad (2.29)$$

The anharmonic coupling can be calculated through

$$\mathcal{A}_{\mathbf{k} \mathbf{k}' \mathbf{k}'' \mathbf{k}'''}^{ss's''s'''} = \sum_{\substack{\text{lmnp} \\ \text{hijk}}} e_{\mathbf{k}_s}^l e_{\mathbf{k}'_{s'}}^m e_{\mathbf{k}''_{s''}}^n e_{\mathbf{k}'''_{s'''}}^p n_h n'_i n''_j n'''_k A_{hijk}^{lmnp} \quad (2.30)$$

2.6 Calculation of Anharmonic Couplings

The explicit calculations of the anharmonic couplings $\mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{ss's''}$ and $\mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}^{ss's's''''}$ in terms of experimental values of elastic constants C_{PQ} proceeds by comparing (2.21) with (2.10) and (2.11), extracting A_{hij}^{lmn} (A_{hijk}^{lmnp}) in terms of C_{PQ} , and inserting this into (2.27). The resulting expressions are

$$\begin{aligned} \mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{ss's''} = & \sum_{i \neq j=1}^2 \left\{ 3C_{11} e_i n_i \sum_p e'_p e''_p n'_i n''_i \right. \\ & + C_{33} e_3 n_3 \sum_p e'_p e''_p n'_3 n''_3 \\ & + 3C_{13} e_i n_i \sum_p e'_p e''_p n'_3 n''_3 \\ & + 3C_{12} e_3 n_3 \sum_p e'_p e''_p n'_j n''_j \\ & + 6C_{66} e_i n_j \sum_p e'_p e''_p n'_i n''_j \\ & \left. + 6C_{44} (e_3 n_i + e_i n_3) \sum_p e'_p e''_p n'_i n''_3 \right\} \end{aligned} \quad (2.31)$$

$$\begin{aligned} \mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}^{ss's's''''} = & \sum_{i \neq j=1}^2 \left\{ 3C_{11} \sum_p e_p e'_p e''_p e'''_p n_i n'_i n''_i n'''_i \right. \\ & + 3C_{33} \sum_p e_p e'_p e''_p e'''_p n_3 n'_3 n''_3 n'''_3 \\ & + 6C_{13} \sum_{p,q} e_p e'_p e''_q e'''_q n_i n'_i n''_3 n'''_3 \\ & + 6C_{12} \sum_p e_p e'_p e''_p e'''_p n_i n'_i n''_j n'''_j \\ & + 12C_{66} \sum_{p,q} e_p e'_p e''_q e'''_q n_i n'_j n''_i n'''_j \\ & \left. + 12C_{44} \sum_{p,q} e_p e'_q e''_p e'''_q n_i n'_i n''_3 n'''_3 \right\} \end{aligned}$$

where e_p, e'_p, e''_p, e'''_p indicate the direction of polarization and $n_j, (j = 1, 2)$ with n_3 are unit vector components of the phonon momenta confined in the 1-2 planes and in 3 direction respectively (There is a slight change in notation: $e'_p = e^p_{\mathbf{k}'_s}$).

It should be pointed out that, since most of the anharmonic modes in HTS are those propagating on the planes with transverse or longitudinal polarizations, we take $n_3 = n'_3 = n''_3 = n'''_3 = 0$.

In order to evaluate the anharmonic couplings we assume isotropy of the medium and the 3 (4) phonons participating in the scattering process to be coplanar.

Let us choose \mathbf{k} along the x-axis, and consider $\mathbf{k}, \mathbf{k}', \mathbf{k}''$ and \mathbf{k}''' to lie on the x-y plane. Let θ', θ'' and θ''' be the angles between \mathbf{k} and \mathbf{k}' , \mathbf{k} and \mathbf{k}'' , and \mathbf{k} and \mathbf{k}''' respectively. If further $\theta_1, \theta_2, \theta_3$ and θ_4 describe (arbitrary) polarization

angles for the transverse phonons.

$$\begin{aligned}
n &= e_L = (1, 0, 0), & e_T &= (0, \cos \theta_1, \sin \theta_1) \\
n' &= e'_L = (\cos \theta', \sin \theta', 0), & e'_T &= (\sin \theta' \cos \theta_2, -\cos \theta' \cos \theta_2, \sin \theta_2) \\
n'' &= e''_L = (\cos \theta'', \sin \theta'', 0), & e''_T &= (\sin \theta'' \cos \theta_3, -\cos \theta'' \cos \theta_3, \sin \theta_3) \\
n''' &= e'''_L = (\cos \theta''', \sin \theta''', 0), & e'''_T &= (\sin \theta''' \cos \theta_4, -\cos \theta''' \cos \theta_4, \sin \theta_4)
\end{aligned} \tag{2.32}$$

Here if we take, as promised, $n_3 = n'_3 = n''_3 = n'''_3 = 0$ and average over θ_n 's ($n = 1, 2, 3, 4$), the resulting anharmonic constants only have planar degrees of freedom $\theta, \theta', \theta'', \theta'''$. Noting that s can be either of T and L we arrive at the expressions

$$\begin{aligned}
|A_{qq'q''}^{TTT}|^2 &= 0 \\
|A_{qq'q''}^{TLL}|^2 &= \frac{1}{4} \left\{ (C_{11} + C_{12}) (\sin 2\theta'' + \sin 2\theta' \right. \\
&\quad \left. + 6 C_{66} \cos(\theta' - \theta'') \sin(\theta' + \theta'')) \right\}^2 \\
|A_{qq'q''}^{TTL}|^2 &= \frac{1}{4} \left\{ (C_{11} + C_{12})^2 \cos^2 \theta' + [-(C_{11} + C_{12}) \cos^2 \theta' \right. \\
&\quad \left. + C_{66} (\sin(\theta' - \theta'') \sin(\theta' + \theta'') + \cos(\theta' - \theta'') \cos(\theta' + \theta'')) \right. \\
&\quad \left. + \sin \theta'' \cos \theta' \sin(\theta' - \theta'')] \right\}^2 + \frac{3}{4} C_{66}^2 [\sin \theta'' \cos \theta' \cos(\theta' - \theta'')]^2 \\
&\quad + \frac{1}{4} C_{66}^2 [\sin \theta'' \cos(\theta' - \theta'')]^2 \left. \right\} \\
|A_{qq'q''}^{LLL}|^2 &= \left\{ (C_{11} + C_{12})^2 [\cos^2(\theta' - \theta'') + \cos^2 \theta'' + \cos 2\theta'] \right. \\
&\quad \left. + C_{66} \cos \theta' \cos \theta'' \cos(\theta' - \theta'') \right\}^2
\end{aligned} \tag{2.33}$$

and the fourth order ones are

$$\begin{aligned}
|A_{qq'q''q'''}^{TTTT}|^2 = & \frac{1}{16} \left\{ \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} II \right] (II - I) \right. \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} III \right] (III - I) \\
& + \left. \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right] (IV - I) \right\}^2 \\
& + \left\{ \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} II \right] + \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} III \right] \right. \\
& + \left. \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right] \right\}^2 \\
& + \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} II \right]^2 [\cos^2 \theta' + \cos^2 (\theta'' - \theta''')] \\
& + \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} III \right]^2 [\cos^2 \theta'' + \cos^2 (\theta' - \theta''')] \\
& + \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right]^2 [\cos^2 \theta''' + \cos^2 (\theta' - \theta'')]
\end{aligned}$$

$$\begin{aligned}
|A_{qq'q''q'''}^{TTTL}|^2 = & \frac{1}{8} \left\{ \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} II \right] [-\cos \theta' \sin (\theta'' - \theta''')] \right. \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} III \right] [-\cos \theta'' \sin (\theta' - \theta''')] \\
& + \left. \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right] [\sin \theta''' \cos (\theta' - \theta'')] \right\}^2 \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} II \right]^2 \sin^2 (\theta'' - \theta''') \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} III \right]^2 \sin^2 (\theta' - \theta''') \\
& + \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right]^2 \sin 2\theta'''
\end{aligned}$$

$$\begin{aligned}
|A_{qq'q''q'''}^{TTLL}|^2 = & \frac{1}{4} \left\{ \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} II \right] [-\cos \theta' \cos (\theta'' - \theta''')] \right. \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} III \right] [\sin \theta'' \sin (\theta' - \theta''')] \\
& + \left. \left[\frac{1}{3} (C_{11} + 2C_{12}) I + 2C_{66} IV \right] [\sin \theta''' \sin (\theta' - \theta'')] \right\}^2 \quad (2.34) \\
& + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2C_{66} II \right]^2 \cos^2 (\theta'' - \theta''')
\end{aligned}$$

$$\begin{aligned}
|A_{qq'q''q'''}^{TLLL}|^2 &= \frac{1}{2} \left\{ \left[\frac{1}{3} (C_{11} + C_{12}) I + 2 C_{66} II \right] [\cos \theta' \sin (\theta''' - \theta'')] \right. \\
&\quad + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2 C_{66} III \right] [\cos \theta'' \sin (\theta' - \theta''')] \\
&\quad + \left. \left[\frac{1}{3} (C_{11} + 2 C_{12}) I + 2 C_{66} IV \right] [\sin \theta''' \cos (\theta' - \theta'')] \right\}^2 \\
&\quad + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2 C_{66} II \right]^2 \sin^2 (\theta'' - \theta''') \\
&\quad + \left[\frac{1}{3} (C_{11} + C_{12}) I + 2 C_{66} III \right]^2 \sin^2 (\theta' - \theta''') \\
&\quad + \left[\frac{1}{3} (C_{11} + 2 C_{12}) I + 2 C_{66} IV \right]^2 \sin^2 \theta''' \\
|A_{qq'q''q'''}^{LLLL}|^2 &= \left\{ \frac{1}{3} (C_{11} + 2 C_{12}) I^2 + 4 C_{66} [\cos \theta' \cos \theta'' \cos (\theta'' - \theta''') \cos (\theta' - \theta''') \right. \\
&\quad + \cos \theta' \cos \theta''' \cos (\theta'' - \theta''') \cos (\theta' - \theta'') \\
&\quad + \left. \cos \theta'' \cos \theta''' \cos (\theta' - \theta''') \cos (\theta' - \theta'')] \right\}^2
\end{aligned}$$

where I, II, III, IV are given by,

$$\begin{aligned}
I &= \cos \theta' \cos (\theta'' - \theta''') + \cos \theta'' \cos (\theta' - \theta''') + \cos \theta''' \cos (\theta' - \theta'') \\
II &= \cos \theta'' \cos (\theta' - \theta''') + \cos \theta''' \cos (\theta' - \theta'') \\
III &= \cos \theta' \cos (\theta'' - \theta''') + \cos \theta''' \cos (\theta' - \theta'') \\
IV &= \cos \theta' \cos (\theta'' - \theta''') + \cos \theta'' \cos (\theta' - \theta''')
\end{aligned} \tag{2.35}$$

Averaging the above equations a second time, over $\theta, \theta', \theta'', \theta'''$ yields

$$\begin{aligned}
|A^{TTT}|^2 &= 0 \\
|A^{TTL}|^2 &= 0.22 (C_{11} + C_{12})^2 + 0.30 C_{66}^2 + 0.09 (C_{11} + C_{12}) C_{66} \\
|A^{TLL}|^2 &= 0.12 (C_{11} + C_{12})^2 + 1.12 C_{66}^2 + 0.75 (C_{11} + C_{12}) C_{66} \\
|A^{LLL}|^2 &= 2.62 (C_{11} + C_{12})^2 + 5.61 C_{66}^2 + 6.75 (C_{11} + C_{12}) C_{66}
\end{aligned} \tag{2.36}$$

and the averaged fourth order couplings are given as,

$$\begin{aligned}
|A^{TTTT}|^2 &= 0.17 (C_{11} + 2C_{12})^2 + 2.75 C_{66}^2 + 0.86 (C_{11} + 2C_{12}) C_{66} \\
|A^{TTTL}|^2 &= 0.04 (C_{11} + 2C_{12})^2 + 0.95 C_{66}^2 + 0.40 (C_{11} + 2C_{12}) C_{66} \\
|A^{TTLL}|^2 &= 0.07 (C_{11} + 2C_{12})^2 + 1.20 C_{66}^2 + 0.57 (C_{11} + 2C_{12}) C_{66} \\
|A^{TLLL}|^2 &= 0.11 (C_{11} + 2C_{12})^2 + 1.80 C_{66}^2 + 0.87 (C_{11} + 2C_{12}) C_{66} \\
|A^{LLLL}|^2 &= 0.62 (C_{11} + 2C_{12})^2 + 9.60 C_{66}^2 + 4.80 (C_{11} + 2C_{12}) C_{66}
\end{aligned} \tag{2.37}$$

From the equations (2.36) and (2.37) the anharmonic couplings can be computed using the measured elastic constants. The results are listed in Table (2.1) for

(GPa)	Bi, Pb ^(a) (2223)	Bi,Pb ^(a) (2212)	Bi ^(a) (2212)	YBCO ^(a) (123)	La ₂ CuO ₄ ^(b)	La _{1.86} Sr _{0.14} CuO ₄ ^(b)	Fused ^(c) Quartz	Pb ^(c)
C ₁₁	36.4	39.9	43.4	136	275.64	397.43	10	15
C ₆₆	14.3	16.0	16.1	45.6	155.12	93.43	3.15	1.83
C ₁₂	17.4	18.6	21.9	75.1	144.23	76.92	3.71	1.83
A ^{TTTT}	27.1	29.7	32.2	100.8	227.5	236.5	6.93	8.1
A ^{LLT}	36.4	39.5	44.3	143.9	313.0	266.8	8.18	7.9
A ^{LLL}	120	131.1	144.2	458.7	1018.8	969.1	28.9	31.1
A ^{TTTTT}	50.3	54.7	61.1	197.7	443.2	347.7	11.26	9.9
A ^{LLLL}	104.7	113.9	126.9	410.1	921.4	721.2	23.4	20.3
A ^{TTTTL}	36.2	39.3	43.9	142	318.5	248.2	8.1	7.0
A ^{TTTTL}	30.3	32.9	36.9	119.7	266.7	203.6	6.6	5.6
A ^{LLLLT}	44.4	48.3	53.9	174.3	390.8	304.0	9.9	8.5

Table 2.1: The measured elastic constants and calculated coupling constants. Third and fourth order anharmonic phonon coupling constants calculated within the elastic potential continuum model. ($1GPa \simeq 0.62410^{-2}eV/\text{\AA}^3$ (a): Ref. [32]; (b): Ref. [19]; (c): Ref. [34]).

YBCO, LSCO, Bi-based compounds, fused quartz (which is known to be a good harmonic crystal) and lead (a strongly coupled conventional superconductor) for comparison.³⁴ The magnitudes of anharmonic energy scales given in Table (2.2) with respect to harmonic energy of typical planar $\omega_0 = 41 meV$ mode as compared to quartz is to be noted.

The third order contribution gives rise to thermal scattering and contributes to the phonon life-time at high temperatures. At temperatures much lower than the characteristic energy $\hbar\omega_0$ we neglect the third order processes. Such terms

(mcV)	Bi, Pb ^(a) (2223)	Bi, Pb ^(a) (2212)	Bi ^(a) (2212)	YBCO ^(a) (123)	La ₂ CuO ₄ ^(b)	La _{0.86} Sr _{0.14} CuO ₄ ^(b)	Fused ^(c) Quartz	Pb ^(d)
ω_0				41	35.6	37.3	150	8.3
E_3	0.60	0.67	0.725	2.32	5.41	5.11	0.031	8.42×10^{-6}
E_4	0.070	0.077	0.083	0.264	0.67	0.52	0.004	3×10^{-7}

Table 2.2: The calculated anharmonic energy scales

also do not play significant role in the low temperature ground state properties due to tetragonal symmetry and hence they will be ignored here. In fourth order, only those terms involving $LLLL$, $TTTT$, $LLTT$ have nonvanishing angular averages. Contrary to the case with the third order, \mathcal{V}_4 can create low temperature anharmonic fluctuations in the ground state. We describe the self consistent mean field solution for the anharmonic model (2.28) in next chapter.

Chapter 3

A DYNAMICAL MODEL FOR LOW TEMPERATURE ANHARMONICITY

3.1 Introduction

It is well known that, lattice anharmonicity becomes important at sufficiently high temperatures.³⁵ Usually, the main source of this behaviour is the increase in the vibrational amplitudes of the individual ions and the strong deviation of the effective ion potential from the usual parabolic one. In this respect, the expansion of the crystal potential upto bilinear terms in displacement becomes insufficient as the need arises to include higher terms in expansion as well. To deal with such cases certain semi-perturbative techniques have been developed. The *quasiharmonic approximation*,³⁵ gives reasonable results for thermodynamic properties of crystals, in which anharmonicity is weak and the frequencies are renormalized by thermal expansion only. The idea behind the quasiharmonic approximation is to map the weakly anharmonic model onto an equivalent harmonic one. Since the harmonic approximation requires the parity of the ground state and the excited states to be a good quantum number, the effect of the third and other higher odd order anharmonic contributions are usually

ignored, particularly in the low temperature formulation. The third order effects usually shift the equilibrium configuration of the lattice. Within the quasiharmonic approximation, dynamical effects, such as renormalization of the phonon frequencies or phonon density of states, are not displayed by the third order terms, provided that one is confined to sufficiently low temperatures.

In crystals with strong anharmonic interactions, however, this approximation breaks down. Few examples are large amplitude vibrations in rare-gas solids, in particular solid helium, soft modes in structural instabilities and melting processes. In particular, crystal field in materials with strong ionic bonds can be largely renormalized due to the induced strong polarization field. It is now understood that, strong ionic character can induce the higher moments of the elastic potential, creating large amplitude oscillations of ions from their equilibrium configurations. These type of materials can undergo structural phase transformations under a certain critical temperature and acquire permanent local electric dipole moments as the large amplitude vibrational modes soften or even freeze in their new equilibrium configurations. Ferroelectric materials are best examples of such low temperature anharmonicity.⁵¹ For these cases a method has been developed, the *self consistent harmonic approximation*, which allows a qualitative description of the effects of strong anharmonicity.⁵⁰

Hence, lattice anharmonicity may be present at low temperatures, i.e. at temperatures much lower than the Debye scale. This effects the ground state properties of the lattice. Large amplitude, low temperature quantum fluctuations, principally induced by light masses, are the major source for low temperature dynamical anharmonicity. There has been a number of experiments showing unusual vibrational and structural properties in the new layered perovskite superconductors. In La_2CuO_4 , for example, the phonon dispersion curves measured by inelastic neutron scattering^{6,12,15} exhibit evidence for pronounced anharmonicity, including the appearance of extra or split modes. A further evidence for low temperature anharmonicity, principally for the buckling and tilting modes in the Cu-O planes, was observed in the second order Raman scattering experiments.²⁵

In cuprate superconductors most of the anharmonic effects are observed near the zone boundaries. Low temperature anharmonicity is unavoidable when a phonon frequency is abnormally softened resulting in large amplitude vibrations of the corresponding mode. Large amplitude vibrations broaden the real space phonon wave function. Conversely, the phonon frequency softening can be observed as a result of low temperature anharmonicity.²⁴ This implies that low temperature anharmonicity and lattice softening interfere. Owing to this dual character, the effects can be accurately formulated only in a self consistent non-perturbative framework. In this chapter we examine the low temperature phonon anharmonicity from this dynamical and self consistent perspective.

3.2 Model Hamiltonian

For our anharmonic model of the crystal lattice we consider the crystal Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} (a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \frac{1}{2}) + \frac{1}{4!} \sum_{\{\mathbf{k}_n\}} V_4(\{\mathbf{k}_n\}) \delta_{\vec{k}+\vec{k}'+\vec{k}''+\vec{k}'''} Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} Q_{\mathbf{k}_4} \quad (3.1)$$

where the first term is the harmonic phonon contribution with dispersion $\omega_{\vec{k}s}$ and $Q_{\mathbf{k}} = a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger}$. The second term gives the fourth order anharmonic contribution as elaborated in Chapter 2. Here, using a collective notation, as compared to that used in Chapter 2,

$$\begin{aligned} V_4(\{\mathbf{k}_n\}) &= V_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \\ &= \frac{1}{N} \left(\frac{\hbar}{2M} \right)^2 \left(\frac{k k' k'' k'''}{\sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'} \omega_{\mathbf{k}''} \omega_{\mathbf{k}'''}}} \right) \mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \end{aligned} \quad (3.2)$$

where hereafter $\mathbf{k} = (\vec{k}, s)$ will denote the phonon variables : wavevector \vec{k} and polarization s . $\mathcal{A}_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$ are the fourth order *anharmonic coupling coefficients* (2.30) which determine the strength of the anharmonicity.

In our calculations we did not include the third order anharmonic term. The effect of third order anharmonicity can be incorporated effectively into

the imaginary part of the phonon self energies. Such thermal broadening effects, however, are negligible at the temperatures of interest and for the model considered, as shown in Appendix A.5.

Besides renormalizing the phonon spectrum low temperature anharmonicity also produces phase space correlations between otherwise independent phonon modes.³⁶ In order to study these correlations, we develop a self consistent formalism, which assumes that the low temperature dynamics is dominated by the lowest order phonon correlations $\phi^{s,s'}(\mathbf{k}) = \langle a_{\mathbf{k},s} a_{-\mathbf{k},s'} \rangle \delta_{s,s'}$. One thereby focuses onto phenomena where strongly anharmonic low temperature multiple phonon quantum fluctuations can lead to qualitative changes in the properties of the ground state. Such considerations of the anharmonic oscillator has been considered intensively in the literature and the approach held by Kaulfusset *al.*³⁷ for a single-mode anharmonic oscillator is very similar to ours. They apply the coupled-cluster method (CCM) to the one-dimensional anharmonic oscillator and find out that fluctuations around the exact energy are small enough to call the method numerically convergent.

In the strongly anharmonic limit (i.e. $|V_{\mathbf{k},\mathbf{k}'}^{s,s'}| \simeq \omega_{\mathbf{k}s}$) one can assume, following CCM, the exact ground state to be a generalized n particle coherent state:

$$|\psi\rangle = \mathcal{S}|0\rangle \quad (3.3)$$

with $a_{\mathbf{k}}|0\rangle = 0$. The operator \mathcal{S} can be expanded in powers of $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$:

$$\mathcal{S} = \exp \left\{ \sum_n S_n - S_n^\dagger \right\} \quad (3.4)$$

$$S_n = \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \xi^n \{ \mathbf{k}_i \} a_{\mathbf{k}_1}^\dagger \cdots a_{\mathbf{k}_n}^\dagger \quad (3.5)$$

The coefficients $\xi^n \{ \mathbf{k}_i \}$ are the so-called correlation amplitudes. Solving the Schrödinger equation is exactly equivalent to evaluating all $\xi^n \{ \mathbf{k}_i \}$ amplitudes. If one tries to solve the problem exactly, one obtains an infinite hierarchy of equations for these amplitudes. This hierarchy is similar to RKKY hierarchy in transport theory and in statistical mechanics, mixing the quantum fluctuations from different orders self consistently.

3.3 T=0 Solution

Here we assume, for weak anharmonicity, that the most dominant amplitude is the two phonon correlation amplitude, which tantamounts to solving the problem in the mean field of $\phi^{s s'}(\mathbf{k}) = \langle a_{\mathbf{k},s} a_{-\mathbf{k},s} \rangle \delta_{s,s'}$. It should be noted that one-phonon amplitude, which is of lower order, has been neglected owing to the well-defined parity of the Hamiltonian and hence the ground state. To take into account the aforementioned leading correction to the ground state, we apply a Bogoliubov transformation to the original phonon creation and annihilation operators and define new bosonic quasi-particle operators $b_{\mathbf{k}}, b_{\mathbf{k}}^\dagger$ as

$$\begin{aligned} b_{\mathbf{k}} &= \mathcal{S}(\{\xi\}) a_{\mathbf{k}} \mathcal{S}^\dagger(\{\xi\}) = C_{\mathbf{k}} a_{\mathbf{k}} - S_{\mathbf{k}} a_{-\mathbf{k}}^\dagger, \\ b_{-\mathbf{k}}^\dagger &= \mathcal{S}(\{\xi\}) a_{-\mathbf{k}}^\dagger \mathcal{S}^\dagger(\{\xi\}) = C_{\mathbf{k}} a_{-\mathbf{k}}^\dagger - S_{\mathbf{k}} a_{\mathbf{k}} \end{aligned} \quad (3.6)$$

where the unitary transformation $\mathcal{S}(\{\xi\})$,

$$\mathcal{S}(\{\xi\}) = \exp\left\{-\sum_{\mathbf{k}} \xi_{\mathbf{k}} (a_{\mathbf{k}} a_{-\mathbf{k}} - a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger)\right\} \quad (3.7)$$

produces the lowest order pair correlations in the ground state of (3.1). Here $C_{\mathbf{k}} = \cosh 2\xi_{\mathbf{k}}$ and $S_{\mathbf{k}} = \sinh 2\xi_{\mathbf{k}}$ where $\xi_{\mathbf{k}}$ is an order parameter for phonon pair correlations to be found self consistently. We considered $\xi_{\mathbf{k}}$ to be real since the phase factor can easily be combined with the phase of the operators $a_{\mathbf{k}}, a_{-\mathbf{k}}^\dagger$ and the wavefunction.

After transforming the Hamiltonian using the equations (3.6) and applying an energy minimization procedure, the new excitation spectrum is given by the effective Hamiltonian

$$\mathcal{H}^{eff} = \sum_{\mathbf{k}} \hbar \Omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{1}{2}) \quad (3.8)$$

where the renormalized phonon frequency is given by

$$\phi(\mathbf{k}) = \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle = C_{\mathbf{k}} S_{\mathbf{k}} = \frac{\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \quad (3.9)$$

The optimum squeezing parameter $\kappa_{\mathbf{k}}$ is determined from the self consistent equation

$$\kappa_{\mathbf{k}} = 6 \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \left[2\phi(\mathbf{k}') + \sqrt{1 + 4\phi^2(\mathbf{k}')} \right] \quad (3.10)$$

$V_{\mathbf{k}\mathbf{k}'}$ is an effective phonon pair-potential given in terms of fourth order anharmonic coupling coefficients by

$$V_{\mathbf{k}\mathbf{k}'} = \frac{1}{N} \left(\frac{\hbar}{2M} \right)^2 \left[\frac{k^2 k'^2}{\omega_{\mathbf{k}} \omega_{\mathbf{k}'}} \right] A_{\mathbf{k}\mathbf{k}\mathbf{k}'\mathbf{k}'} \quad (3.11)$$

We assume that the interaction potential is essentially isotropic on the Cu-O planes. The details of the calculation leading to the above self consistent mean field solution of $\phi^s s'(\mathbf{k})$ is given in Appendix A.3. We solve Equation (3.10) self consistently in two dimensions for $\omega_{\mathbf{k}_s} = \omega_0 = 41meV$ optical B_{1g} phonon. For small couplings the zero temperature solution is given analytically by,

$$\kappa_{\mathbf{k}}/\omega_0 \simeq \left(\frac{k}{k_0} \right)^2 \lambda_{p-p} \quad (3.12)$$

here k_0 describes the upper momentum cutoff which is fixed at the X point and $\lambda_{p-p} = 3/8 \pi^2 V_0/\omega_0$ is the dimensionless anharmonic coupling constant. Here V_0 is given by Eq.(3.11) evaluated at $k = k' = k_0$. For YBCO, $\lambda_{p-p} = 0.05$. The approximate linear dependence of zero temperature $\kappa_{\mathbf{k}=X}$ is also displayed in the exact numerical solution of the Equation (3.10) shown in Figure (3.1).

3.4 Finite Temperature Solution

We have shown in Appendix A.4 that for a pure lattice system finite temperature depairing effects due to third order anharmonicity are suppressed in the presence of momentum correlations in the ground state. This implies that Eq.(3.10) can be reliably extended to finite temperatures. Below we pursue this by using the finite temperature Green's function of the system corresponding to the effective mean field Hamiltonian \mathcal{H}^{eff} .

For our purposes, the phonon and the anomalous phonon Green's functions are defined for arbitrary state $|\Psi\rangle = \mathcal{S}(\{\xi^{ph}\})|0\rangle$ as

$$\mathcal{D}_{\mathbf{k}}(t, t') = -i \langle \Psi | T Q_{\mathbf{k}}(t) Q_{-\mathbf{k}}(t') | \Psi \rangle \quad (3.13)$$

$$\mathcal{F}_{\mathbf{k}}(t, t') = -i \langle \Psi | T a_{\mathbf{k}}(t) a_{-\mathbf{k}}(t') | \Psi \rangle \quad (3.14)$$

where \mathcal{T} defines the proper time ordering in the action of the operators onto the state $|\Psi\rangle$. The calculations given in Appendix (A.4) yield

$$\mathcal{D}_{\mathbf{k}}(t, t') = -i(C_{\mathbf{k}} + S_{\mathbf{k}})^2 [(N_{\mathbf{k}} + 1)e^{-i\Omega_{\mathbf{k}}|t-t'|} + N_{\mathbf{k}}e^{i\Omega_{\mathbf{k}}|t-t'|}] \quad (3.15)$$

$$\mathcal{F}_{\mathbf{k}}(t, t') = C_{\mathbf{k}}S_{\mathbf{k}}[(N_{\mathbf{k}} + 1)e^{i\Omega_{\mathbf{k}}|t-t'|} + N_{\mathbf{k}}e^{-i\Omega_{\mathbf{k}}|t-t'|}] \quad (3.16)$$

where $N_{\mathbf{k}} = \langle \Psi | b_{\mathbf{k}}^\dagger b_{\mathbf{k}} | \Psi \rangle$. Note that for $\kappa_{\mathbf{k}} = 0$, Equation (3.15) reduces to the normal phonon Green's functions and the anomalous part $\mathcal{F}_{\mathbf{k}}(t, t')$ vanishes.

The finite temperature self consistent equation for $\kappa_{\mathbf{k}}$ can be obtained by using the Green's function Eq.(3.16) in the zero temperature equation (3.10), as derived in Appendix A.4.

$$\kappa_{\mathbf{k}} = 6 \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}\mathbf{k}') \left[2 \frac{\kappa_{\mathbf{k}'}}{\Omega_{\mathbf{k}'}} \coth \frac{\Omega_{\mathbf{k}'}}{2kT} + \sqrt{1 + 4 \frac{\kappa_{\mathbf{k}'}}{\Omega_{\mathbf{k}'}}^2 \coth^2 \frac{\Omega_{\mathbf{k}'}}{2kT}} \right] \quad (3.17)$$

This nonlinear integral equation can only be solved numerically. In the course of the solution, the only external parameter is the pair-potential $V(\mathbf{k}, \mathbf{k}')$ given by the model (3.11). We calculate $V(\mathbf{k}, \mathbf{k}')$ for the optical B_{1g} phonon i.e. $\omega_{\mathbf{k}} = \omega_0 = 42 \text{ meV}$ and TTTT coupling. Since we use an isotropic continuum model for $V(\mathbf{k}, \mathbf{k}')$ the solution turns out to be isotropic in the momentum space as well. The solution of (3.17) at $k = k_0 = X$ for various values of λ_{p-p} as a function of temperature is shown in Figure (3.2).

The results show that the order parameter of low temperature anharmonicity, $\kappa_{\mathbf{k}}$, is a monotonically increasing function of temperature, in other words, phonon-phonon correlations seem to be an increasing function of temperature. But this is only true for low temperatures, low in Debye scale. High temperature anharmonicity will dominate at higher temperatures, and depairing rate due to third order anharmonicity will increase. These effects will blur the correlated order and above some temperature $\kappa_{\mathbf{k}}$ is expected to decline.

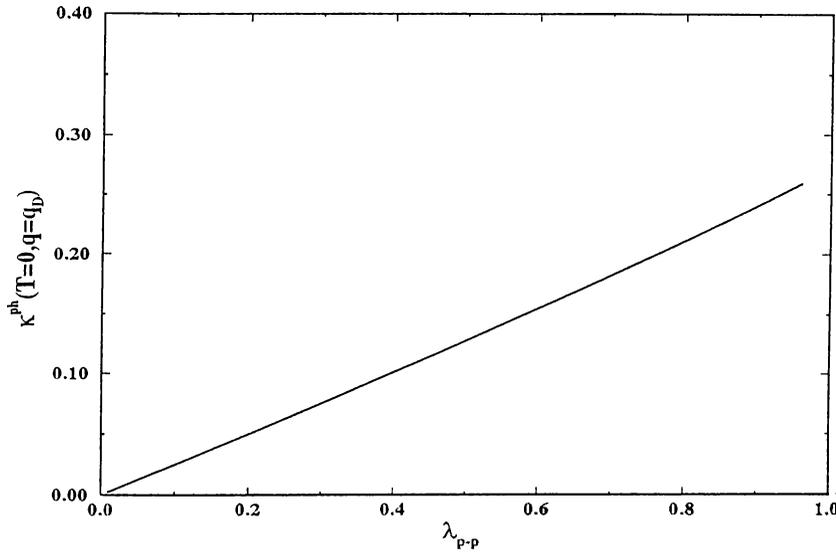


Figure 3.1: $\kappa(\mathbf{q} = X, T = 0)$ as a function of λ_{p-p}
 $\kappa(\mathbf{q})$ is calculated using the zero-temperature solution of the self-consistent equation (3.17) which is in conformity with the analytic solution (3.12) indicating linear dependence of $\kappa(\mathbf{q})$ on λ_{p-p}

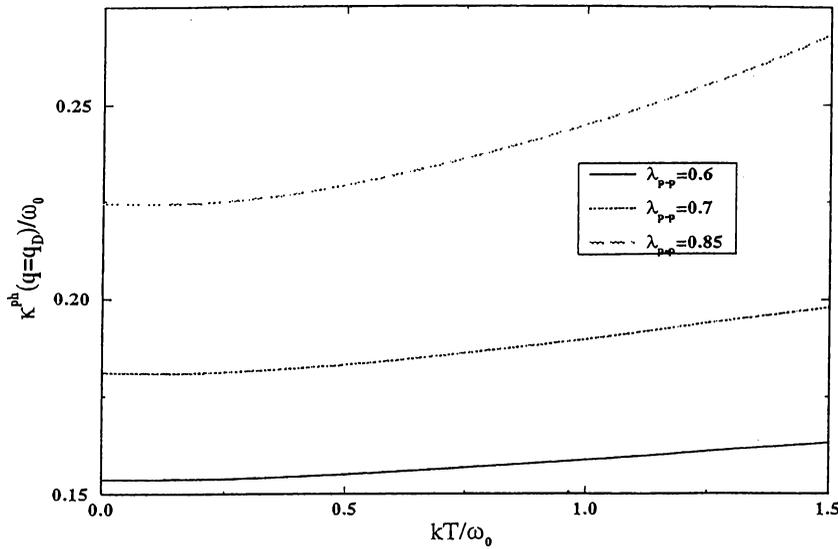


Figure 3.2: Finite Temperature Solution $\kappa(\mathbf{q} = X, T)$
 $\kappa(\mathbf{q} = X, T)$ is solved numerically from the non-linear self-consistent equation (3.17) for various λ_{p-p}

Chapter 4

ELECTRON-PHONON INTERACTION IN THE PRESENCE OF ANHARMONICITY

4.1 Introduction

There are numerous experimental findings which show undoubtedly that for oxide superconductors, electronic and vibrational degrees of freedom are strongly coupled in at least some portions of the phase space.

Several Raman scattering experiments have noted anomalous line shifts of specific lattice vibrational modes as the sample undergoes a normal to superconducting phase transition by lowering T across T_c . Most notable of all is the anomalous softening of the planar, z-polarized, optical mode at 340cm^{-1} first reported by Macfarlane *et al.*³⁸ in ceramic samples of $YBa_2Cu_3O_{7-x}$. Experiments performed on single crystals have shown that, the widths of the corresponding line shifts in temperature scale are rather sharp, i.e. within 20 K of T_c . Based on the polarization selection rules observed in light scattering, it has been proven³⁹ that this mode propagates in the CuO_2 -planes with its eigenvectors

in the z-direction (perpendicular to the planes); thus highlighting the relevance of these planes for the electron-phonon interaction. However, the intriguing fact is that, only selected phonon modes are modified by the superconducting transition, while others are not. These observed positive and negative shifts have been quantitatively explained by Zeyher and Zwicky by the conventional superconducting state, but assuming a strong coupling between electrons and phonons. According to their theory, a T_c of 91 K would correspond to an electron-phonon coupling constant of $\lambda \sim 2.9$ and to gap ratio $\Delta/\Delta_{BCS} = 1.41$. Their results, with the electron-phonon coupling constant of $\lambda \sim 2.9$, explains practically all the experimental data, obtained from optical experiments, concerning phonon self-energy effects due to superconductivity, namely, the absence of superconductivity-induced effects in 4 of the 5 Raman modes and the signs, relative magnitudes and the temperature dependence of the phonon shifts and widths.

Despite the success of the strong electron-phonon theory of Zeyher and Zwicky, this theory fails to explain some anomalies in the dynamical structure factor (DSF) observed at T_c . In recent inelastic neutron scattering experiments, performed by Arai *et al.*²³ an anomalous increase of approximately % 10 in DSF is observed in the vicinity of T_c for some specific high frequency optical vibrations, corresponding to Cu and O modes. Similar experiments performed by Toby *et al.*⁴⁰ have been reported to display an anomalous increase at T_c in the pair distribution function, and gave evidence on the anomalous correlations between the vibrations of the Cu and O atoms within a single unit cell. It can be concluded from these experimental findings that the apparent anomaly in phonon states in the short-wavelength region is associated with a local structural distortion of polaronic origin (Here the coupling of spin fluctuations to the externally polarized neutrons is ruled out, because of two reasons. Firstly, the observed wavevector shift is larger than 5\AA^{-1} , where the magnetic response dies out. Secondly, experiments with unpolarized neutron sources yield the same anomalies). It has been suggested that the characterization of these local structures in terms of a dynamical model naturally suggests polaronic mechanisms.^{41,42} In the most

general understanding, such effects imply the realization of a dynamical entangled ground state mixing electronic and vibrational degrees of freedom. As a result of strong electron-phonon interaction the ground state of the system can accommodate fluctuations with a finite number of phonons at very low temperatures.⁴¹

There are also arguments questioning the importance of electron-ion coupling for superconducting cuprates. Microscopic calculations of electron-phonon coupling and subsequent solutions of the Eliashberg's equations can explain T_c 's upto only 30 – 40 K thus proving that electron-phonon coupling by itself cannot account for $T_c = 92$ K in $YBa_2Cu_3O_7$. This theoretical result is supported by the virtually missing isotope shift in this compound.³

This conclusion is only valid if the ionic displacements δR caused by lattice polarization are small compared to lattice spacing R , $\delta R/R \ll 1$. In that case the harmonic approximation holds, and we are dealing with electrons, phonons and their interaction, the accurate description being Eliashberg's theory. If, however, the condition $\delta R/R \ll 1$ does not hold at least for some selected ionic movements, the harmonic approximation breaks down and phonons are no longer good quantum states. In this anharmonic regime, Eliashberg's theory is no longer the suitable frame. In this context, recent neutron-scattering experiments performed on single crystals of La_2CuO_4 indicate strong anharmonic effects, at least for some certain phonon modes.^{6,9} The most striking departure from harmonic behaviour is the existence of more peaks in phonon spectral density at a given wavenumber Q than the number for a harmonic crystal (three times the number of atoms in the unit cell). For Q along the (110) direction in La_2CuO_4 , for example, there would be 7 modes of Σ_1 symmetry in a harmonic crystal, while 8 or 9 spectral peaks are detected away from the zone center.

The aforementioned experimental results in this and previous chapters suggest that we use a model for the HTS which takes into account

- enhanced electron-phonon coupling in the planes
- low temperature anharmonicity of some phonon modes

for the study of the dynamical anomalies.

Low temperature anharmonicities of the lattice was discussed in Chapter 2, with the result that low temperature anharmonicity could effectively lead to a squeezed and momentum correlated ground state of the phonon subsystem with the degree of correlation ensued by a non-zero $\kappa_{\mathbf{k}}$, which is determined variationally. We now add the electron-phonon coupling into this picture in order to examine the influence of low temperature phonon anharmonicity on the coupled system. Similar non-perturbative, strongly coupled electron-phonon models have been suggested within the context of polaronic models of HTS.⁴¹⁻⁴³

Some preliminary qualitative estimates can be made by examining the effect of correlations on the ionic ground state in the real space. The ground state in question is connected with the broadened harmonic oscillator ionic ground state wavefunction⁴⁵ (super Gaussian). This corresponds (in the coordinate- $Q_{\mathbf{k}}$ -representation) to $\psi_0(Q_{\mathbf{k}}) = \langle Q_{\mathbf{k}} | \mathcal{S}(\{\xi_{\mathbf{k}}\}) | 0 \rangle$ and is given by,

$$\psi_0(Q_{\mathbf{k}}) = \sqrt{\frac{1}{\pi}} \left(\frac{M \omega_{\mathbf{k}}}{\hbar} \right) e^{-2\xi_{\mathbf{k}}} \exp\left\{ -\left(\frac{M \omega_{\mathbf{k}}}{2\hbar} e^{-4\xi_{\mathbf{k}}} \right) Q_{\mathbf{k}}^2 \right\} \quad (4.1)$$

Here the broadening factor $\exp(-2\xi_{\mathbf{k}})$ is due to $\xi_{\mathbf{k}} \neq 0$, and, $\langle (Q_{\mathbf{k}}^0)^2 \rangle = \frac{\hbar}{2M\omega_{\mathbf{k}}}$ is the average harmonic zero point fluctuation of ions with mass M and vibrational frequency $\omega_{\mathbf{k}}$. Hence the mean square displacement is enhanced by a factor $e^{4\xi_{\mathbf{k}}}$, i.e. $\langle Q_{\mathbf{k}}^2 \rangle = \langle (Q_{\mathbf{k}}^0)^2 \rangle e^{4\xi_{\mathbf{k}}}$. It should be noted that if we consider (A.6.4)

$$e^{4\xi_{\mathbf{k}}} = \frac{1}{2} \left\{ \left(\frac{\omega_{\mathbf{k}} + \Omega_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \right)^{1/2} + \left(\frac{\omega_{\mathbf{k}} - \Omega_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \right)^{1/2} \right\}^2 = \frac{\omega_{\mathbf{k}} + 2\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \quad (4.2)$$

we see that the same enhancement factor appears in the electron-phonon coupling (see Appendix A.6)

$$V^{e-e}(\mathbf{k}) = -\frac{|g_{\mathbf{k}}|^2}{\Omega_{\mathbf{k}}} \left[\frac{\omega_{\mathbf{k}} + 2\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \right] = -\frac{|g_{\mathbf{k}}|^2}{\Omega_{\mathbf{k}}} e^{4\xi_{\mathbf{k}}} \quad (4.3)$$

From above, $\langle (Q_{\mathbf{k}}^0)^2 \rangle \simeq (0.07)^2 \text{\AA}^2$ (M being the oxygen mass and $\omega_0 = 41 \text{meV}$), and from inelastic neutron scattering experiments¹⁵ we have $\langle Q_{\mathbf{k}}^2 \rangle \simeq (0.1)^2 \text{\AA}^2$ giving $\langle Q_{\mathbf{k}}^2 \rangle / \langle (Q_{\mathbf{k}}^0)^2 \rangle \simeq 2.04$. Hence, a crude estimate for the *order parameter* $\kappa_{\mathbf{k}}$ of the low temperature phonon correlations can be made using this simple

argument giving $\kappa_{\mathbf{k}}/\omega_0 \simeq 0.3$. This would lead to an enhancement factor of ~ 2.5 for the electron-phonon coupling.

Our model Hamiltonian consists of two parts: first part is the prominent Fröhlich Hamiltonian which describes the *linear* electron-phonon coupling and includes only the harmonic phonon contribution, whereas the second part describes the anharmonic contribution of the crystal potential.

4.2 Fröhlich Hamiltonian

The conventional theory of superconductivity⁴⁶ as well as many models for high T_c superconductivity are based on this model. To derive it we start with the first quantized formulation of the problem including harmonic phonons and a single band of Bloch electrons in a periodic lattice potential.

The Hamiltonian

$$\mathcal{H}_e = \sum_{i=1}^{N_e} \left(-\frac{\nabla_i^2}{2m_e} + V(\mathbf{r}_i) \right) \quad (4.4)$$

describes the dynamics of the electrons moving in the static lattice potential $V(\mathbf{r}_i)$. Here N_e is the total number of electrons and m_e is the bare electron mass.

$$V(\mathbf{r}) = \sum_{\mathbf{l}} v(\mathbf{r} - \mathbf{R}_{\mathbf{l}}) \quad (4.5)$$

is the potential energy in a crystal field distorted by phonons. The interaction of an electron with the crystal field at a single site is described in the Hartree approximation by the potential $v(\mathbf{r})$. In many solids the displacement of ions $\mathbf{u}_{\mathbf{l}} = \mathbf{R}_{\mathbf{l}} - \mathbf{l}$ from the equilibrium positions \mathbf{l} is small compared with a lattice constant a , which allows us to expand $v(\mathbf{r} - \mathbf{R}_{\mathbf{l}})$ near equilibrium

$$v(\mathbf{r} - \mathbf{R}_{\mathbf{l}}) \simeq v(\mathbf{r} - \mathbf{l}) - \mathbf{u}_{\mathbf{l}} \cdot \nabla v(\mathbf{r} - \mathbf{l}). \quad (4.6)$$

Furthermore we have the ionic Hamiltonian consisting of the ion kinetic energies and the ion-ion potential (crystal potential), the form of which is discussed in Appendix A.1. Here we will consider the expansion of crystal potential upto second order, i.e we will remain in harmonic approximation.

A zero order hamiltonian \mathcal{H}_0 , which includes the electron and ion kinetic energies, the periodic part of the crystal field and the ion-ion interaction can be diagonalized with the one particle Bloch states $\Psi_{\mathbf{q}}(\mathbf{r})$ and with vibrational field \mathbf{u}_l , given by

$$\mathbf{u}_l = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}}}} \mathbf{e}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{l}} (a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger) \quad (4.7)$$

where \mathbf{k} is the composite index representing phonon momenta and polarization, (\vec{k}, s) ; \mathbf{q} includes electron momentum, spin and band index, (\vec{q}, n, σ) ; $\mathbf{e}_{\mathbf{k}}$ is the unit polarization vector and $\omega_{\mathbf{k}}$ is the phonon frequency. As a result, the total Hamiltonian of an ionic crystal, including electron-phonon interaction \mathcal{H}_{e-ph} , in second quantized form becomes

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{e-ph} \quad (4.8)$$

where

$$\mathcal{H}_0 = \sum_{\mathbf{q}} \mathcal{E}_{\mathbf{q}} c_{\mathbf{q}}^\dagger c_{\mathbf{q}} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \quad (4.9)$$

and

$$\mathcal{H}_{e-ph} = \sum_{\mathbf{k}, \mathbf{q}} \gamma(\mathbf{k}, \mathbf{q}) c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{q}} (a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger) \quad (4.10)$$

with dimensionless electron-phonon matrix elements

$$\gamma(\mathbf{k}, \mathbf{q}) = -\sqrt{\frac{N}{2M\omega_{\mathbf{k}}^3}} \int d^3r (\mathbf{e}_{\mathbf{k}} \cdot \nabla v(\mathbf{r})) \psi_{\mathbf{k}+\mathbf{q}}^*(\mathbf{r}) \psi_{\mathbf{q}}(\mathbf{r}). \quad (4.11)$$

If

$$\gamma(\mathbf{k}, \mathbf{q}) = \gamma(\mathbf{k}) \quad (4.12)$$

the interaction is translationally invariant and is the origin of what we call Fröhlich interaction.

4.3 Superconducting Fröhlich Interaction in Presence of Anharmonicity

To the Fröhlich Hamiltonian derived in last section we add now the fourth order anharmonic phonon interaction term to account for the anharmonicities reported

in the experiments. The full hamiltonian then becomes

$$\begin{aligned} \mathcal{H} = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}} \omega_{\mathbf{k}} (a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + 1/2) + \sum_{\mathbf{q}, \mathbf{k}} \gamma(\mathbf{k}) c_{\mathbf{k}+\mathbf{q}} c_{\mathbf{q}}^{\dagger} (a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger}) \\ + \frac{1}{4!} \sum_{\mathbf{q}, \mathbf{k}} V_{\mathbf{k} \mathbf{k}'} Q_{\mathbf{k}} Q_{-\mathbf{k}} Q_{\mathbf{k}'} Q_{-\mathbf{k}'} \end{aligned} \quad (4.13)$$

where the last term was defined in Chapter 2. We consider for the electron-phonon coupling $\gamma_b(\mathbf{k})$ of the out-of-plane-polarized planar high frequency buckling mode as,³⁹

$$|\gamma_b(\mathbf{k})|^2 = 4 \lambda_b^2 (\sin^2 k_x / 2 + \sin^2 k_y / 2) . \quad (4.14)$$

Using tight binding effective single band diagonalization, Song and Annett⁴⁷ have obtained the magnitudes of the coupling constant λ_b for the LSCO compound at the $\vec{k} = X$ point of the BZ. Naturally for YBCO similar magnitudes are expected due to the common Cu-O planar bonding. However we will keep λ_b as a phenomenological parameter in our model.

The linearization of the anharmonic hamiltonian is accomplished as described in Appendix A.3. Following the procedure outlined there

$$\begin{aligned} \mathcal{H}^{eff} &= \hat{S}(\{\xi^{ph}\}) \mathcal{H} \hat{S}^{\dagger}(\{\xi^{ph}\}) \\ &= \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}}^{ph} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + 1/2) \\ &\quad + \sum_{\mathbf{q}, \mathbf{k}} \gamma(\mathbf{k}) (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph}) c_{\mathbf{k}+\mathbf{q}}^{\dagger} c_{\mathbf{q}} (b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger}) \end{aligned} \quad (4.15)$$

where $C_{\mathbf{k}}^{ph} = \cosh 2\xi_{\mathbf{k}}^{ph}$, $S_{\mathbf{k}}^{ph} = \sinh 2\xi_{\mathbf{k}}^{ph}$, the renormalized dispersion is

$$\Omega_{\mathbf{k}}^{ph} = e^{-4\xi_{\mathbf{k}}^{ph}} \omega_{\mathbf{k}} = \sqrt{\tilde{\omega}_{\mathbf{k}}^2 - 4(\kappa_{\mathbf{k}}^{ph})^2} \quad (4.16)$$

and $b_{\mathbf{k}}(b_{\mathbf{k}}^{\dagger})$ are given by the Bogoliubov transformation (A.3.3) in terms of $a_{\mathbf{k}}(a_{\mathbf{k}}^{\dagger})$. All the relations given in Appendices A.3 and A.4 hold here too, with $(\xi_{\mathbf{k}}^{ph} \leftrightarrow \xi_{\mathbf{k}})$.

Following Lang and Firsov (1962)^{48,49} one can apply on \mathcal{H}^{eff} a canonical unitary transformation to decouple electronic and vibrational degrees of freedom within \mathcal{H}^{eff} . For our case, this unitary transformation is given by

$$\mathcal{U} = \exp \left\{ \sum_{\mathbf{k}, \mathbf{q}} \frac{\gamma_{\mathbf{k}}}{\hbar \Omega_{\mathbf{k}}^{ph}} (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph}) c_{\mathbf{q}}^{\dagger} c_{\mathbf{k}+\mathbf{q}} (b_{\mathbf{k}}^{\dagger} - b_{-\mathbf{k}}) \right\} \quad (4.17)$$

Applying (4.17) onto \mathcal{H}^{eff} the transformed decoupled hamiltonian is given by

$$\begin{aligned} \mathcal{H}' &= \mathcal{U}^{\dagger} \mathcal{S}^{\dagger} \mathcal{H} \mathcal{S} \mathcal{U} \\ &= \sum_{\mathbf{q}} \tilde{\mathcal{E}}_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}}^{ph} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + 1/2) \\ &\quad + \sum_{\mathbf{q}, \mathbf{k}, \mathbf{q}'} \frac{|\gamma(\mathbf{k})|^2}{\Omega_{\mathbf{k}}^{ph}} (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^2 c_{\mathbf{k}+\mathbf{q}}^{\dagger} c_{\mathbf{q}'-\mathbf{k}}^{\dagger} c_{\mathbf{q}} c_{\mathbf{q}'} \end{aligned} \quad (4.18)$$

Note that the four-electron term is in conventional BCS-ordered form, where $\tilde{\mathcal{E}}_{\mathbf{q}}$ now accomodates the polaron binding and band narrowing effects. The perturbative expansion of $\tilde{\mathcal{E}}_{\mathbf{q}}$ including second order terms with respect to $\gamma(\mathbf{k})$ is given in the polaronic ground state by,

$$\begin{aligned} \tilde{\mathcal{E}}_{\mathbf{q}} &= \mathcal{E}_{\mathbf{q}} - \sum_{\mathbf{k}'} \left(\frac{|\gamma(\mathbf{k}')|}{\hbar \Omega_{\mathbf{k}'}} \right)^2 e^{-4\xi_{\mathbf{k}'}} (\mathcal{E}_{\mathbf{q}+\mathbf{k}'} + \mathcal{E}_{\mathbf{q}-\mathbf{k}'} - 2\mathcal{E}_{\mathbf{k}'}) \\ &\quad + \sum_{\mathbf{k}'} \frac{|\Upsilon(\mathbf{q} + \mathbf{k}')|^2}{\hbar \Omega_{\mathbf{q}+\mathbf{k}'}} \end{aligned} \quad (4.19)$$

In the strong coupling limit Eq. (4.19) provides a similar band narrowing effect as Holstein reduction factor with the main difference being the $e^{-4\xi_{\mathbf{k}'}}$ factor arising from the momentum correlations in the ground state.⁴³ The factor in the bracket of the second term is equal to $(\partial^2 \mathcal{E}_{\mathbf{k}'} / \partial \mathbf{k}'^2) \mathbf{q}^2$ and contributes to the polaron effective mass. The third term comes from reordering of the electron operators into the conventional BCS normal ordered form.

The intricate physics inherent in and between the two successive transformations can be elucidated. The transformation \mathcal{U} in simplest terms, is analogous

to the displacement operator for phonons i.e. it *formally* shifts the equilibrium position of the phonon ground state such that the displacements of the normal mode $|\mathbf{k}\rangle$ is displaced by $\rho^\dagger(\mathbf{k})|\Psi_e\rangle = \sum_{\mathbf{q}} c_{\mathbf{q}}^\dagger c_{\mathbf{k}+\mathbf{q}}|\Psi_e\rangle$, where $|\Psi_e\rangle$ is the electronic part of the wavefunction. This allows us to treat part of the recoil energy of the k^{th} phonon mode from the scattered Bloch electrons in a convenient way. It is well known that the recoil cuts off the energy transfer between the particles and the phonon field. Hence this is a way to pass the coupling of the phonons to electrons from the hamiltonian to the wave functions. The Hamiltonian \mathcal{H}' is now seperable, and we can now factor out the eigenfunction as

$$|\Psi\rangle = |\Psi_{ph}\rangle \otimes |\Psi_e\rangle \quad (4.20)$$

where $|\Psi\rangle$ is the eigenfunction of \mathcal{H}' , $|\Psi_{ph}\rangle$ and $|\Psi_e\rangle$ that of phononic and *polaronic* seperable parts. But in spite of this, the transformation \mathcal{U} mixes the two degrees of freedom *dynamically*. This way of dealing with the electron-phonon interaction is quite prominent in the polaron theory. However, in our treatment we introduce a new ground state for the phonon subsystem, namely a squeezed vacuum state (see Appendix A.2), contrary to the generally held practice to take a normal vacuum state. At low temperatures this is a good approximation due to the suppression of the thermal excitations of the phonon spectrum. Thus the phonon state is given by

$$|\Psi_{ph}\rangle = \mathcal{U}\mathcal{S}|0\rangle \quad (4.21)$$

and is a dynamically displaced, two-phonon correlated ground state.

In addition to a simple shift from squeezed vacuum to a coherent squeezed state which is parametrized by the mean occupation $\langle\rho(\mathbf{k})\rangle = \langle\sum_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{q}}\rangle$, the transformation \mathcal{U} also permits fluctuations around this shift, since it includes the shift in operator form. Conversely since \mathcal{U} also acts on the electronic ground state $|\Psi_e\rangle$ and the action includes phonon momentum $i(a_{\mathbf{k}}^\dagger - a_{\mathbf{k}})$ the fluctuations around $\langle\rho(\mathbf{k})\rangle$ are determined by the phonon variables. At this stage we assert that

- the *incoherent* fluctuations of the phonon state around the coherent mean

value $\langle \rho(\mathbf{k}) \rangle$ can to lowest order be represented by an effective squeezed state.

At this point we should also mention that $|\Psi_e\rangle$ for the electron subsystem is assumed to be of BCS type⁴⁶

$$|BCS\rangle = \prod_{\mathbf{q}} (u_{\mathbf{q}} + v_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{-\mathbf{q}}^{\dagger}) |vac\rangle \quad (4.22)$$

here $|vac\rangle$ is the electronic vacuum state and

$$u_{\mathbf{q}}^2 = \frac{1}{2} \left(1 + \frac{\tilde{\mathcal{E}}_{\mathbf{q}}}{E_{\mathbf{q}}} \right), \quad (4.23)$$

$$v_{\mathbf{q}}^2 = \frac{1}{2} \left(1 - \frac{\tilde{\mathcal{E}}_{\mathbf{q}}}{E_{\mathbf{q}}} \right), \quad (4.24)$$

$$E_{\mathbf{q}} = (\tilde{\mathcal{E}}_{\mathbf{q}}^2 + \Delta_{\mathbf{q}}^2)^{1/2} \quad (4.25)$$

as usual, and $\Delta_{\mathbf{q}}$ is the superconducting gap. Obviously such a treatment of $|\Psi_e\rangle$ is based on the assumption that the phonon-induced attraction between polarons overcompensates for the Coulomb repulsion between them.

Then *coherent* part of the phonon ground state fluctuations is given by

$$\langle a_{\mathbf{k}} \rangle = \langle \Psi | a_{\mathbf{k}} | \Psi \rangle = (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^2 \frac{\gamma(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \langle \rho^{\dagger}(\mathbf{k}) \rangle_{BCS} \quad (4.26)$$

where as promised, $|\Psi\rangle = \mathcal{U}S(\xi^{ph})|0\rangle \otimes |BCS\rangle$.

Thus a transformation defined by

$$\begin{aligned} \mathcal{U}_c &= \exp \left\{ \sum_{\mathbf{k}} \frac{\gamma(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}} (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^2 \langle \rho^{\dagger}(\mathbf{k}) \rangle (a_{\mathbf{k}}^{\dagger} - a_{-\mathbf{k}}) \right\} \\ &= \exp \left\{ \sum_{\mathbf{k}} \frac{\gamma(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}} (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph}) \langle \rho^{\dagger}(\mathbf{k}) \rangle (b_{\mathbf{k}}^{\dagger} - b_{-\mathbf{k}}) \right\} \end{aligned} \quad (4.27)$$

would extract from the ground state $|\Psi_{ph}\rangle = \mathcal{U}S|0\rangle$ the pure coherent component.

So, our assertion is that the fluctuating part of the ground state, which is responsible for all incoherent fluctuations, can be reached if we transform out (shift in phase space) the pure coherent part as

$$|\Psi_{ph}\rangle_{ic} = \mathcal{U}_c^\dagger \mathcal{U} \mathcal{S}(\xi^{ph}) |0\rangle \quad (4.28)$$

where *ic* stands for incoherent fluctuations. If such fluctuations are nonzero then $\xi_{\mathbf{q}} \neq 0$ and $|\Psi_{ph}\rangle_{ic}$ is different from the vacuum state with the leading corrections arising from the two-phonon correlations. Let's consider a unitary operator $\mathcal{S}(\tilde{\xi}) \simeq [\mathcal{U}_c^\dagger \mathcal{U}] \mathcal{S}(\xi^{ph})$ such that $|\Psi_{ph}\rangle_{ic} = \mathcal{S}(\tilde{\xi})|0\rangle$. Then $\mathcal{S}(\{\tilde{\xi}\})$ is the effective operator creating these two-phonon correlations. This operation decouples the phonon ground state $|\Psi_{ph}\rangle$ from its one-phonon coherent part enabling to extract the genuine two-phonon correlations. Hence $|\Psi_{ph}\rangle = \mathcal{U}_c |\Psi_{ph}\rangle_{ic}$.

Above, $\{\tilde{\xi}_{\mathbf{k}}\}$ must be determined in such a way that $|\Psi_{ph}\rangle_{ic}$ can properly account for all dynamical phonon correlations including the low temperature anharmonic phonon [i.e. $\xi_{\mathbf{k}}^{ph}$ as in Equations (4.31) and (3.7)] as well as electron-phonon origin. Namely, one can define an effective phonon correlation order parameter $\kappa_{\mathbf{k}}$ such that,

$$\phi(\mathbf{k}) =_{ic} \langle \Psi_{ph} | a_{\mathbf{k}} a_{-\mathbf{k}} | \Psi_{ph} \rangle_{ic} = \frac{\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} . \quad (4.29)$$

The left hand side can be calculated using the following relations

$$\begin{aligned} \mathcal{U}^\dagger \mathcal{U}_c a_{\mathbf{k}} \mathcal{U}_c^\dagger \mathcal{U} &= (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^2 \frac{\gamma(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \delta \rho^\dagger(\mathbf{k}) + a_{\mathbf{k}} \\ \mathcal{U}^\dagger \mathcal{U}_c a_{-\mathbf{k}} \mathcal{U}_c^\dagger \mathcal{U} &= (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^2 \frac{\gamma(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \delta \rho(\mathbf{k}) + a_{-\mathbf{k}} \end{aligned} \quad (4.30)$$

where $\delta \rho(\mathbf{k}) = \rho(\mathbf{k}) - \langle \rho(\mathbf{k}) \rangle$. Writing out (4.29) explicitly

$$\begin{aligned} &\langle BCS | \otimes \langle \xi^{ph} | \mathcal{U}^\dagger \mathcal{U}_c a_{\mathbf{k}} a_{-\mathbf{k}} \mathcal{U}_c^\dagger \mathcal{U} | \xi^{ph} \rangle \otimes | BCS \rangle \\ &= \frac{\kappa_{\mathbf{k}}^{ph}}{\Omega_{\mathbf{k}}^{ph}} + (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})^4 \frac{|\gamma(\mathbf{k})|^2}{(\hbar \Omega_{\mathbf{k}}^{ph})^2} \langle \delta \rho^\dagger(\mathbf{k}) \delta \rho(\mathbf{k}) \rangle_{BCS} \end{aligned} \quad (4.31)$$

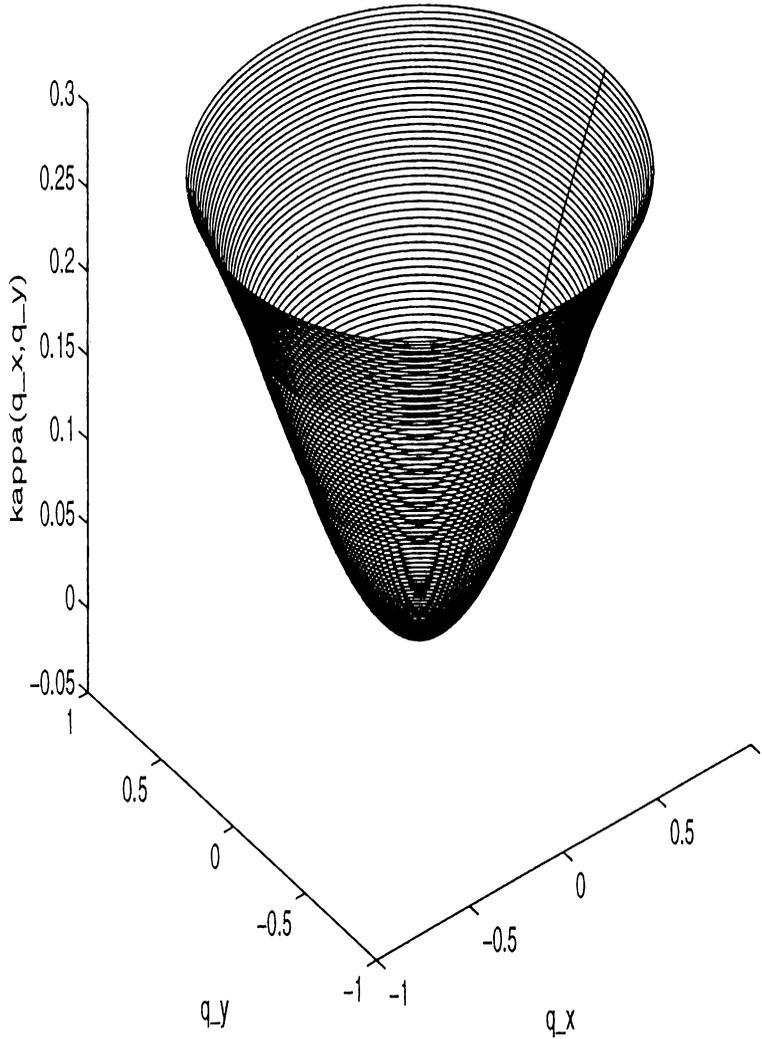


Figure 4.1: Full dependence of $\kappa_{\mathbf{q}}(T=0)$ on momenta for a typical coupling

where $|\xi^{ph}\rangle = \mathcal{S}(\xi^{ph})|0\rangle$. Finally we obtain a self-consistent equation for the effective squeezing parameter $\kappa_{\mathbf{k}}$ as

$$\frac{\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} = \frac{\kappa_{\mathbf{k}}^{ph}}{\Omega_{\mathbf{k}}^{ph}} + \frac{\omega_{\mathbf{k}}^2 |\gamma(\mathbf{k})|^2}{\hbar^2 (\Omega_{\mathbf{k}}^{ph})^4} \langle \delta\rho^\dagger(\mathbf{k}) \delta\rho(\mathbf{k}) \rangle_{BCS} \quad (4.32)$$

where we used the result (A.3.19). Note that the above equation reduces to

the previously derived result for anharmonic phonons in the absence of Fröhlich interaction ($\gamma(\mathbf{k}) = 0$).

4.4 Results

It was shown in the Appendix A.6, remaining in weak coupling formalism, that externally driven phonon correlations enhance the electron-electron interaction

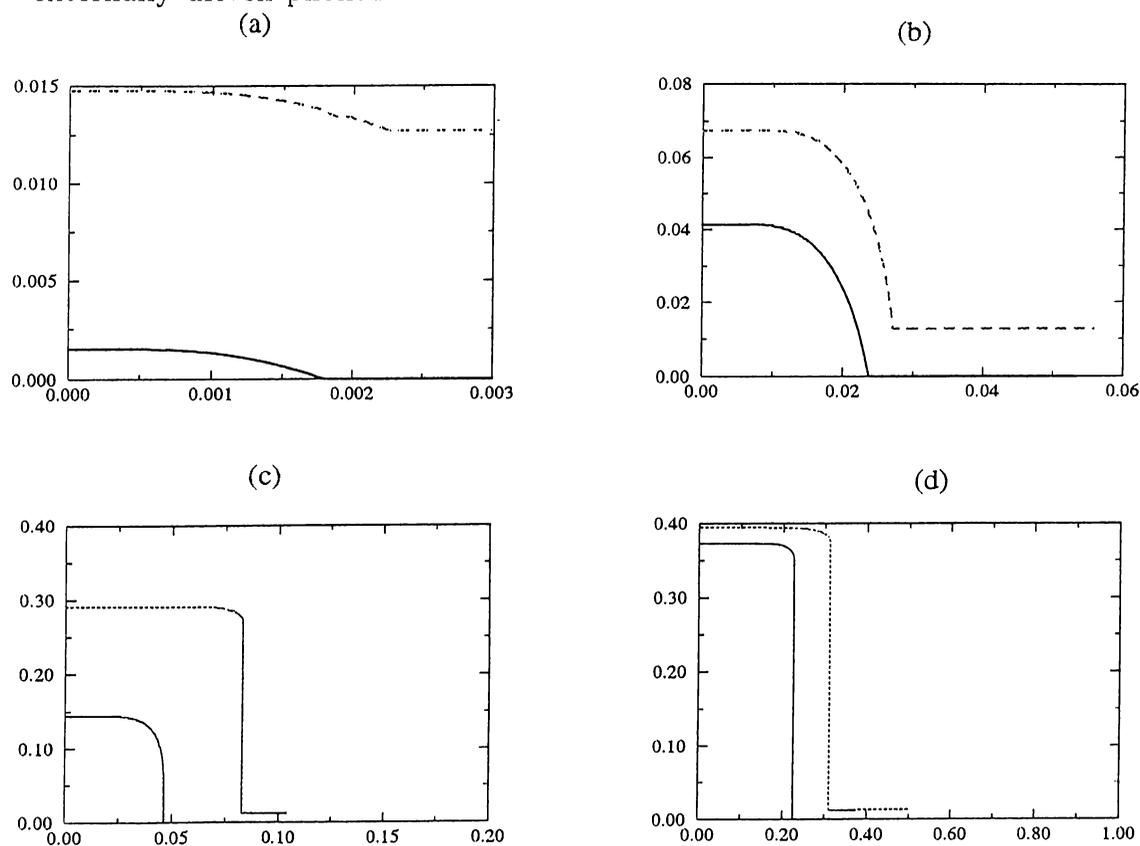


Figure 4.2: Temperature dependence of the low temperature phonon correlations $\kappa(\mathbf{q} = \mathbf{X}, T)/\omega_0$ vs. kT/ω_0 for particular values of λ_{p-p} and λ_{e-e} . dashed: $\lambda_{p-p} = 0.05$, solid: $\lambda_{p-p} = 0$ (a) $\lambda_{e-e} = 0.15$ (b) $\lambda_{e-e} = 0.25$ (c) $\lambda_{e-e} = 0.30$ (d) $\lambda_{e-e} = 0.35$

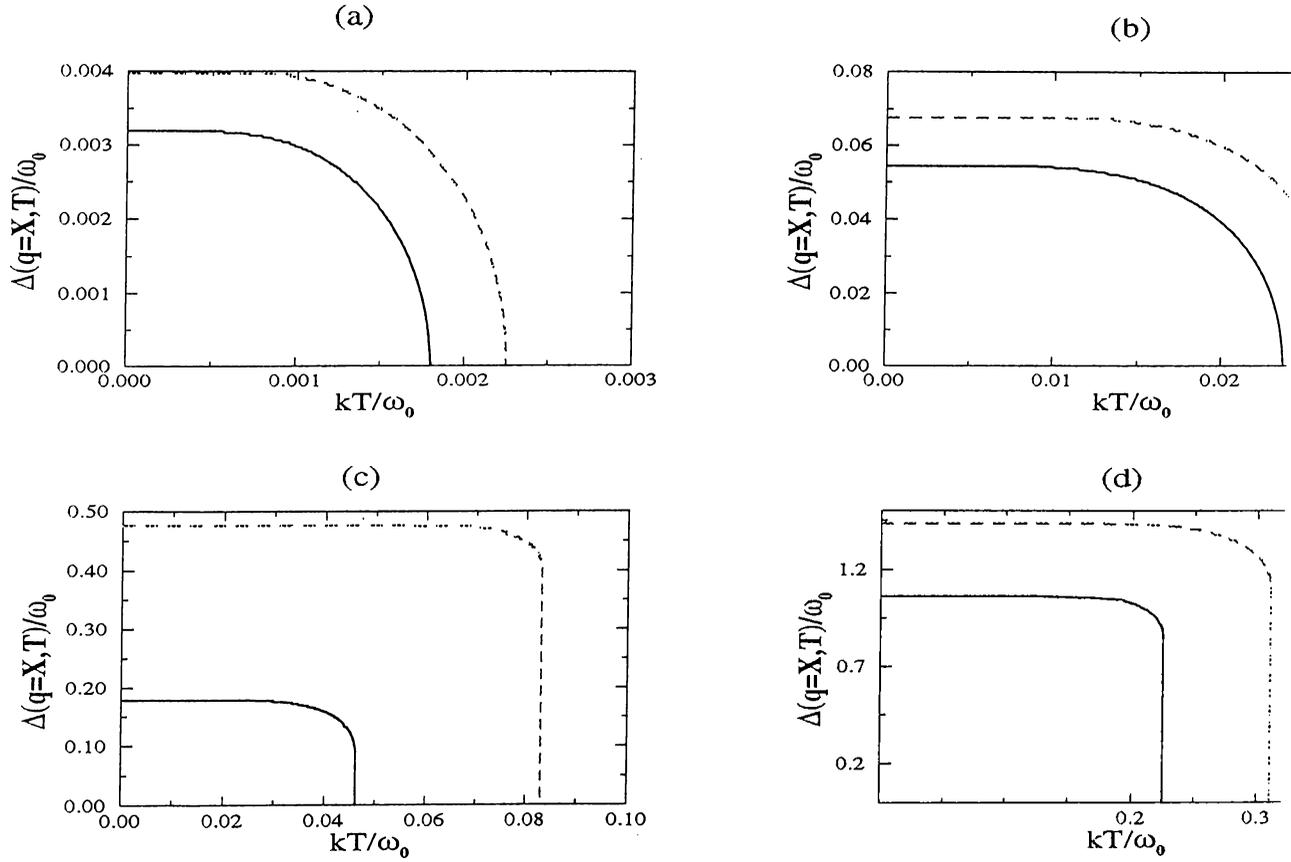


Figure 4.3: Temperature dependence of $\Delta(\mathbf{q} = \mathbf{X}, \mathbf{T})$

The BCS like gap energy $\Delta(\mathbf{q} = \mathbf{X}, \mathbf{T})$ for particular values of λ_{p-p} and λ_{e-e} . dashed: $\lambda_{p-p} = 0.05$, solid: $\lambda_{p-p} = 0$ (a) $\lambda_{e-e} = 0.15$ (b) $\lambda_{e-e} = 0.25$ (c) $\lambda_{e-e} = 0.30$ (d) $\lambda_{e-e} = 0.35$

(A.6.9). In our self-consistent scheme here, phonon correlations are driven internally and they are coupled to superconducting ground state properties given by Equations (4.22-4.25). Hence we can close our self consistency loop by including the BCS gap equations. The set of equations to be solved self-consistently becomes

$$\Delta(\mathbf{q}) = - \int \frac{d\mathbf{q}'}{(2\pi)^2} V^{e-e}(\mathbf{q} - \mathbf{q}') \mathcal{F}(\mathbf{q}') \quad (4.33)$$

$$\mathcal{F}(\mathbf{q}) = -\frac{1}{\beta} \sum_n \frac{\Delta(\mathbf{q})}{\omega_n^2 + \xi_{\mathbf{q}}^2 + \Delta^2(\mathbf{q})} \quad (4.34)$$

$$V^{e-e}(\mathbf{q}) = -\frac{|\gamma(\mathbf{q})|^2}{\Omega_{\mathbf{q}}} \left[\frac{\omega_{\mathbf{q}} + 2\kappa_{\mathbf{q}}}{\Omega_{\mathbf{q}}} \right] \quad (4.35)$$

$$\frac{\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} = \frac{\kappa_{\mathbf{k}}^{ph}}{\Omega_{\mathbf{k}}^{ph}} + \frac{\omega_{\mathbf{k}}^2 |\gamma(\mathbf{k})|^2}{\hbar^2 (\Omega_{\mathbf{k}}^{ph})^4} \langle \delta\rho^\dagger(\mathbf{k}) \delta\rho(\mathbf{k}) \rangle_{BCS} \quad (4.36)$$

$$\kappa_{\mathbf{k}}^{ph} = 6 \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}\mathbf{k}') \left[2 \frac{\kappa_{\mathbf{k}'}^{ph}}{\Omega_{\mathbf{k}'}^{ph}} \coth \frac{\Omega_{\mathbf{k}'}^{ph}}{2kT} + \sqrt{1 + 4 \left(\frac{\kappa_{\mathbf{k}'}^{ph}}{\Omega_{\mathbf{k}'}^{ph}} \right)^2 \coth^2 \frac{\Omega_{\mathbf{k}'}^{ph}}{2kT}} \right] \quad (4.37)$$

and $\mathcal{F}(\mathbf{q}) = \langle BCS | c_{\mathbf{q}\sigma} c_{-\mathbf{q}-\sigma} | BCS \rangle$ describes the anomalous pairing.

These complicated coupled non-linear integral equations can be solved numerically for the superconductive gap $\Delta_{\mathbf{q}}(T)$ and the effective squeezing parameter $\kappa_{\mathbf{q}}(T)$. First $\kappa_{\mathbf{q}}^{ph}(T)$ is calculated for a specific phonon-phonon coupling constant λ_{p-p} . This was accomplished in Chapter 3. Next, Equations (4.33-4.36) are solved self-consistently. Note that the self-consistency in Equation (4.36) derives from the fact that, $\kappa_{\mathbf{q}}$ depends on charge fluctuations $\langle \delta\rho^\dagger(\mathbf{k}) \delta\rho(\mathbf{k}) \rangle_{BCS}$, which in turn depend on $\Delta_{\mathbf{q}}(T)$ and hence on the form of $V^{e-e}(\mathbf{q})$ which is enhanced by $\kappa_{\mathbf{q}}$. A typical momentum dependent zero temperature solution of $\kappa_{\mathbf{q}}$ is given in Fig.(4.1). The temperature dependent solutions for $\Delta_{\mathbf{q}}(T)$ and $\kappa_{\mathbf{q}}(T)$ at a specific \mathbf{q} -point, namely at X-point of the Brillouin zone is given in Fig.(4.3) and Fig.(4.2) respectively, for various values of electron-electron coupling λ_{e-e} and phonon-phonon coupling λ_{e-p} .

Two parameters play a role in determining the specific form of $\Delta_{\mathbf{q}}(T)$ and $\kappa_{\mathbf{q}}(T)$. These are the phonon-phonon coupling constant λ_{p-p} defined in Chapter 3 and an effective electron-electron coupling λ_{e-e} , which is identified by the $\kappa_{\mathbf{q}} = 0$ solution, having the form $\lambda_{e-e} = \frac{\langle |\gamma_{\mathbf{b}}(\mathbf{k})|^2 \rangle_{FS}}{\omega_0} \rho(0)$ with $\rho(0)$ representing the electron density of states on the Fermi surface. They determine the relative contributions of phonon-anharmonicity and electron-phonon coupling to the correlated phonon subsystem. Depending on relative strength of these parameters, we obtain different values for T_c , Δ and Δ/T_c ratio or the effective

λ_{e-e}	λ_{p-p}	Δ/T_c
0.15	0.05	1.767
	0.0	1.765
0.25	0.05	2.48
	0.0	2.28
0.30	0.05	5.75
	0.0	3.86

Table 4.1: The variation of the dimensionless Δ/T_c ratio around the BCS value 1.76 for different values of λ_{p-p} and λ_{e-e} .

order parameter $\kappa\mathbf{q}(T)$.

The results are shown for the case of $\lambda_{p-p} = 0.05$, which is the calculated value from Table 2.1 for YBCO, and for $\lambda_{p-p} = 0$. Four values of electron-electron coupling is considered for each of λ_{p-p} . The results at the first sight indicate that there is an enhancement in $\Delta\mathbf{q}(0)$ and $\kappa\mathbf{q}(0)$ for increasing values of λ_{e-e} . Furthermore it is also observed that, for higher λ_{e-e} the transition to normal state becomes sharper. In Table 4.1 below the deviation of the dimensionless $\Delta(0)/T_c$ ratio is shown for different λ_{e-e} and λ_{p-p} . Results are always larger than the BCS limit of $\Delta(0)/T_c \simeq 1.76$ as expected and within the range of physical coupling strengths the electronic contribution is considerably larger than that of λ_{p-p} .

4.5 Dynamical Structure Factor

The main motivation of this self consistent approach is the observation of the temperature dependent critical anomaly of the dynamical structure factor²³

$S(\mathbf{k}, \omega)$ in the vicinity of T_c for YBCO and LSCO based compounds using inelastic neutron scattering. Similar anomalies have also been observed for the Tl(2212) compound⁴⁰ in the dynamical pair distribution function measurements. The fluctuation of the pair distribution function is the crucial quantity to examine the observed temperature anomalies and is simply related to the Fourier transform of the static structure factor $S(\mathbf{k})$ as,

$$\delta g(\mathbf{r}) = \int_{-\infty}^{\infty} \frac{d\mathbf{k}}{(2\pi)^2} e^{-i\mathbf{k}\cdot\mathbf{r}} [1 - S(\mathbf{k})] \quad (4.38)$$

where $S(\mathbf{k}) = \int d\omega S(\mathbf{k}, \omega)$ and,

$$S(\mathbf{k}, \omega) = \int dt e^{-i\omega t} \frac{1}{N} \sum_{\langle i,j \rangle} e^{-\mathbf{k}\cdot\Delta\mathbf{R}_{ij}} \langle e^{-i\mathbf{k}\cdot\mathbf{u}_i(t)} e^{i\mathbf{k}\cdot\mathbf{u}_j(0)} \rangle \quad (4.39)$$

In Eq.(4.38), the anomalous temperature dependence of $\delta g(\mathbf{r})$ is given by that of the structure factors. Hence, to examine the effects of the low temperature dynamics of (4.13) on the DSF, one has to follow the prescription to calculate $S(\mathbf{k}, \omega)$ exclusively in the dynamically correlated polaronic ground state $|\Psi_{ph}\rangle_{ic} = S(\tilde{\xi})|0\rangle$. A routine calculation yields,

$$S(\mathbf{k}) = \frac{1}{N} \sum_{\langle ij \rangle} \exp\left\{-\frac{1}{N} \sum_{\mathbf{k}',s} \frac{\hbar}{M\Omega_{\mathbf{k}'}} |\mathbf{k}\cdot\mathbf{e}_{\mathbf{k}'}|^2 (C_{\mathbf{k}'} + S_{\mathbf{k}'})^2 (2N_{\mathbf{k}'} + 1) [1 - \cos(\mathbf{k}'\cdot\Delta\mathbf{R}_{ij})]\right\} \quad (4.40)$$

In (4.40), the Debye-Waller factor $W_{\mathbf{k}}$ is identified by,

$$W_{\mathbf{k}} = \frac{1}{N} \sum_{\mathbf{k}'} \frac{\hbar}{2M\Omega_{\mathbf{k}'}} |\mathbf{k}\cdot\mathbf{e}_{\mathbf{k}'}|^2 (C_{\mathbf{k}'} + S_{\mathbf{k}'})^2 (2N_{\mathbf{k}'} + 1) \quad (4.41)$$

and, $(C_{\mathbf{k}'} + S_{\mathbf{k}'})^2 = e^{4\xi_{\mathbf{k}'}}$ as the temperature dependent enhancement factor of the zero point fluctuations as given by the solution of (4.32). In (4.40) the thermal occupation factor is $N_{\mathbf{k}} = [\exp(\beta\Omega_{\mathbf{k}}) + 1]^{-1}$ where $\Omega_{\mathbf{k}}$ is as given above Eq. (A.3.19). For $\tilde{\xi}_{\mathbf{k}} = 0$ the Equations(4.40) and (4.41) reduce to their well-known harmonic limit. In real crystals, the anomalous temperature dependence of the Debye-Waller factor is usually considered as a signature for multiphonon interaction.^{50,51} However, such anharmonic effects are usually calculated either

perturbatively or by using self-consistent harmonic approximation without inquiring in detail the specific properties of the low temperature, non-perturbative ground state. The temperature anomalies considered arise from the temperature dependence of $\tilde{\xi}_{\mathbf{k}}$. From the solution of Equations (4.33)-(4.37) the temperature dependence of the Debye-Waller factor can be calculated in the vicinity of T_c . At temperatures below T_c two factors contribute to the anomalous temperature dependence of the structure factor. These are the dynamically enhanced electron-phonon interaction due to phonon coupling to superconducting charge density fluctuations and the low temperature anharmonic phonons. Both factors increase the amplitude of the zero point vibrations which results in an enhancement in the Debye-Waller factor at low temperatures below T_c . The harmonic contribution as well as the thermal anharmonic scattering produce a hyperbolic increase in Debye-Waller factor with respect to temperature. The numerical solution of $\exp(-W_{\mathbf{q}})$ as a function of temperature is given in Fig.(4.4,4.5). The structure factor data of Arai *et al.*²³ is shown in the inset. The theory has the qualitative features of the data within a reasonable range of coupling constants.

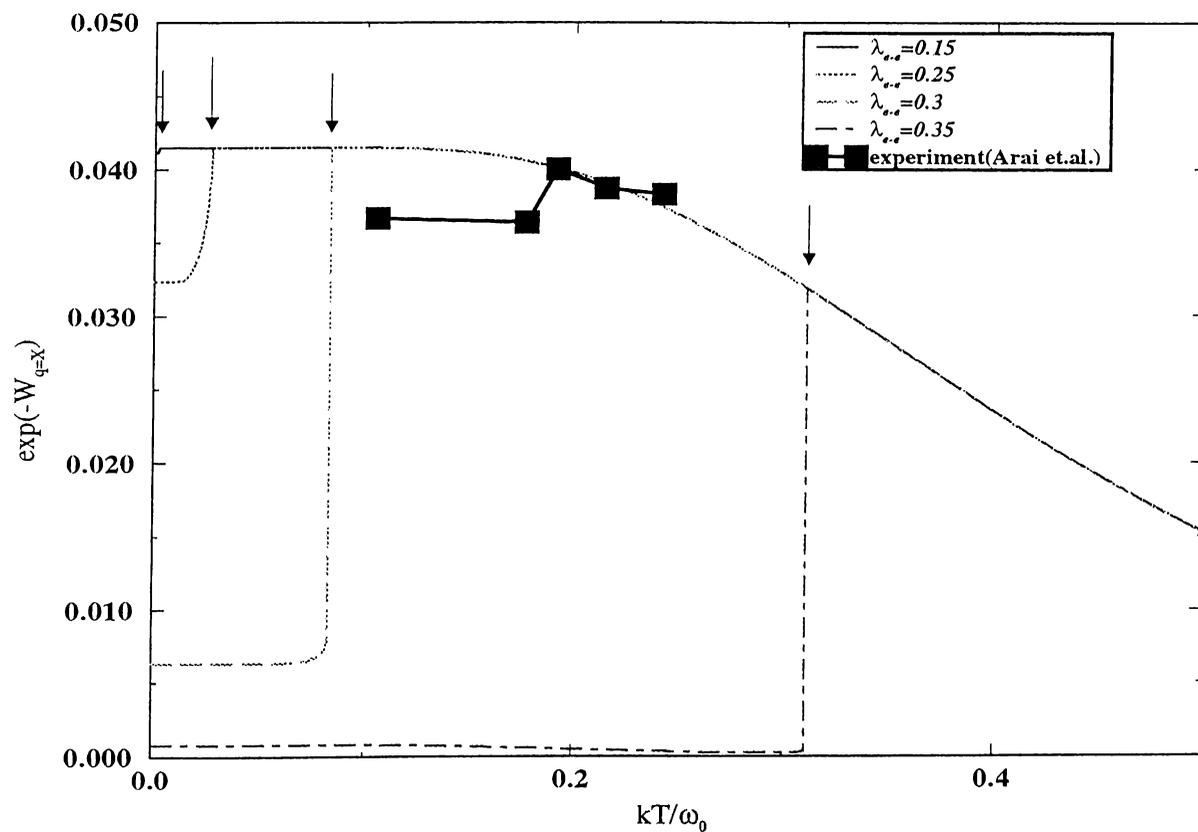


Figure 4.4: Calculated Debye-Waller factors showing anomaly at T_c for YBCO $\exp(-W_{\mathbf{q}})$ vs. Temperature for YBCO, $\lambda_{p-p} = 0.05$ for various electron-electron couplings λ_{e-e}

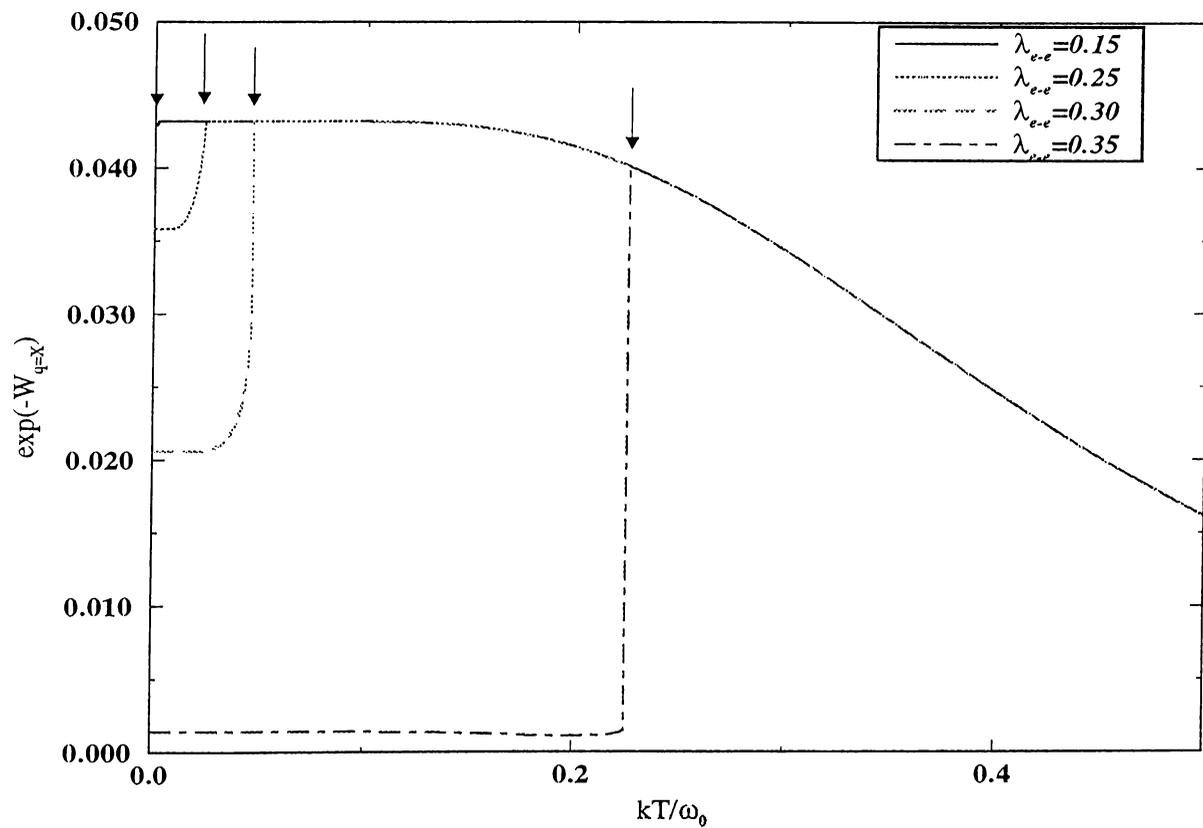


Figure 4.5: Calculated Debye-Waller factors showing anomaly at T_c for a harmonic crystal
 $\exp(-W_{\mathbf{q}})$ vs. Temperature for a harmonic crystal, $\lambda_{p-p} = 0$ for various electron-electron couplings λ_{e-e}

Chapter 5

CONCLUSION

We examined the effects of low-temperature phonon anharmonicity on the vibrational ground state and the electron-phonon interaction. In particular, we have applied our formalism to the recently observed anomalous temperature behaviour in the dynamical structure factor measurements in certain high temperature superconductors.

The interatomic potentials in most solids are in fair approximation parabolic. In those cases, anharmonicity has to be taken into account at high temperatures. This is accomplished perturbatively, by including successively higher terms in the expansion of the interatomic potential, in order to take into account slight deviations from the parabolic approximation for increasing mean-square deviations of ions from their equilibrium positions. In such treatments, at most quartic terms are taken into account and in this context, anharmonic parameters such as phonon mean life-time and frequency shifts are considered. In contrast, for a number of solids, the interatomic potentials are far from being parabolic, resembling rather a wine-bottle or a square well.⁵¹ In these solids, anharmonicity exists even at $T \rightarrow 0$, and is usually termed as *low temperature anharmonicity*. Such cases cannot be treated by the conventional perturbative scheme. Rather a non-perturbative variational treatment, specifying the explicit form of the ground state, is suited.

Our approach consists mainly of two parts. In the first part (Chapter 3),

we considered the pure lattice system, which is described by an anharmonic Hamiltonian. Elaborating on the effect of anharmonicity to generate correlations between different phonon modes, we assumed that these effects could be represented to lowest order by a squeezed correlated ground state. This assumption allowed us to linearize the anharmonic Hamiltonian and to define an order parameter for the phonon-subsystem giving the magnitude of phonon correlations.

In the second part (Chapter 4), results of the former part was implemented into a more realistic framework of interacting electrons and phonons assuming a Fröhlich interaction mediated by squeezed correlated phonons. The source of the squeezing was shown to be twofold: squeezing generated by anharmonic lattice interactions and by the action of charge-density fluctuations. We applied a self-consistent non-perturbative treatment to this situation to arrive at a new electron-phonon ground state typical of polarons. Our results indicate that, these effects not only enhance T_c , but also give rise to a number of non-perturbative polaronic effects, resulting in larger low temperature quantum fluctuations than otherwise expected. Further, we have reproduced anomalous DSF features of Arai *et al.*,²³ at least qualitatively, and have shown that this anomaly is connected with charge density fluctuations in the polaronic ground state. A variety of other anomalous temperature features as observed in the measurements of specific heat,²⁰ ultrasound propagation,⁵⁴ penetration depth etc. can be explained within our model. In this context, I believe that this extension leads to a more complete treatment of our theory, as well as of Zeyher and Zwicknagel.

Similar approaches as ours has been employed in the context of polaronic and bi-polaronic mechanisms of superconductivity by numerous authors (see Alexandrov *et al.*⁵⁵ and the references therein). In contrast to our approach, where we employed the BCS weak coupling theory, in which only those electron states near the Fermi surface are coupled to electrons, and to the so called strong coupling theory employed by Zeyher (for a review, see Scalapino⁵⁶), these theories rest on the fact that in strong coupling narrow band systems, the well known Migdal theorem, on which the former theories rely, breaks down because in such

systems one may be in the so called anti-adiabatic limit⁵⁷⁻⁵⁹

$$\omega > W$$

where ω is the characteristic phonon frequency and W is the renormalized band halfwidth. Yet, some other theories^{57,58,60,61} are concerned with the strong coupling narrow-band systems, in which *all* the electron states in the Fermi sea are involved in the superconductivity. In such systems, the strong electron-phonon interaction leads to lattice instabilities and the result of it is the formation of the so-called small polarons. In accordance with the magnitude of the effective attraction between polarons, which is denoted by V , research belonging to this class could be divided into two subclasses. If the effective attraction is small ($V < W$), Alexandrov⁶² and Robaszkiewicz *et al.*^{63,64} have shown that the small polarons form spatially overlapping Cooper pairs with superconducting properties similar to ordinary BCS theory. There are nevertheless differences in the gap equations and in the expressions for the critical temperature T_c . In the case of strong polaron-polaron coupling ($V > W$), Alexandrov and Ranninger⁶⁵ have shown that a new type of superconductivity, the so-called bipolaronic superconductivity could result, and its properties are different in many ways from the BCS properties, but are similar to those of the superfluidity of liquid helium. It is clear that the magnitude of W plays an important role in polaronic mechanisms. In the low temperature region, W is connected to the bare band halfwidth D via polaronic narrowing factor⁶⁰

$$W = D \exp(-\gamma^2/\hbar^2\omega^2)$$

where γ represents the strength of the electron-phonon interaction. However, this renormalization effect is obtained by averaging the effective electron-phonon Hamiltonian over the displaced phonon vacuum state, under the assumption that phonon subsystem does not change as electrons move. However, this adiabatic approximation turns out to be inadequate, physically. It is generally accepted that the movement of charge carriers is in some extent related to the softening of local structures. This softening, in turn, leads to strong coupling between the

charge carriers and the environmental lattice vibrations. This effect is unfavorable for application of the adiabatic approximation. Sethna⁶⁶ has shown that, due to the coupling with the phonon bath, the charge carriers not only move in an adiabatic potential, but are also influenced by a retarded potential, which originates from the fact that the phonons are not always in equilibrium with the charge carriers. The motion of the particle at time t disturbs the phonon state, which in turn acts on the motion of the particle at a later time t' , and the process turns out to be nonmarkovian. In other words, the adiabatic approximation breaks down, and the displaced oscillator state does not properly represent the real phonon ground state. Recently, displaced-squeezed phonon state was proposed as the variational function to obtain a more stable approximate ground state in polaronic systems. Such a route was also followed in our approach, with the difference that

- we included the anharmonic modes of the lattice besides the harmonic modes,
- we remained in weak coupling regime.

In our calculation a similar band narrowing factor was obtained.

As far as future prospectives are concerned, the strong coupling formalism of Zeyher and Zwicknagel as applied to our non-perturbative framework would be natural extension, since then the inclusion of experimental results would enable us to check the quantitative reliability of our theory. In addition to the temperature anomalies taken into account by our model, the anomalous softening and hardening of certain phonon modes can also be explained in the context of such a non-perturbative formalism.

As an experimental justification of our assumptions inherent to our model, we need a probe of quantum statistical properties of the lattice subsystem. A suitable, and a recent method is furnished by correlated Raman spectroscopy.⁶⁷ The ability to measure the correlation between photons, demonstrated first by Hanbury-Brown and Twiss,⁶⁸ makes spectroscopic correlation measurements possible in their application to condensed matter systems, to obtain more

information about the quantum statistical properties of collective excitations studied therein.

Appendix

A.1 Derivation of Anharmonic Hamiltonian

Consider a general three dimensional crystal in which a unit cell is situated at position vector \mathbf{l} and let \mathbf{b} be the position of basis atoms in it. One can define the displacement vector of the atom situated at \mathbf{lb} to be $\mathbf{u}(\mathbf{lb})$.

We can now expand the crystal potential energy \mathcal{V} in Taylor series for small displacements $\mathbf{u}(\mathbf{lb})$ around \mathbf{lb} as

$$\begin{aligned}
 \mathcal{V} = & \mathcal{V}_0 + \sum_{\mathbf{lb}} \frac{\partial \mathcal{V}}{\partial u_\alpha(\mathbf{lb})} \Big|_0 u_\alpha(\mathbf{lb}) + \frac{1}{2!} \sum_{\substack{\{\mathbf{lb}\} \\ \alpha\beta}} \frac{\partial^2 \mathcal{V}}{\partial u_\alpha(\mathbf{lb}) \partial u_\beta(\mathbf{l'b'})} \Big|_0 u_\alpha(\mathbf{lb}) u_\beta(\mathbf{l'b'}) \\
 & + \frac{1}{3!} \sum_{\substack{\{\mathbf{lb}\} \\ \alpha\beta\gamma}} \frac{\partial^3 \mathcal{V}}{\partial u_\alpha(\mathbf{lb}) \partial u_\beta(\mathbf{l'b'}) \partial u_\gamma(\mathbf{l''b''})} \Big|_0 u_\alpha(\mathbf{lb}) u_\beta(\mathbf{l'b'}) u_\gamma(\mathbf{l''b''}) \\
 & + \frac{1}{4!} \sum_{\substack{\{\mathbf{lb}\} \\ \alpha\beta\gamma\eta}} \frac{\partial^4 \mathcal{V}}{\partial u_\alpha(\mathbf{lb}) \partial u_\beta(\mathbf{l'b'}) \partial u_\gamma(\mathbf{l''b''}) \partial u_\eta(\mathbf{l''''b''''})} \Big|_0 \\
 & \times u_\alpha(\mathbf{lb}) u_\beta(\mathbf{l'b'}) u_\gamma(\mathbf{l''b''}) u_\eta(\mathbf{l''''b''''})
 \end{aligned} \tag{A.1.1}$$

For the equilibrium state to be a minimum

$$\frac{\partial \mathcal{V}}{\partial u_\alpha(\mathbf{lb})} \Big|_0 = 0 \tag{A.1.2}$$

After fixing the constant term \mathcal{V}_0 to zero, one can write the crystal Hamiltonian upto fourth order in potential energy as

$$\begin{aligned}
\mathcal{H} &= \mathcal{T} + \mathcal{V}_2 + \mathcal{V}_3 + \mathcal{V}_4 \\
&= \sum_{\mathbf{R}} \frac{\mathbf{p}(\mathbf{R}) \cdot \mathbf{p}(\mathbf{R})}{2m} + \frac{1}{2!} \sum_{\substack{\{\mathbf{R}\} \\ \alpha\beta}} \Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') u_{\alpha}(\mathbf{R}) u_{\beta}(\mathbf{R}') \\
&\quad + \frac{1}{3!} \sum_{\substack{\{\mathbf{R}\} \\ \alpha\beta\gamma}} \Psi_{\alpha\beta\gamma}(\mathbf{R}, \mathbf{R}', \mathbf{R}'') u_{\alpha}(\mathbf{R}) u_{\beta}(\mathbf{R}') u_{\gamma}(\mathbf{R}'') \\
&\quad + \frac{1}{4!} \sum_{\substack{\{\mathbf{R}\} \\ \alpha\beta\gamma\eta}} \Xi_{\alpha\beta\gamma\eta}(\mathbf{R}, \mathbf{R}', \mathbf{R}'', \mathbf{R}''') u_{\alpha}(\mathbf{R}) u_{\beta}(\mathbf{R}') u_{\gamma}(\mathbf{R}'') u_{\eta}(\mathbf{R}''')
\end{aligned} \tag{A.1.3}$$

where $\mathbf{p}(\mathbf{R})$ is the momentum operator of the atom located at \mathbf{R} , and \mathbf{R} is a shorthand notation for $l\mathbf{b}$. Φ, Ψ and Ξ are tensors of second, third and fourth rank respectively

$$\Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = \left. \frac{\partial^2 \mathcal{V}}{\partial u_{\alpha}(\mathbf{R}) \partial u_{\beta}(\mathbf{R}')} \right|_0 \tag{A.1.4}$$

$$\Psi_{\alpha\beta\gamma}(\mathbf{R}, \mathbf{R}', \mathbf{R}'') = \left. \frac{\partial^3 \mathcal{V}}{\partial u_{\alpha}(\mathbf{R}) \partial u_{\beta}(\mathbf{R}') \partial u_{\gamma}(\mathbf{R}'')} \right|_0 \tag{A.1.5}$$

$$\Xi_{\alpha\beta\gamma\eta}(\mathbf{R}, \mathbf{R}', \mathbf{R}'', \mathbf{R}''') = \left. \frac{\partial^4 \mathcal{V}}{\partial u_{\alpha}(\mathbf{R}) \partial u_{\beta}(\mathbf{R}') \partial u_{\gamma}(\mathbf{R}'') \partial u_{\eta}(\mathbf{R}''')} \right|_0 \tag{A.1.6}$$

If we assume Born-von Kármán cyclic boundary conditions we may introduce a new set of coordinates (a *normal set*) via the definition

$$u_{\alpha}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, s, \mathbf{b}} \sqrt{\frac{\hbar}{2m\omega_{\mathbf{k}_s}}} e_{\mathbf{k}_s}^{\alpha}(\mathbf{b}) e^{i\mathbf{k} \cdot l} (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^{\dagger}) \tag{A.1.7}$$

where \mathbf{k} denotes the direction of propagation of phonon modes, s is the branch index, $e_{\mathbf{k}_s}(\mathbf{b})$ is the polarization vector and $\omega_{\mathbf{k}_s}$ is the corresponding frequency.

The latter are determined by solving the relevant eigenvalue equation (i.e. diagonalizing $\mathcal{T} + \mathcal{V}_2$). The Hamiltonian becomes after diagonalization

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}_3 + \mathcal{V}_4 \quad (\text{A.1.8})$$

where

$$\mathcal{H}_0 = \sum_{\mathbf{k}_s} \hbar \omega_{\mathbf{k}_s} (a_{\mathbf{k}_s}^\dagger a_{\mathbf{k}_s} + \frac{1}{2}) \quad (\text{A.1.9})$$

$$\mathcal{V}_3 = \frac{1}{3!} \sum_{\mathbf{k}_s, \mathbf{k}'_{s'}, \mathbf{k}''_{s''}} \delta_{\mathbf{G}, \mathbf{k} + \mathbf{k}' + \mathbf{k}''} V_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{ss's''} Q_{\mathbf{k}_s} Q_{\mathbf{k}'_{s'}} Q_{\mathbf{k}''_{s''}} \quad (\text{A.1.10})$$

$$\mathcal{V}_4 = \frac{1}{4!} \sum_{\mathbf{k}_s, \mathbf{k}'_{s'}, \mathbf{k}''_{s''}, \mathbf{k}'''_{s'''}} \delta_{\mathbf{G}, \mathbf{k} + \mathbf{k}' + \mathbf{k}'' + \mathbf{k}'''} V_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}^{ss's''s'''} Q_{\mathbf{k}_s} Q_{\mathbf{k}'_{s'}} Q_{\mathbf{k}''_{s''}} Q_{\mathbf{k}'''_{s'''}} \quad (\text{A.1.11})$$

Here \mathbf{G} is a reciprocal space vector and $Q_{\mathbf{k}} = a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger$. The anharmonic coefficients are given by

$$V_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^{ss's''} = \frac{1}{\sqrt{N}} \sum_{\{\mathbf{b}\}} \left(\frac{\hbar}{2M} \right)^{\frac{3}{2}} \frac{e_{\mathbf{k}_s}^\alpha(\mathbf{b}) e_{\mathbf{k}'_{s'}}^\beta(\mathbf{b}') e_{\mathbf{k}''_{s''}}^\gamma(\mathbf{b}'')}{\sqrt{\omega_{\mathbf{k}_s} \omega_{\mathbf{k}'_{s'}} \omega_{\mathbf{k}''_{s''}}}} \mathcal{F}_3^{\alpha\beta\gamma}(\{\mathbf{k}, \mathbf{b}\})_{\alpha\beta\gamma} \quad (\text{A.1.12})$$

$$V_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}^{ss's''s'''} = \frac{1}{N} \sum_{\{\mathbf{b}\}} \left(\frac{\hbar}{2M} \right)^2 \frac{e_{\mathbf{k}_s}^\alpha(\mathbf{b}) e_{\mathbf{k}'_{s'}}^\beta(\mathbf{b}') e_{\mathbf{k}''_{s''}}^\gamma(\mathbf{b}'') e_{\mathbf{k}'''_{s'''}}^\eta(\mathbf{b}''')}{\sqrt{\omega_{\mathbf{k}_s} \omega_{\mathbf{k}'_{s'}} \omega_{\mathbf{k}''_{s''}} \omega_{\mathbf{k}'''_{s'''}}}} \mathcal{F}_4^{\alpha\beta\gamma\eta}(\{\mathbf{k}, \mathbf{b}\})_{\alpha\beta\gamma\eta}$$

Here $\mathcal{F}_3^{\alpha\beta\gamma}$ and $\mathcal{F}_4^{\alpha\beta\gamma\eta}$ are the Fourier transformed anharmonic tensors of third and fourth order, respectively, given in terms of derivatives of the crystal potential (A.1.5, A.1.6) by

$$\mathcal{F}_3^{\alpha\beta\gamma}(\{\mathbf{k}, \mathbf{b}\}) = \sum_{\mathbf{h}, \mathbf{h}'} e^{-i\mathbf{q}' \cdot \mathbf{h}'} e^{-i\mathbf{q}'' \cdot \mathbf{h}''} \Psi_{\alpha\beta\gamma} \quad (\text{A.1.13})$$

$$\mathcal{F}_4^{\alpha\beta\gamma\eta}(\{\mathbf{k}, \mathbf{b}\}) = \sum_{\mathbf{h}, \mathbf{h}', \mathbf{h}''} e^{-i\mathbf{q}' \cdot \mathbf{h}'} e^{-i\mathbf{q}'' \cdot \mathbf{h}''} e^{-i\mathbf{q}''' \cdot \mathbf{h}'''} \Xi_{\alpha\beta\gamma\eta} \quad (\text{A.1.14})$$

A.2 Coherent and Squeezed Phonon States

The concepts of coherent and squeezed states originate from various non-classical photon states of quantum optics, which recently find an ever increasing application domain in condensed matter problems as well.^{44,52,53}

A coherent state is a phase coherent sum of number states. For this state, the quantum fluctuations in any pair of conjugate variables are at the lower limit of the corresponding canonical Heisenberg uncertainty relations. In this respect, coherent states are the most "classical" non-classical pure quantum states. Coherent state is as "quiet" as the vacuum state. Squeezed states are interesting because they can have smaller quantum noise than the vacuum state in one of the conjugate variables at the expense of an increased asymmetric noise in the other conjugate variable.

The application of the above concepts to lattice subsystem is best accomplished in the second quantization formalism taking into account the collective nature of lattice oscillations i.e. phonons. A phonon with quasimomentum $\mathbf{p} = \hbar\mathbf{k}$ and branch subscript s has energy $\epsilon_{\mathbf{k}_s} = \hbar\omega_{\mathbf{k}_s}$. The corresponding creation and annihilation operators satisfy the boson commutation relations

$$[a_{\mathbf{k}'_{s'}}, a_{\mathbf{k}_s}^\dagger] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'} \quad , \quad [a_{\mathbf{k}'_{s'}}, a_{\mathbf{k}'_{s'}}] = 0. \quad (\text{A.2.1})$$

The atomic displacements $u_{i\alpha}$ of a crystal lattice are given by

$$u_{i\alpha} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}_s}^N \sqrt{\frac{\hbar}{2M\omega_{\mathbf{k}_s}}} \epsilon_{\mathbf{k}_s}^\alpha Q_{\mathbf{k}_s} e^{i\mathbf{k}\cdot\mathbf{R}_i} \quad (\text{A.2.2})$$

Here \mathbf{R}_i refers to the equilibrium lattice positions, α to a particular direction, $\epsilon_{\mathbf{k}_s}^\alpha$ to the polarization eigenvector, and $Q_{\mathbf{k}_s}$ is the normal mode amplitude operator given by

$$Q_{\mathbf{k}_s} = (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^\dagger) \quad (\text{A.2.3})$$

An experimentally observable quantity is the real part of the Fourier transform of the atomic displacement:

$$\text{Re}[u_\alpha(\mathbf{k})] = \sum_s \sqrt{\frac{\hbar}{8m\omega_{\mathbf{k}_s}}} \{ \epsilon_{\mathbf{k}_s}^\alpha (a_{\mathbf{k}_s} + a_{-\mathbf{k}_s}^\dagger) + \epsilon_{\mathbf{k}_s}^{\alpha*} (a_{-\mathbf{k}_s} + a_{\mathbf{k}_s}^\dagger) \}$$

Dropping for simplicity the branch subscript s , assuming $\epsilon_{\mathbf{k}s}^\alpha$ real we may define a \mathbf{k} -mode dimensionless lattice amplitude operator:

$$u(\pm\mathbf{k}) = a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger + a_{-\mathbf{k}} + a_{\mathbf{k}}^\dagger \quad (\text{A.2.4})$$

This operator is the phonon analog of the electric field in the photon case.

The phonon number states $|n_{\mathbf{k}}\rangle$, eigenstates of the harmonic phonon Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{k}s} \hbar\omega_{\mathbf{k}s} (a_{\mathbf{k}} a_{\mathbf{k}}^\dagger + 1/2) \quad (\text{A.2.5})$$

satisfying $a_{\mathbf{k}}|n_{\mathbf{k}}\rangle = \sqrt{n_{\mathbf{k}}}|n_{\mathbf{k}}-1\rangle$ are states for which the number of phonons for each \mathbf{k} is a good quantum number. Since phase and phonon number are conjugate variables, the phase is uniformly random in these states and the expectation values of the atomic displacement $\langle n_{\mathbf{k}}|u_{i\alpha}|n_{\mathbf{k}}\rangle$ and \mathbf{k} -mode lattice amplitude $\langle n_{\mathbf{k}}|u(\pm\mathbf{k})|n_{\mathbf{k}}\rangle$ vanish as a consequence. The relevant quantum fluctuations in a number state $|n_{\mathbf{k}}\rangle$ are

$$\langle [\Delta u(\pm\mathbf{k})]^2 \rangle_{n_{\mathbf{k}}} = 2 + 2\bar{n}_{\mathbf{k}} \quad (\text{A.2.6})$$

$$\langle (\Delta u_{i\alpha})^2 \rangle_{n_{\mathbf{k}}} = \frac{\hbar|\epsilon_{\mathbf{k}\alpha}^2|^2 \bar{n}_{\mathbf{k}}}{Nm\omega_{\mathbf{k}\alpha}} + \sum_{\mathbf{k}' \neq \mathbf{k}}^N \frac{\hbar|\epsilon_{\mathbf{k}'\alpha}^2|^2}{2Nm\omega_{\mathbf{k}'\alpha}} \quad (\text{A.2.7})$$

Note that for the phonon vacuum state $|n_{\mathbf{k}}=0\rangle$, then the vacuum fluctuations

$$\langle [\Delta u(\pm\mathbf{k})]^2 \rangle_{n_{\mathbf{k}}} = 2 \quad (\text{A.2.8})$$

$$\langle (\Delta u_{i\alpha})^2 \rangle_{n_{\mathbf{k}}} = \sum_{\mathbf{k}'}^N \frac{\hbar|\epsilon_{\mathbf{k}'\alpha}^2|^2}{2Nm\omega_{\mathbf{k}'\alpha}} \quad (\text{A.2.9})$$

are minimum.

A single mode coherent state is defined to be the eigenstate of the phonon annihilation operator:

$$a_{\mathbf{k}}|\alpha_{\mathbf{k}}\rangle = \alpha_{\mathbf{k}}|\alpha_{\mathbf{k}}\rangle \quad (\text{A.2.10})$$

It can also be generated by applying a phonon displacement operator $\mathcal{D}_{\mathbf{k}}(\alpha_{\mathbf{k}})$ to the phonon vacuum state

$$|\alpha_{\mathbf{k}}\rangle = \mathcal{D}_{\mathbf{k}}(\alpha_{\mathbf{k}})|0\rangle = \exp\left(-\frac{|\alpha_{\mathbf{k}}|^2}{2}\right) \sum_{n_{\mathbf{k}}=0}^{\infty} \frac{\alpha_{\mathbf{k}}^{n_{\mathbf{k}}}}{\sqrt{n_{\mathbf{k}}!}} |n_{\mathbf{k}}\rangle \quad (\text{A.2.11})$$

$$\mathcal{D}_{\mathbf{k}}(\alpha_{\mathbf{k}}) = \exp(\alpha_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} - \alpha_{\mathbf{k}}^* a_{\mathbf{k}}) \quad (\text{A.2.12})$$

Thus it can be seen that a phonon coherent state is a phase-coherent superposition of number states. Moreover, coherent states are a set of minimum-uncertainty states which have the same noise level as the vacuum state (this is called "shot noise limit" in quantum optics). Coherent states are also the set of quantum states which are excited by a classical driving force. They can be best used in the classical description of the harmonic oscillator. In a single mode coherent state $|\alpha_{\mathbf{k}}\rangle$ the expectation value of \mathbf{k} - mode lattice amplitude $\langle n_{\mathbf{k}} | u(\pm \mathbf{k}) | n_{\mathbf{k}} \rangle$ is:

$$\langle u(\pm \mathbf{k}) \rangle_{\alpha_{\mathbf{k}}} = 2|\alpha_{\mathbf{k}}| \cos \omega_{\mathbf{k}} t \quad (\text{A.2.13})$$

and the fluctuations can be given as

$$\langle [\Delta u(\pm \mathbf{k})]^2 \rangle_{\alpha_{\mathbf{k}}} = 2 \langle (\Delta u_{i\alpha})^2 \rangle_{\alpha_{\mathbf{k}}} = \sum_{\mathbf{k}'}^N \frac{\hbar |\epsilon_{\mathbf{k}'s}|^2}{2Nm\omega_{\mathbf{k}'\alpha}} \quad (\text{A.2.14})$$

Thus the noise is the same as that of the vacuum state although contrary to the vacuum state the coherent state has non-zero expectations for the amplitudes.

Since the (quadrature) squeezed states are generalized coherent states, one can achieve smaller variances for one of the quadratures during certain time intervals at the expense of increasing the variance of the conjugate quadrature in conformity with the Heisenberg uncertainty principle. Here quadrature refers to dimensionless coordinate and momentum.

A single mode squeezed state is generated from a vacuum state as:

$$|\alpha_{\mathbf{k}}, \xi\rangle = \mathcal{D}_{\mathbf{k}}(\alpha_{\mathbf{k}}) \mathcal{S}_{\mathbf{k}}(\xi) |0\rangle \quad (\text{A.2.15})$$

similarly a two-mode quadrature squeezed state is generated as

$$|\alpha_{\mathbf{k}_1}, \alpha_{\mathbf{k}_2}, \xi\rangle = \mathcal{D}_{\mathbf{k}_1}(\alpha_{\mathbf{k}_1}) \mathcal{D}_{\mathbf{k}_2}(\alpha_{\mathbf{k}_2}) \mathcal{S}_{\mathbf{k}_1, \mathbf{k}_2}(\xi) |0\rangle \quad (\text{A.2.16})$$

Here $\mathcal{D}_{\mathbf{k}}(\alpha_{\mathbf{k}})$ is the coherent state displacement operator with $\alpha_{\mathbf{k}} = |\alpha_{\mathbf{k}}| e^{i\phi}$ and

$$\mathcal{S}_{\mathbf{k}}(\xi) = \exp\left(\frac{\xi^*}{2} a_{\mathbf{k}}^2 - \frac{\xi}{2} a_{\mathbf{k}}^{\dagger 2}\right) \quad (\text{A.2.17})$$

$$\mathcal{S}_{\mathbf{k}_1, \mathbf{k}_2}(\xi) = \exp(\xi^* a_{\mathbf{k}_1} a_{\mathbf{k}_2} - \xi a_{\mathbf{k}_1}^{\dagger} a_{\mathbf{k}_2}^{\dagger}) \quad (\text{A.2.18})$$

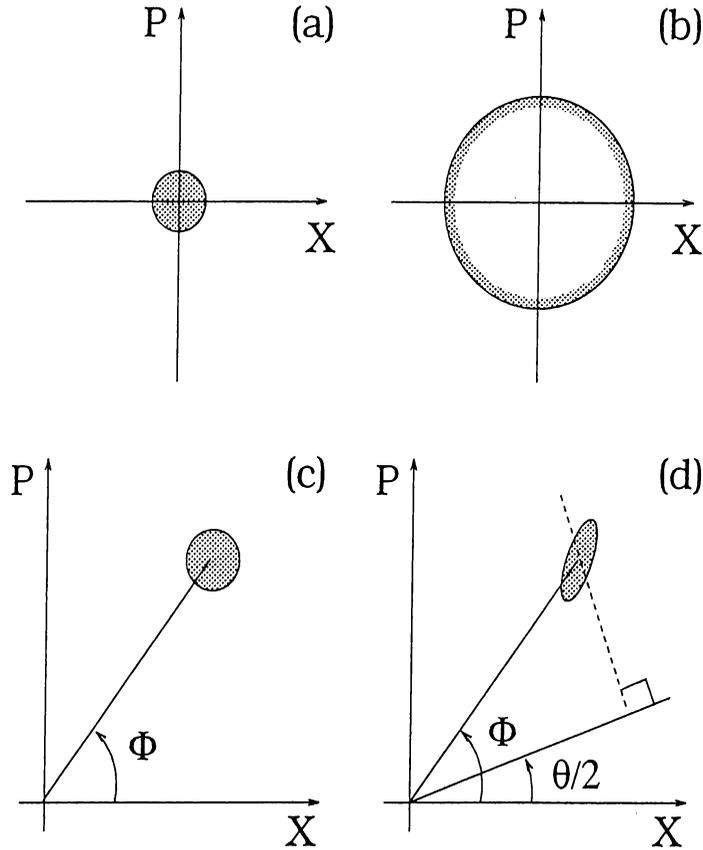


Figure A.1: Variances of vacuum, number, coherent and squeezed states
 Schematic diagram of the uncertainty areas (shaded) in the generalized coordinate and momentum ($X(\mathbf{q}, -\mathbf{q})$, $P(\mathbf{q}, -\mathbf{q})$) phase space of (a) the phonon vacuum state, (b) a phonon number state, (c) a phonon coherent state, and (d) a phonon squeezed state. Here $X(\mathbf{q}, -\mathbf{q})$ and $P(\mathbf{q}, -\mathbf{q})$ are the two mode ($\pm\mathbf{q}$) coordinate and momentum operators, which are the direct generalizations of their corresponding single-mode operators. Notice that the phonon coherent state has the same uncertainty area as the vacuum state, and that both areas are circular, while the squeezed state has an elliptical uncertainty area. Therefore, in the direction parallel to the $\theta/2$ line, the squeezed state has a smaller noise than both the vacuum and coherent states.

are the single-mode and two-mode squeezing mode operators with $\xi = re^{i\theta}$. For the case of squeezed states involved in modes $\pm\mathbf{k}$ the two mode quadrature

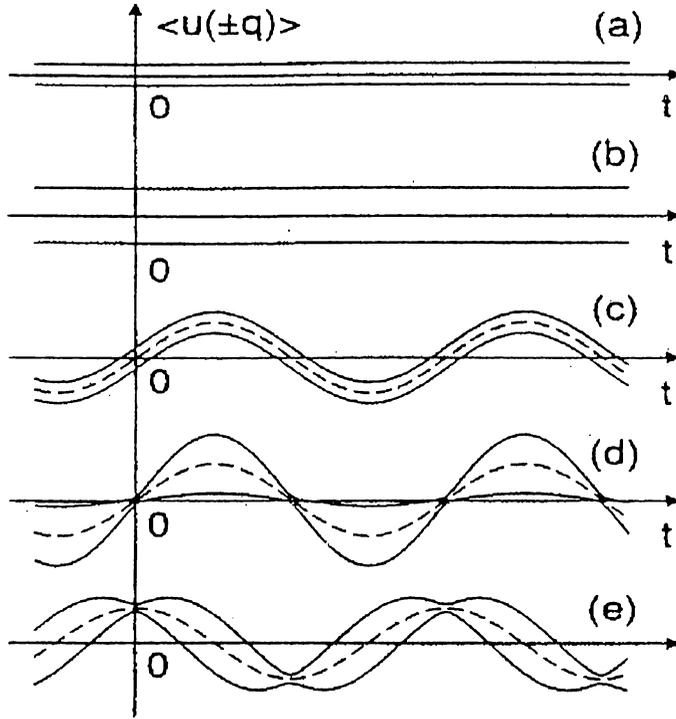


Figure A.2: Evolution of vacuum, number, coherent and squeezed states
Schematic diagram of the time evolution of the expectation value and the fluctuation of the lattice amplitude operator $u(\pm \mathbf{q})$ in different states. Dashed line represents $\langle u(\pm \mathbf{q}) \rangle$, while the solid line represents $\langle u(\pm \mathbf{q}) \rangle \pm \sqrt{\langle [\delta u(\pm \mathbf{q})]^2 \rangle}$. (a) The phonon vacuum state $|0\rangle$, where $\langle u(\pm \mathbf{q}) \rangle = 0$ and $\langle [\delta u(\pm \mathbf{q})]^2 \rangle = 2$. (b) A phonon number state $|n_{\mathbf{q}}, n_{-\mathbf{q}}\rangle$, where $\langle u(\pm \mathbf{q}) \rangle = 0$ and $\langle [\delta u(\pm \mathbf{q})]^2 \rangle = 2(n_{\mathbf{q}} + n_{-\mathbf{q}}) + 2$. (c) A single mode phonon coherent state $\alpha_{\mathbf{q}}$, where $\langle u(\pm \mathbf{q}) \rangle = 2|\alpha_{\mathbf{q}}| \cos \omega_{\mathbf{q}} t$, and $\langle [\delta u(\pm \mathbf{q})]^2 \rangle = 2(e^{-2r} \cos^2 \omega_{\mathbf{q}} t + e^{2r} \sin^2 \omega_{\mathbf{q}} t)$. (d) A single mode phonon squeezed state, as in (c); now the expectation value of u is $\langle u(\pm \mathbf{q}) \rangle = 2|\alpha_{\mathbf{q}}| \sin \omega_{\mathbf{q}} t$ (i.e. $\alpha_{\mathbf{q}}$ is purely imaginary), and the fluctuation has the same time dependence as in (c). Notice that the squeezing effect now appears at the times when the lattice amplitude $\langle u(\pm \mathbf{q}) \rangle$ reaches its maxima while in (c) the squeezing effect is present at the times when $\langle u(\pm \mathbf{q}) \rangle$ is close to zero.

operators have the form

$$\begin{aligned} X(\mathbf{k}, -\mathbf{k}) &= 2^{-3/2}(a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger + a_{-\mathbf{k}} + a_{\mathbf{k}}^\dagger) \\ &= 2^{-3/2}u(\pm \mathbf{k}) \end{aligned} \tag{A.2.19}$$

$$P(\mathbf{k}, -\mathbf{k}) = -i2^{-3/2}(a_{\mathbf{k}} - a_{-\mathbf{k}}^\dagger + a_{-\mathbf{k}} - a_{\mathbf{k}}^\dagger)$$

In this squeezed state $|\alpha_{\mathbf{k}}, \alpha_{-\mathbf{k}}, \xi\rangle$ the amplitude expectations and fluctuations are:

$$\langle u(\pm \mathbf{k}) \rangle_{\alpha_{\mathbf{k}}} = 2|\alpha_{\mathbf{k}}| \cos \omega_{\mathbf{k}} t \quad (\text{A.2.20})$$

$$\langle [\Delta u(\pm \mathbf{k})]^2 \rangle_{\alpha_{\mathbf{k}}} = 2 \left(e^{-2r} \cos^2 \frac{\theta}{2} + e^{2r} \sin^2 \frac{\theta}{2} \right) \quad (\text{A.2.21})$$

It can be seen that the variances can be smaller than the vacuum value of 2.

A.3 Derivation of $T = 0$ Self-Consistent Equation

To linearize the fourth order anharmonic Hamiltonian we pursue a method quite similar to that of BCS method, but here the system being bosonic in nature. We assume that the ground state is properly described by a squeezed vacuum state of phonons defined by

$$|\xi\rangle = \mathcal{S}(\{\xi\})|0\rangle \quad (\text{A.3.1})$$

where the unitary transformation $\mathcal{S}(\{\xi\})$ acting on the phonon vacuum state $|0\rangle$ is given by

$$\mathcal{S}(\{\xi\}) = \exp\left\{-\sum_{\mathbf{k}} \xi_{\mathbf{k}} (a_{\mathbf{k}} a_{-\mathbf{k}} - a_{\mathbf{k}}^{\dagger} a_{-\mathbf{k}}^{\dagger})\right\} \quad (\text{A.3.2})$$

Here and throughout the derivation \mathbf{k} denotes the composite quantum number (\vec{k}, s) where s is the polarization index and $-\mathbf{k} = (-\vec{k}, s)$.

The calculation of the ground state energy and the excitation spectrum is simplified by introducing a canonical transformation (named after its inventor, N. N. Bogoliubov) :

$$\begin{aligned} b_{\mathbf{k}} &= \mathcal{S}(\{\xi\}) a_{\mathbf{k}} \mathcal{S}^{\dagger}(\{\xi\}) = C_{\mathbf{k}} a_{\mathbf{k}} - S_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger}, \\ b_{-\mathbf{k}}^{\dagger} &= \mathcal{S}(\{\xi\}) a_{-\mathbf{k}}^{\dagger} \mathcal{S}^{\dagger}(\{\xi\}) = C_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger} - S_{\mathbf{k}} a_{\mathbf{k}} \end{aligned} \quad (\text{A.3.3})$$

Here $C_{\mathbf{k}} = \cosh 2(\xi_{\mathbf{k}})$ and $S_{\mathbf{k}} = \sinh 2(\xi_{\mathbf{k}})$ where $\xi_{\mathbf{k}}$ is a parameter for phonon pair correlations to be found self consistently through an energy minimization procedure. These new operators annihilate and create a kind of quasi-particle excitation. It is easy to verify that

$$b_{\mathbf{k}}|\xi\rangle = 0 \quad (\text{A.3.4})$$

Hence $|\xi\rangle$ is a state of zero quasi-particles. This fact and the fact that the quasi-particle operators satisfy the canonical commutation relations allow us to adopt the *Wick's theorem* to the squeezed vacuum state and the Bogoliubov transformation:

1. *Normal ordering* is taken with respect to the Bogoliubov quasi particle operators, with $b_{\mathbf{k}}^\dagger$ taken to the left of $b_{\mathbf{k}}$
2. The *contraction* of two operators X and Y is defined as the matrix element in the squeezed vacuum state

$$\langle XY \rangle = \langle \xi | XY | \xi \rangle \quad (\text{A.3.5})$$

The anharmonic part of the crystal Hamiltonian

$$\frac{1}{4!} \sum_{\{\mathbf{k}_n\}} \delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''+\mathbf{k}'''} V_4(\{\mathbf{k}_n\}) Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} Q_{\mathbf{k}_4}, \quad (\text{A.3.6})$$

includes the phonon operators in the specific form of displacements $Q_{\mathbf{k}}$ which transform under the Bogoliubov transformation in a relatively simple way

$$\begin{aligned} Q_{\mathbf{k}} &= a_{\mathbf{k}} + a_{-\mathbf{k}}^\dagger = (C_{\mathbf{k}} + S_{\mathbf{k}})(b_{\mathbf{k}} + b_{-\mathbf{k}}^\dagger) \\ &= e^{2\xi_{\mathbf{k}}} (b_{\mathbf{k}} + b_{-\mathbf{k}}^\dagger) \end{aligned} \quad (\text{A.3.7})$$

Thus it is appropriate to consider the normal order expansion of the four-displacement-product

$$\begin{aligned} Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} Q_{\mathbf{k}_4} &= \mathcal{N}(Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} Q_{\mathbf{k}_4}) + \mathcal{N}(Q_{\mathbf{k}_1} Q_{\mathbf{k}_2}) \langle Q_{\mathbf{k}_3} Q_{\mathbf{k}_4} \rangle \\ &\quad + \mathcal{N}(Q_{\mathbf{k}_1} Q_{\mathbf{k}_3}) \langle Q_{\mathbf{k}_2} Q_{\mathbf{k}_4} \rangle + \mathcal{N}(Q_{\mathbf{k}_1} Q_{\mathbf{k}_4}) \langle Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} \rangle \\ &\quad + \mathcal{N}(Q_{\mathbf{k}_2} Q_{\mathbf{k}_3}) \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_4} \rangle + \mathcal{N}(Q_{\mathbf{k}_2} Q_{\mathbf{k}_4}) \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_3} \rangle \\ &\quad + \mathcal{N}(Q_{\mathbf{k}_3} Q_{\mathbf{k}_4}) \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} \rangle + \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_2} \rangle \langle Q_{\mathbf{k}_3} Q_{\mathbf{k}_4} \rangle \\ &\quad + \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_3} \rangle \langle Q_{\mathbf{k}_2} Q_{\mathbf{k}_4} \rangle + \langle Q_{\mathbf{k}_1} Q_{\mathbf{k}_4} \rangle \langle Q_{\mathbf{k}_2} Q_{\mathbf{k}_3} \rangle \end{aligned} \quad (\text{A.3.8})$$

The normal products and the contractions are calculated as

$$\mathcal{N}(Q_{\mathbf{k}} Q_{\mathbf{k}'}) = e^{2(\xi_{\mathbf{k}} + \xi_{\mathbf{k}'})} \left[b_{\mathbf{k}} b_{\mathbf{k}'} + b_{-\mathbf{k}}^\dagger b_{\mathbf{k}'} + b_{-\mathbf{k}'}^\dagger b_{\mathbf{k}} + b_{-\mathbf{k}}^\dagger b_{-\mathbf{k}'}^\dagger \right] \quad (\text{A.3.9})$$

$$\langle Q_{\mathbf{k}} Q_{\mathbf{k}'} \rangle = e^{2(\xi_{\mathbf{k}} + \xi_{\mathbf{k}'})} \delta_{\mathbf{k}, -\mathbf{k}'} \quad (\text{A.3.10})$$

Here, it must be noted that, the anharmonic potential includes a delta function $\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4,\mathbf{G}}$ implicitly (conservation of crystal momentum) and together with the delta function in the contractions, splits into two delta functions. But we will exclude umklapp scatterings and only $\mathbf{G} = 0$ will be possible in what follows.

Assuming that

$$V_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4} = V_{\mathcal{P}\{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4\}} \quad (\text{A.3.11})$$

where \mathcal{P} stands for permutation operator, and $\xi_{-\mathbf{k}} = \xi_{\mathbf{k}}$, which follows from momentum conservation in the ground state, we may write down the anharmonic Hamiltonian in reduced form as

$$\mathcal{H}^{eff} = \mathcal{H}_0 + \mathcal{H}_{11} + \mathcal{H}_{20} + \mathcal{H}_4 \quad (\text{A.3.12})$$

where \mathcal{H}_0 contains no uncontracted operators, each term of \mathcal{H}_{11} contains one creation and one annihilation operator, each term in \mathcal{H}_{20} contains two creation and two annihilation operators, and \mathcal{H}_4 contains four operators in normal order. The term \mathcal{H}_4 contains four phonon operators in normal order and represents an interaction between the *quasi-particles*, and will be neglected. Calculation of these terms is straightforward but tedious and one must keep track of the symmetry factors:

$$\mathcal{H}_0 = \sum_{\mathbf{k}\mathbf{k}'} \hbar\omega_{\mathbf{k}}(S_{\mathbf{k}}^2 + \frac{1}{2}) + 3\tilde{V}(\mathbf{k}, \mathbf{k}')e^{4(\xi_{\mathbf{k}}+\xi_{\mathbf{k}'})} \quad (\text{A.3.13})$$

$$\mathcal{H}_{11} = \sum_{\mathbf{k}\mathbf{k}'} \left[\hbar\omega_{\mathbf{k}}(C_{\mathbf{k}}^2 + S_{\mathbf{k}}^2) + 12\tilde{V}(\mathbf{k}, \mathbf{k}')e^{4(\xi_{\mathbf{k}}+4\xi_{\mathbf{k}'})} \right] b_{\mathbf{k}}^\dagger b_{\mathbf{k}} \quad (\text{A.3.14})$$

$$\mathcal{H}_{20} = \sum_{\mathbf{k}\mathbf{k}'} \left[\hbar\omega_{\mathbf{k}}C_{\mathbf{k}}S_{\mathbf{k}} + 6\tilde{V}(\mathbf{k}, \mathbf{k}')e^{4(\xi_{\mathbf{k}}+4\xi_{\mathbf{k}'})} \right] (b_{\mathbf{k}}b_{-\mathbf{k}} + b_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger) \quad (\text{A.3.15})$$

The ground state energy is given just by the fully contracted part \mathcal{H}_0

$$E = \langle \xi | \mathcal{H}^{eff} | \xi \rangle = \mathcal{H}_0 \quad (\text{A.3.16})$$

Minimizing E with respect to the squeezing parameter $\xi_{\mathbf{k}}$ we obtain the self consistency equation

$$\hbar\omega_{\mathbf{k}}C_{\mathbf{k}}S_{\mathbf{k}} = 6e^{4\xi_{\mathbf{k}}} \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}, \mathbf{k}')e^{4\xi_{\mathbf{k}'}} \quad (\text{A.3.17})$$

Now the minimization condition (A.3.17) implies \mathcal{H}_{20} to vanish identically, therefore with the approximation of neglecting \mathcal{H}_4 we find that $\mathcal{H}^{eff} = \mathcal{H}_0 + \mathcal{H}_{11}$ is diagonal and its spectrum can be obtained trivially.

The excitation spectrum is given directly by \mathcal{H}_{11} which may be written in the form

$$\mathcal{H}_{11} = \sum_{\mathbf{k}} \hbar \Omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{1}{2}) \quad (\text{A.3.18})$$

where the renormalized frequency is expressed as

$$\Omega_{\mathbf{k}} = (C_{\mathbf{k}} - S_{\mathbf{k}})^2 \omega_{\mathbf{k}} = e^{-4\xi_{\mathbf{k}}} \omega_{\mathbf{k}} \quad (\text{A.3.19})$$

An effective squeezing parameter $\kappa_{\mathbf{k}}$ may be defined, if we assume that the linearized effective Hamiltonian \mathcal{H}^{eff} was derived from an Hamiltonian \mathcal{H}_{sq}

$$\mathcal{H}_{sq} = \sum_{\mathbf{k}} \hbar \tilde{\omega}_{\mathbf{k}} (a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \frac{1}{2}) + \sum_{\mathbf{k}} \kappa_{\mathbf{k}} (a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger + a_{\mathbf{k}} a_{-\mathbf{k}}) \quad (\text{A.3.20})$$

$$\downarrow (a_{\mathbf{k}} = C_{\mathbf{k}} b_{\mathbf{k}} + S_{\mathbf{k}} b_{-\mathbf{k}}^\dagger)$$

$$\mathcal{H}^{eff} = \sum_{\mathbf{k}} \hbar \Omega_{\mathbf{k}} (b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{1}{2}) \quad (\text{A.3.21})$$

It can be shown that, in this case we have the relation

$$\phi(\mathbf{k}) = C_{\mathbf{k}} S_{\mathbf{k}} = \frac{\kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \quad (\text{A.3.22})$$

where the expression for the renormalized frequency $\Omega_{\mathbf{k}}$ is given in terms of the squeezing parameter $\kappa_{\mathbf{k}}$ by

$$\Omega_{\mathbf{k}} = \sqrt{\tilde{\omega}_{\mathbf{k}}^2 - 4\kappa_{\mathbf{k}}^2}. \quad (\text{A.3.23})$$

Furthermore, $\phi(\mathbf{k}) = \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle$ is the anomalous pair correlation and $\tilde{\omega}_{\mathbf{k}}$ is a 'dressed' frequency which, by comparing (A.3.23), (A.3.22) and (A.3.19), is found to be related to the bare frequency $\omega_{\mathbf{k}}$ by

$$\tilde{\omega}_{\mathbf{k}} = \frac{1}{2} (1 + e^{-8\xi_{\mathbf{k}}}) \omega_{\mathbf{k}} \quad (\text{A.3.24})$$

Using the relations above, our zero-temperature self-consistency equation (A.3.17) takes the final form

$$\begin{aligned}\kappa_{\mathbf{k}} &= 6 \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}\mathbf{k}') e^{4\xi\mathbf{k}'} \\ &= 6 \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}\mathbf{k}') \left[2\phi(\mathbf{k}') + \sqrt{1 + 4\phi^2(\mathbf{k}')} \right].\end{aligned}\quad (\text{A.3.25})$$

It must be noted that, the above formalism tantamounts to solving the anharmonic Hamiltonian (3.1) in the mean field of $\phi(\mathbf{k}) = \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle$. In this formalism one replaces for example a typical term $a_{\mathbf{k}_1} a_{-\mathbf{k}_2} a_{\mathbf{k}_3} a_{-\mathbf{k}_4}$ in the expansion of the four-displacement product by

$$a_{\mathbf{k}_1} a_{-\mathbf{k}_2} a_{\mathbf{k}_3} a_{-\mathbf{k}_4} = 6 \phi(\mathbf{k}_3) [a_{\mathbf{k}_1} a_{-\mathbf{k}_1} + C_{\mathbf{k}_1} S_{\mathbf{k}_1}] \delta_{\mathbf{k}_1, \mathbf{k}_2} \delta_{\mathbf{k}_3, \mathbf{k}_4} \quad (\text{A.3.26})$$

The final equations will exactly be equivalent to those produced by the former approach.

A.4 Green's Functions and Finite Temperature Solution

The finite temperature self-consistent equation and various physical properties of the anharmonic phonon system can be determined trivially through the Green's function formalism.

We shall define two types of finite-temperature Green's functions

$$\mathcal{D}_{\mathbf{k}}(t, t') = -i\langle\Psi|\mathcal{T}Q_{\mathbf{k}}(t)Q_{-\mathbf{k}}(t')|\Psi\rangle \quad (\text{A.4.1})$$

$$\mathcal{F}_{\mathbf{k}}(t, t') = -i\langle\Psi|\mathcal{T}a_{\mathbf{k}}(t)a_{-\mathbf{k}}(t')|\Psi\rangle \quad (\text{A.4.2})$$

In the definitions (A.4.2), \mathcal{T} is the time ordering operator, $\langle\Psi|\cdots|\Psi\rangle$ denotes a thermal average over the canonical ensemble generated by the spectrum of effective Hamiltonian \mathcal{H}^{eff} at temperature T and

$$Q_{\mathbf{k}} = a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger} \quad (\text{A.4.3})$$

Now, let's define a "squeezed displacement operator" $Q_{\mathbf{k}}^{sq}$ in terms of the squeezed quasi-particle operators (A.3.3) by

$$Q_{\mathbf{k}}^{sq} = b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger} \quad (\text{A.4.4})$$

From (A.3.3) follows $Q_{\mathbf{k}} = (C_{\mathbf{k}} + S_{\mathbf{k}})Q_{\mathbf{k}}^{sq}$. These relations enable us to find $\mathcal{D}_{\mathbf{k}}(t, t')$ easily from the form of normal-phonon temperature Green's function

$$\mathcal{D}_{\mathbf{k}}(t, t') = -i(C_{\mathbf{k}} + S_{\mathbf{k}})^2 [(N_{\mathbf{k}} + 1)e^{-i\Omega_{\mathbf{k}}|t-t'|} + N_{\mathbf{k}}e^{i\Omega_{\mathbf{k}}|t-t'|}] \quad (\text{A.4.5})$$

where $N_{\mathbf{k}} = (\exp(\beta\Omega_{\mathbf{k}}) - 1)^{-1}$ is the mean occupation number in state $b_{\mathbf{k}}^{\dagger}|\xi\rangle$.

To calculate $\mathcal{F}_{\mathbf{k}}(t, t')$ consider first the Matsubara Green's function

$$\mathcal{G}_{\mathbf{k}}(\sigma, \sigma') = \langle\mathcal{T}a_{\mathbf{k}}(\sigma)a_{-\mathbf{k}}(\sigma')\rangle \quad (\text{A.4.6})$$

σ is some real parameter at this stage, and

$$a_{\mathbf{k}}(\sigma) = e^{\sigma\mathcal{H}^{eff}} a_{\mathbf{k}} e^{-\sigma\mathcal{H}^{eff}} \quad (\text{A.4.7})$$

Using the canonical transformations (A.3.3) we have

$$a_{\mathbf{k}}(\sigma) = C_{\mathbf{k}} b_{\mathbf{k}} e^{-\sigma \Omega_{\mathbf{k}}} + S_{\mathbf{k}} b_{-\mathbf{k}}^{\dagger} e^{\sigma \Omega_{\mathbf{k}}} \quad (\text{A.4.8})$$

Inserting this expression and that for $a_{-\mathbf{k}}(\sigma)$ into (A.4.6) we obtain

$$\mathcal{G}_{\mathbf{k}}(\sigma, \sigma') = C_{\mathbf{k}} S_{\mathbf{k}} [(N_{\mathbf{k}} + 1) e^{\Omega_{\mathbf{k}} |\sigma - \sigma'|} + N_{\mathbf{k}} e^{-\Omega_{\mathbf{k}} |\sigma - \sigma'|}] \quad (\text{A.4.9})$$

Analytic Continuation of this function into the complex plane gives us the desired Green's function $\mathcal{F}_{\mathbf{k}}(t, t')$ trivially

$$\mathcal{F}_{\mathbf{k}}(t, t') = C_{\mathbf{k}} S_{\mathbf{k}} [(N_{\mathbf{k}} + 1) e^{i\Omega_{\mathbf{k}} |t - t'|} + N_{\mathbf{k}} e^{-i\Omega_{\mathbf{k}} |t - t'|}] \quad (\text{A.4.10})$$

The anomalous pair correlation $\phi_{\mathbf{k}} = \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle$ can then be naturally extended to finite temperatures

$$\phi_{\mathbf{k}}(T) = \mathcal{F}_{\mathbf{k}}(t, t) = 2C_{\mathbf{k}} S_{\mathbf{k}} \coth \frac{\Omega_{\mathbf{k}}}{2kT} \quad (\text{A.4.11})$$

and the finite temperature generalization of our self consistent equation (A.3.25) becomes finally

$$\kappa_{\mathbf{k}} = 6 \sum_{\mathbf{k}'} \tilde{V}(\mathbf{k}\mathbf{k}') \left[2 \frac{\kappa_{\mathbf{k}'}}{\Omega_{\mathbf{k}'}} \coth \frac{\Omega_{\mathbf{k}'}}{2kT} + \sqrt{1 + 4 \frac{\kappa_{\mathbf{k}'}}{\Omega_{\mathbf{k}'}} \coth^2 \frac{\Omega_{\mathbf{k}'}}{2kT}} \right] \quad (\text{A.4.12})$$

A.5 Third Order Anharmonicity and Effect of Depairing

In this section we will derive the expression for the three phonon scattering rate $\Gamma_{\mathbf{k}}$ of *squeezed phonons* through the expression of the matrix elements for three-phonon processes from first order time-dependent perturbation theory. Let us consider an initial state of the *squeezed phonon* system in which three squeezed phonons are identified with their modes

$$|i\rangle = |n_{\mathbf{k}}, n_{\mathbf{k}'}, n_{\mathbf{k}''}\rangle = \frac{(b_{\mathbf{k}}^\dagger)^{n_{\mathbf{k}}}}{\sqrt{n_{\mathbf{k}}}} \frac{(b_{\mathbf{k}'}^\dagger)^{n_{\mathbf{k}'}}}{\sqrt{n_{\mathbf{k}'}}} \frac{(b_{\mathbf{k}''}^\dagger)^{n_{\mathbf{k}''}}}{\sqrt{n_{\mathbf{k}''}}} |\xi\rangle \quad (\text{A.5.1})$$

where $b_{\mathbf{k}}$ are the squeezed phonon quasi particle operators defined in (A.3.3) and $|\xi\rangle$ is the squeezed vacuum state (A.3.1). We consider the presence of anharmonic third order perturbation \mathcal{V}_3 to cause the system to change in time t to a final state :

- for *class 1* three phonon events $|f\rangle = |n_{\mathbf{k}} - 1, n_{\mathbf{k}'} - 1, n_{\mathbf{k}''} + 1\rangle$
- for *class 2* three phonon events $|f\rangle = |n_{\mathbf{k}} - 1, n_{\mathbf{k}'} + 1, n_{\mathbf{k}''} + 1\rangle$

The rate of occurrence of such a process per unit time, or the transition probability, is given by the golden rule formula

$$P_i^f = \frac{2\pi}{\hbar} |\langle f | \mathcal{V}_3 | i \rangle|^2 \delta(E_f - E_i) \quad (\text{A.5.2})$$

where $E_i(E_f)$ is the initial(final) state energy of the three (squeezed-) phonon system. For class 1 events $E_f - E_i = \hbar(\Omega_{\mathbf{k}''} - \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}})$, and for class 2 events $E_f - E_i = -\hbar(\Omega_{\mathbf{k}} - \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}''})$.

So explicit expressions for class 1 and class 2 events become

$$P_{\mathbf{k}, \mathbf{k}'}^{\mathbf{k}''} = \frac{2\pi}{\hbar^2} |\langle n_{\mathbf{k}} - 1, n_{\mathbf{k}'} - 1, n_{\mathbf{k}''} + 1 | \mathcal{V}_3 | n_{\mathbf{k}}, n_{\mathbf{k}'}, n_{\mathbf{k}''} \rangle|^2 \delta(\Omega_{\mathbf{k}} + \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}''}) \quad (\text{A.5.3})$$

$$P_{\mathbf{k}}^{\mathbf{k}', \mathbf{k}''} = \frac{2\pi}{\hbar^2} |\langle n_{\mathbf{k}} - 1, n_{\mathbf{k}'} + 1, n_{\mathbf{k}''} + 1 | \mathcal{V}_3 | n_{\mathbf{k}}, n_{\mathbf{k}'}, n_{\mathbf{k}''} \rangle|^2 \delta(\Omega_{\mathbf{k}} - \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}''}) \quad (\text{A.5.4})$$

The third order anharmonic potential is given by

$$\mathcal{V}_3 = \frac{1}{3!} \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \left(\frac{\hbar}{2M}\right)^{\frac{3}{2}} \frac{k k' k''}{\sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'} \omega_{\mathbf{k}''}}} A_{\mathbf{k}\mathbf{k}'\mathbf{k}''} Q_{\mathbf{k}} Q_{\mathbf{k}'} Q_{\mathbf{k}''} \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \quad (\text{A.5.5})$$

Here $Q_{\mathbf{k}}$ are the normal phonon displacement operators as defined in (3.1). This anharmonic term will contribute to the effective mean field Hamiltonian (3.8) as

$$\mathcal{H}^{eff} = \sum_{\mathbf{k}} \hbar \Omega_{\mathbf{k}} \left(b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + \frac{1}{2} \right) + \mathcal{V}_3^{eff} \quad (\text{A.5.6})$$

the effective third order potential being

$$\begin{aligned} \mathcal{V}_3^{eff} &= \mathcal{S}^\dagger \mathcal{V}_3 \mathcal{S} \\ &= \frac{1}{3!} \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \left(\frac{\hbar}{2M}\right)^{\frac{3}{2}} \frac{k k' k''}{\sqrt{\Omega_{\mathbf{k}} \Omega_{\mathbf{k}'} \Omega_{\mathbf{k}''}}} A_{\mathbf{k}\mathbf{k}'\mathbf{k}''} Q_{\mathbf{k}}^{sq} Q_{\mathbf{k}'}^{sq} Q_{\mathbf{k}''}^{sq} \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \end{aligned} \quad (\text{A.5.7})$$

where $\Omega_{\mathbf{k}}$ is the renormalized frequency (A.3.19) and $Q_{\mathbf{k}}^{sq}$ are the squeezed displacement operators defined by (A.4.4).

The calculated three phonon scattering matrix elements are then

$$P_{\mathbf{k},\mathbf{k}'}^{\mathbf{k}''} = \frac{2\pi}{\hbar^2 N} \left(\frac{\hbar}{2M}\right)^3 \frac{(k k' k'')^2}{\sqrt{\Omega_{\mathbf{k}} \Omega_{\mathbf{k}'} \Omega_{\mathbf{k}''}}} |A_{\mathbf{k}\mathbf{k}'\mathbf{k}''}|^2 N_{\mathbf{k}} N_{\mathbf{k}'} (N_{\mathbf{k}''} + 1) \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \quad (\text{A.5.8})$$

$$P_{\mathbf{k}}^{\mathbf{k}',\mathbf{k}''} = \frac{N_{\mathbf{k}'} + 1}{N_{\mathbf{k}'}} P_{\mathbf{k},\mathbf{k}'}^{\mathbf{k}''}$$

Here, $N_{\mathbf{k}}$ is the average renormalized thermal occupation factor given in (A.4.5).

The three phonon scattering rate can be expressed in terms of the above matrix elements

$$\Gamma_{\mathbf{k}} = \int \frac{d^3 k}{(2\pi)^3} \frac{d^3 k'}{(2\pi)^3} \left[\frac{1}{2} P_{\mathbf{k}}^{\mathbf{k}',\mathbf{k}''} \delta(\Omega_{\mathbf{k}} - \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}''}) + P_{\mathbf{k}\mathbf{k}'}^{\mathbf{k}''} \delta(\Omega_{\mathbf{k}} + \Omega_{\mathbf{k}'} - \Omega_{\mathbf{k}''}) \right] \quad (\text{A.5.9})$$

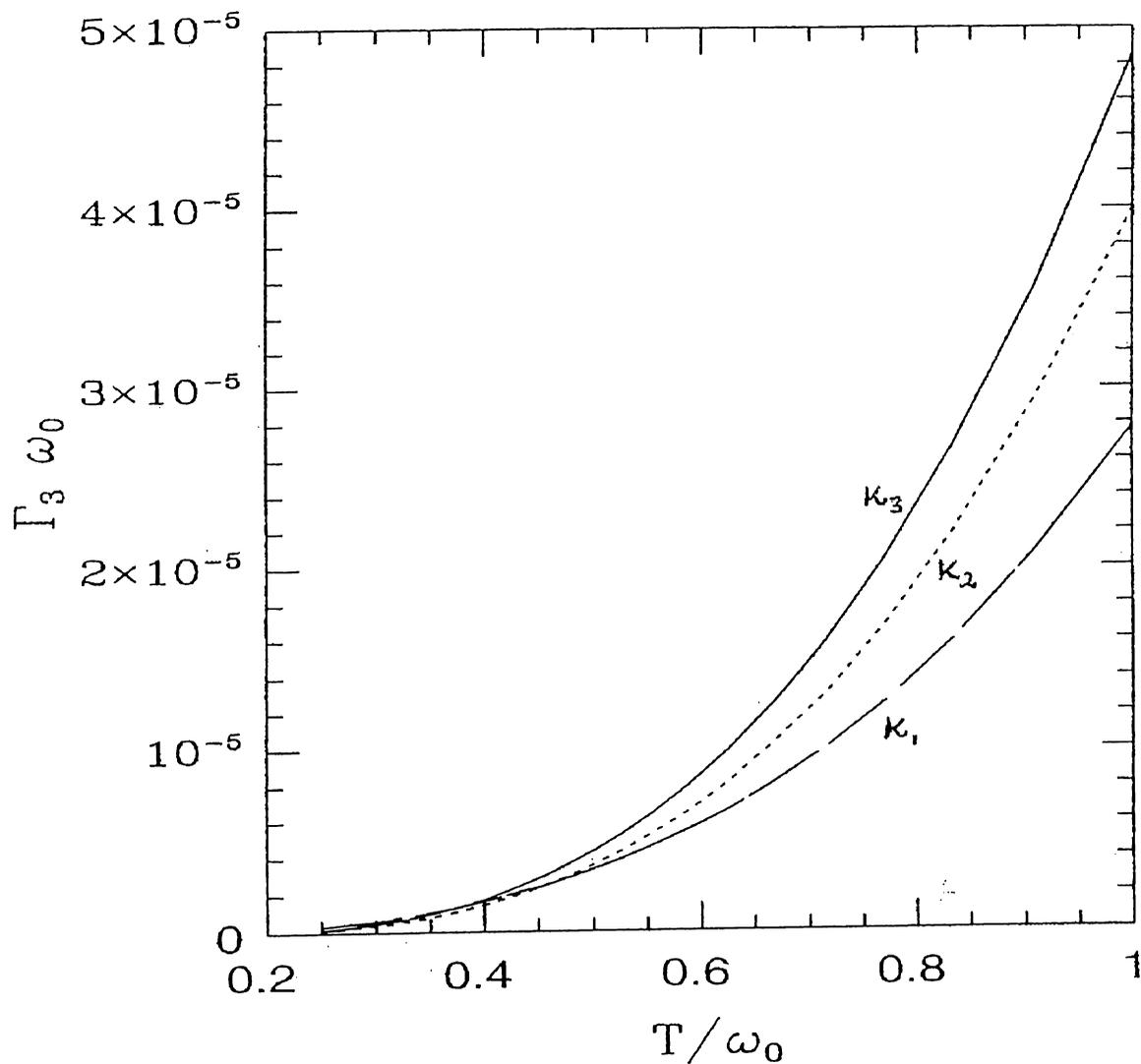


Figure A.3: Phonon scattering rate in squeezed state

Temperature variation of third order scattering rate Γ_3 for various squeezing parameters κ_q : $\kappa_1 > \kappa_2 > \kappa_3$. Note the suppression of the scattering rate with increasing squeezing parameter.

A.6 Electron-Electron Coupling in Presence of Correlated Phonons

For the derivation of the effective electron-electron coupling in the presence of correlated squeezed phonons we start with the Fröhlich Hamiltonian including

the simplest anharmonic phonon interaction term

$$\mathcal{H} = \sum_{\mathbf{q}, \sigma} \mathcal{E}_{\mathbf{q}} c_{\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}, \sigma} + \sum_{\mathbf{k}} \omega_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{k}} \gamma(\mathbf{k}) \rho_{\mathbf{k}} (a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger}) + \sum_{\mathbf{k}} (\kappa_{\mathbf{k}} a_{\mathbf{k}} a_{-\mathbf{k}} + \kappa_{\mathbf{k}}^* a_{\mathbf{k}}^{\dagger} a_{-\mathbf{k}}^{\dagger}) \quad (\text{A.6.1})$$

where $c_{\mathbf{q}, \sigma}$'s and $a_{\mathbf{k}}$'s are fermion and phonon annihilation operators and $\mathcal{E}_{\mathbf{q}}$ and $\omega_{\mathbf{k}}$ are the single particle electron energy and phonon frequency, respectively. We use the composite index $\mathbf{k} = (\vec{k}, s)$ for the phonon variables, \vec{k} being a phonon wavevector, and s a polarization. Here $\gamma(\mathbf{q})$ describes the Fröhlich type electron-phonon interaction and $\kappa_{\mathbf{q}} = |\kappa_{\mathbf{q}}| e^{i\theta_{\mathbf{q}}}$ describes the squeezed phonon coupling constant. $\rho_{\mathbf{k}}$ is the momentum dependent electron density operator given by

$$\rho_{\mathbf{k}} = \sum_{\mathbf{q}, \sigma} c_{\mathbf{k}+\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}, \sigma} \quad (\text{A.6.2})$$

Squeezing can be the simplest realization of a non-linearity of interaction between different phonon modes. Squeezing, which is synonymously used with correlation, is known to exist in some real superconducting materials.

The pure phonon part of the Hamiltonian \mathcal{H} may be diagonalized by the Bogoliubov transformation

$$\begin{aligned} b_{\mathbf{k}} &= C_{\mathbf{k}} a_{\mathbf{k}} - S_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger}, \\ b_{-\mathbf{k}}^{\dagger} &= C_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger} - S_{\mathbf{k}} a_{\mathbf{k}}. \end{aligned} \quad (\text{A.6.3})$$

For the transformation to be canonical, i.e to conserve the form of the commutation relations, it is necessary that $|C_{\mathbf{k}}|^2 - |S_{\mathbf{k}}|^2 = 1$. The coefficients are given by

$$\begin{aligned} C_{\mathbf{k}} &= \frac{i}{\sqrt{2}} \left(\frac{\omega_{\mathbf{k}} + \Omega_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \right)^{\frac{1}{2}} e^{i\theta_{\mathbf{k}}/2} \\ S_{\mathbf{k}} &= \frac{i}{\sqrt{2}} \left(\frac{\omega_{\mathbf{k}} - \Omega_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \right)^{\frac{1}{2}} e^{i\theta_{\mathbf{k}}/2} \end{aligned} \quad (\text{A.6.4})$$

where $\Omega_{\mathbf{k}} = \sqrt{\omega_{\mathbf{k}}^2 - 4|\kappa_{\mathbf{k}}|^2}$ is the new spectrum. We can take $\theta_{\mathbf{k}} = 0$ without any loss of generality. By using the equations (A.6.1), (A.6.3) and (A.6.4), an

effective Hamiltonian describing exchange of virtual correlated phonons can be obtained as

$$\mathcal{H} = \sum_{\mathbf{q}, \sigma} \mathcal{E}_{\mathbf{q}} c_{\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}, \sigma} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \sum_{\mathbf{k}} \gamma(\mathbf{k}) (C_{\mathbf{k}} + S_{\mathbf{k}}) \rho_{\mathbf{k}} (b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger}). \quad (\text{A.6.5})$$

Decoupling of phonons from the electrons can be achieved by an *infinitesimal* Lang-Firsov transformation

$$B_{\mathbf{k}} = b_{\mathbf{k}} - f_{\mathbf{k}} \rho_{\mathbf{k}}. \quad (\text{A.6.6})$$

Here the renormalized phonon operators $B_{\mathbf{k}}, B_{\mathbf{k}}^{\dagger}$ obey the bosonic canonical commutation relation $[B_{\mathbf{k}}, B_{\mathbf{k}}^{\dagger}] = 1$. The appropriate $f_{\mathbf{k}}$ has to be chosen as

$$f_{\mathbf{k}} = -\frac{\gamma(\mathbf{k})}{\Omega_{\mathbf{k}}} (C_{\mathbf{k}} + S_{\mathbf{k}}) \quad (\text{A.6.7})$$

in order to kill the linear term in $g_{\mathbf{k}}$. The decoupled Hamiltonian can be written as

$$\mathcal{H} = \sum_{\mathbf{q}, \sigma} \tilde{\mathcal{E}}_{\mathbf{q}, \sigma} c_{\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}, \sigma} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}} B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}} + \sum_{\substack{\mathbf{k}, \mathbf{q}, \mathbf{q}' \\ \sigma, \sigma'}} V_{\mathbf{k}} c_{\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}'+\mathbf{k}, \sigma'}^{\dagger} c_{\mathbf{q}+\mathbf{k}, \sigma} c_{\mathbf{q}', \sigma'}. \quad (\text{A.6.8})$$

In the renormalization of the single-particle electron energy $\tilde{\mathcal{E}}_{\mathbf{q}, \sigma}$ by squeezed phonons there is a contribution from the direct Hartree term which originates from reorganizing the four electron term to the conventional normal ordered BCS form.

The important result of this calculation shows up in the form of the effective electron-pair interaction potential, given by

$$V_{\mathbf{k}} = -\frac{|\gamma(\mathbf{k})|^2}{\Omega_{\mathbf{k}}} \frac{\omega_{\mathbf{k}} + \kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \quad (\text{A.6.9})$$

Note that there is an enhancement factor of $\frac{\omega_{\mathbf{k}}}{\Omega_{\mathbf{k}}} \frac{\omega_{\mathbf{k}} + \kappa_{\mathbf{k}}}{\Omega_{\mathbf{k}}}$ due to the squeezing of interaction-mediating phonons.

A.7 Lang-Firsov Transformation

In this section the explicit derivation of the formula (4.18) is given.

We will begin with the Fröhlich Hamiltonian of interacting electrons and squeezed phonons.

$$\mathcal{H} = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}}^{ph} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + 1/2) + \sum_{\mathbf{k}} \Upsilon(\mathbf{k}) \rho(\mathbf{k}) (b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger}) \quad (\text{A.7.1})$$

where we have redefined $\Upsilon(\mathbf{k}) = \gamma(\mathbf{k}) (C_{\mathbf{k}}^{ph} + S_{\mathbf{k}}^{ph})$ and $\rho(\mathbf{k}) = \sum_{\mathbf{q}, \sigma} c_{\mathbf{k}+\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}, \sigma}$.

The Lang-Firsov transformation is defined by

$$\mathcal{U} = \exp \left\{ \sum_{\mathbf{k}} \frac{\Upsilon_{\mathbf{k}}}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho^{\dagger}(\mathbf{k}) (b_{\mathbf{k}}^{\dagger} - b_{-\mathbf{k}}) \right\} \quad (\text{A.7.2})$$

Now since \mathcal{U} is unitary $\mathcal{U}^{\dagger} \mathcal{H} \mathcal{U}$ describes the same physics as \mathcal{H} . The explicit realization of the transformation involves the use of Baker-Hausdorff Lemma:

$$e^A Q e^{-A} = Q + [A, Q] + \frac{1}{2} [A, [A, Q]] + \dots \quad (\text{A.7.3})$$

The transformation of the Hamiltonian can then be obtained by the transformed operators:

$$\mathcal{U} \rho(\mathbf{k}) \mathcal{U}^{\dagger} = \rho(\mathbf{k}) \quad (\text{A.7.4})$$

$$\mathcal{U} b_{\mathbf{k}}^{\dagger} \mathcal{U}^{\dagger} = b_{\mathbf{k}}^{\dagger} - \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(\mathbf{k}) \quad (\text{A.7.5})$$

$$\mathcal{U} b_{\mathbf{k}} \mathcal{U}^{\dagger} = b_{\mathbf{k}} - \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(-\mathbf{k}) \quad (\text{A.7.6})$$

$$\mathcal{U} Q_{\mathbf{k}} \mathcal{U}^{\dagger} = Q_{\mathbf{k}} - 2 \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(-\mathbf{k}) \quad (\text{A.7.7})$$

where $Q_{\mathbf{k}} = b_{\mathbf{k}} + b_{\mathbf{k}}^{\dagger}$ and $\Upsilon(\mathbf{k}) = \Upsilon(-\mathbf{k})$, $\rho^{\dagger}(\mathbf{k}) = \rho(-\mathbf{k})$. Then the transformed Hamiltonian $\mathcal{H}' = \mathcal{U} \mathcal{H} \mathcal{U}^{\dagger}$ becomes

$$\mathcal{H}' = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} \mathcal{U} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} \mathcal{U}^{\dagger}$$

$$\begin{aligned}
& + \sum_{\mathbf{k}} \hbar \Omega_{\mathbf{k}} \left\{ [b_{\mathbf{k}}^{\dagger} - \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(\mathbf{k})] [b_{\mathbf{k}} - \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(-\mathbf{k})] + \frac{1}{2} \right\} \\
& + \sum_{\mathbf{k}} \Upsilon(\mathbf{k}) \rho(\mathbf{k}) (Q_{\mathbf{k}} - 2 \frac{\Upsilon(\mathbf{k})}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(-\mathbf{k})) \quad (\text{A.7.8})
\end{aligned}$$

The second term kills the last term, which results in decoupling of electrons from phonons.

$$\mathcal{H}' = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}} \mathcal{U} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} \mathcal{U}^{\dagger} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}}^{ph} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + 1/2) - \sum_{\mathbf{k}} \frac{|\Upsilon(\mathbf{k})|^2}{\hbar \Omega_{\mathbf{k}}^{ph}} \rho(\mathbf{k}) \rho(-\mathbf{k}) \quad (\text{A.7.9})$$

The first term cannot be calculated exactly and must be handled through the use of perturbation theory. We replace

$$\begin{aligned}
\mathcal{U}^{\dagger} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} \mathcal{U} & \simeq \langle \xi | \mathcal{U} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} \mathcal{U}^{\dagger} | \xi \rangle \\
& = 1 - \sum_{\mathbf{k}'} \left(\frac{|\Upsilon(\mathbf{k}')|}{\hbar \Omega_{\mathbf{k}'}} \right)^2 e^{-4\varepsilon_{\mathbf{k}'}} (\delta_{\mathbf{q}, \mathbf{q}+\mathbf{k}'} + \delta_{\mathbf{q}, \mathbf{q}-\mathbf{k}'} - 2\delta_{\mathbf{q}, \mathbf{k}'}) \quad (\text{A.7.10})
\end{aligned}$$

i.e by its average over the phonon ground state. This corresponds to a renormalization of the single electron spectrum. Lastly, the density-density term in (A.7.10) must be converted into BCS-ordered form, which brings a further contribution to this renormalization. Final form of the Hamiltonian becomes

$$\begin{aligned}
\mathcal{H}' & = S^{\dagger} \mathcal{U}^{\dagger} \mathcal{H} S \mathcal{U} \\
& = \sum_{\mathbf{q}} \tilde{\varepsilon}_{\mathbf{q}} c_{\mathbf{q}}^{\dagger} c_{\mathbf{q}} + \sum_{\mathbf{k}} \Omega_{\mathbf{k}}^{ph} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + 1/2) \\
& \quad + \sum_{\substack{\mathbf{k}, \mathbf{q}, \mathbf{q}' \\ \sigma, \sigma'}} \frac{|\Upsilon(\mathbf{k})|^2}{\Omega_{\mathbf{k}}^{ph}} c_{\mathbf{k}+\mathbf{q}, \sigma}^{\dagger} c_{\mathbf{q}'-\mathbf{k}, \sigma'}^{\dagger} c_{\mathbf{q}, \sigma'} c_{\mathbf{q}', \sigma} \quad (\text{A.7.11})
\end{aligned}$$

where the renormalized single electron spectrum is given by

$$\tilde{\varepsilon}_{\mathbf{q}} = \varepsilon_{\mathbf{q}} - \sum_{\mathbf{k}'} \left(\frac{|\Upsilon(\mathbf{k}')|}{\hbar \Omega_{\mathbf{k}'}} \right)^2 e^{-4\varepsilon_{\mathbf{k}'}} (\varepsilon_{\mathbf{q}+\mathbf{k}'} + \varepsilon_{\mathbf{q}-\mathbf{k}'} - 2\varepsilon_{\mathbf{k}'})$$

$$+ \sum_{\mathbf{k}'} \frac{|\Upsilon(\mathbf{q} + \mathbf{k}')|^2}{\hbar \Omega_{\mathbf{q} + \mathbf{k}'}} \quad (\text{A.7.12})$$

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