The Nature of Vibrations of a 2-D Disordered Lattice Model with Nano-scale Order

Prasenjit Ghosh and Umesh V Waghmare

Theoretical Sciences Unit,
Jawaharlal Nehru Centre for Advanced Scientific Research,
Jakkur PO, Bangalore 560 064, India

Motivated by the unusual soft mode anomalies in the relaxor ferroelectrics, we present a numerical study of vibrational excitations of a disordered lattice model with chemical order on the nano-scale. We find an Ioffe-Regel crossover in acoustic modes separating propagating low-frequency modes from the intermediate frequency diffusons, and localized modes at the high-frequency end of the spectrum. At a fixed degree of disorder, we find increasing uncertainty in the momentum of long wave-length optical modes with decrease in the size of nano-ordered regions. We determine the cause for this to be a strong mixing between acoustic and optical modes, believed to be central to the model of waterfall phonon anomalies.

PACS numbers: 63.22.+m 63.20.Dj 74.25.Kc

Nano-scale structure of materials has interesting effects on their macroscopic behavior and become yet another control parameter in tuning material properties[1]. For example, relaxor ferroelectrics, such as PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN)[2] and PbSc\textsubscript{2/3}Nb\textsubscript{1/3}O\textsubscript{3} (PSN)[3], have tremendous technological potential in applications based on solid state transducers[4], due to their giant electromechanical and dielectric response. Randomness and nano-scale regions in the ordering of polar fields are known to be central to these interesting properties[3, 5]. In contrast to conventional ferroelectrics such as PbTiO\textsubscript{3} with a sharp ferroelectric transition, relaxors exhibit a diffuse ferroelectric transition, with a broad peak in dielectric constant as a function of temperature.

Ferroelectricity in conventional ferroelectric materials is essentially a phonon-related property characterized by a soft mode near the ferroelectric phase transition[7, 8]. The soft phonon anomalies in the context of relaxors[9] were observed as “waterfall phonons” recently using neutron scattering, with a speculation that these are linked with nano-polar regions. Further studies of the “waterfall” phenomena based on neutron scattering were explained using a mode-coupling theory[10, 11] for the coupling between acoustic and optical modes. While the model used in our analysis is a great simplification of relaxors, it allows us to determine some general aspects of phonons in a nano-ordered system. In particular, we find localization of modes at high frequencies and an Ioffe-Regel crossover at low frequencies, similar to that found in amorphous systems[12, 13]. Our findings about the nature of long-wavelength optical modes helps in uncovering possible links between nano-scale order and waterfall phonons in terms of the mode coupling analysis of Hlinka et al.[11].

For the ordered case, our model system consists of two types of atoms A and B occupying (0,0)\textsubscript{a} and (1/2, 1/2)\textsubscript{a} sites of a square lattice respectively, \(a\) being the lattice constant. The interaction between two atoms displaced from their mean position by \(\mathbf{u}_i\) and \(\mathbf{u}_j\) is given by

\[
U_{ij} = k_L (\hat{\mathbf{b}}_i \cdot \mathbf{u}_i)(\hat{\mathbf{b}}_j \cdot \mathbf{u}_j) + k_T (\hat{\mathbf{b}}_i \cdot \mathbf{u}_i)(\hat{\mathbf{b}}_j \cdot \mathbf{u}_j)
\]

(1)

where \(\hat{\mathbf{b}}_i\) and \(\hat{\mathbf{b}}_j\) are the unit vectors parallel (longitudinal) and perpendicular (transverse) to the line joining two atoms respectively, \(k_L\) and \(k_T\) being the longitudinal and transverse force constants respectively. Only harmonic interactions up to the second nearest neighbors ((1,1)\textsubscript{a}) have been included, giving 10 distinct interatomic force constants \(k_{L,T}^{AA,nn}, k_{L,T}^{AA,2nn}, k_{L,T}^{BB,nn}, k_{L,T}^{BB,2nn}, k_{L,T}^{AB,nn}\) and two onsite interactions \(k_A\) and \(k_B\), where \(nn\) and \(2nn\) stand for the nearest and next nearest neighbors respectively. Values of the force constants (Table I) have been chosen such that the acoustic sum rule is obeyed, there are stable modes throughout the Brillouin zone, and acoustic and optical branches are well-separated.

Disorder is introduced by randomly selecting two different types of atoms and interchanging their positions
making sure that a given atom is interchanged only once. A configuration with nano-scale order is obtained by excluding such an interchange in the circular nano-ordered regions (NORs) with a fixed diameter of a few nanometers. Centres of these circular regions are taken randomly, but avoiding any overlap between them. The degree of disorder is quantified with a disorder parameter \( \delta \) defined as

\[
\delta = \frac{\text{No. of A-A or B-B nearest neighbors}}{\text{Total no. of nearest neighbor}}. \quad (2)
\]

For a fully ordered case, \( \delta = 0.0 \), whereas \( \delta \) is 0.5 for the completely disordered case. For a disordered configuration A and B occupy one of the two sites of the square lattice with equal probability, resulting in new types of neighboring pairs of atoms, such as (A-B)\(_{2n}\) and (A-B)\(_{3n}\). The force constants for their interactions are taken as \((k^{AAnn}_X + k^{BBnn}_X)/2.0\) and \((k^{A2nn}_X + k^{B2nn}_X)/2.0\) respectively, where \(X = L, T\). Similarly, nearest neighbor atoms of the same type can possibly be separated by \((0.5,0,5)\), for which the force constants are given by \(k^{Y2nn}_X\), where \(Y = A, B\). The \((Y-Y)_{nn}\) interactions for the ordered case are now the \((Y-Y)_{2nn}\) and \((Y-Y)_{3nn}\), respectively. The acoustic sum rule is imposed by correcting the diagonal elements of the force constant matrix\[21\]. Using this model, we study vibrational modes of configurations consisting of \(32 \times 32\) lattice sites (2048 atoms) with different number of nano-ordered regions and \(\delta \approx 0.4\).

**TABLE I: Force constants (in ar. units) for different interactions along different directions**

| Force Constants Values | Force Constants Values |
|------------------------|------------------------|
| \(k_A\)               | \(k^{BBnn}_B\)         |
| -19.0                  | -2.5                   |
| \(k_B\)               | \(k^{BBnn}_A\)         |
| -16.0                  | -0.5                   |
| \(k^{AAnn}_L\)        | \(k^{BB2nn}_B\)        |
| 2.0                    | -0.25                  |
| \(k^{A2nn}_L\)        | \(k^{BB2nn}_B\)        |
| -0.5                   | 0.0                    |
| \(k^{A2nn}_T\)        | \(k^{BB2nn}_B\)        |
| -1.25                  | -2.25                  |
| \(k^{A42nn}_T\)       | \(k^{BBnn}_B\)         |
| 0.0                    | -1.25                  |

The spectral density function \(S_k(\omega)\) is calculated for different configurations, which allows us to relate to the constant energy scan and constant momentum transfer scan obtained in the neutron scattering experiments. We use the contour plot of \(S_k(\omega)\) in visualizing the dispersion of phonon modes for systems with disorder. The spectral density function\[21\] is given by

\[
S_k(\omega) = \frac{\sum_{j=1}^{N} |\tilde{\alpha}_j|^2 \delta(\omega - \omega^j)}{2N} \quad (3)
\]

where \(N\) is the total number of atoms. \(\omega^j\) is the frequency of the \(j^{th}\) eigenmode, \(|\tilde{\alpha}_k|\) is the Fourier transform of the real space eigenvector of the \(j^{th}\) mode. Phonon dispersion of the ordered system along the \(\langle 10 \rangle\) direction obtained from dynamical matrix and from \(S_k(\omega)\) are compared in Fig. 1. At \(X\) point, the longitudinal optical branch has the highest energy, whereas the transverse optical branch is degenerate with the longitudinal acoustic branch. Finite width of the peaks in the contour plot of \(S_k(\omega)\) arise from the width of Gaussian used to approximate the delta function in Eqn 3. Based on a reasonable agreement between the two descriptions, we use \(S_k(\omega)\)-based description in the study of phonons of systems with disorder. Our results for phonons of nano-ordered and disordered configurations (Fig. 1(c)-(d)) show that the introduction of disorder results in mixing of the phonon modes and subsequent broadening of peaks in \(S_k(\omega)\) as a function of both \(k\) and \(\omega\); \(k\) is no longer a good quantum number to describe these modes. While new modes with intermediate energies appear near the \(\Gamma\) point, long wavelength acoustic modes for \(k \lesssim 0.22\) are least affected. This is consistent with the error-bars on phonon measurements using inelastic neutron scattering technique\[8\].

To probe extended versus localized nature of modes in the presence of disorder and nano-ordered regions we calculate inverse participation ratio (IPR):

\[
IPR(\omega_j) = N \frac{\sum_i |\tilde{\alpha}_i^j|^4}{(\sum_i |\tilde{\alpha}_i^j|^2)^2} \quad (4)
\]

where \(\tilde{\alpha}_i^j\) are the eigenstates of the phonon modes. IPR is \(N\) (1) for a fully localized (extended) mode. For a configuration with fourteen nano-ordered regions, IPR as a function of energy (Fig. 2(a)) is found to be quite similar.
function is used to obtain the decay time \( \tau \) width at half maxima (function of frequency. In the frequency domain, the full propagons, but not for diffusons. The Ioffe-Regel (I-R) sons. Wave vector

wavelength modes (evident in Fig 1) and the latter do ever, the former have non-negligible character of long-wavevector, point of their crossover is indicated by a circle.

to that obtained for amorphous Si\(^{18}\). The high energy modes, between 5.0 and 6.0 units of energy, are highly localized and are called locons, while the rest are called extendons\(^{18}\). Some modes around \( \epsilon = 2.0 \) have intermediate values of IPR exhibiting moderate localization. We investigated these modes further by examining distribution of number of atoms as a function of their contribution to the IPR and find that they are similar to the localized modes with the same IPR and \( 5 < \epsilon < 6 \). However, the former have non-negligible character of long-wavelength modes (evident in Fig 1) and the latter do not.

Extendons can be classified into two categories, the propagons (these propagate ballistically) and the diffusons. Wave vector \( k \) is a good quantum number for propagons, but not for diffusons. The Ioffe-Regel (I-R) cross-over \(^{17}\) separates propagons and diffusons as a function of frequency. In the frequency domain, the full width at half maxima (\( \zeta \)) of a peak in the spectral density function is used to obtain the decay time \( \tau \) of a propagating mode due to scattering (\( \tau_{k}^{-1} \approx \pi \zeta \omega(k) \))\(^{18}\). The crossover point between \( \omega \) vs. \( k \) and \( \tau^{-1} \) vs. \( k \) gives the location (\( k \)) of the I-R cross-over. For the configuration with fourteen nano-ordered regions (Fig. 2(b)), we find the I-R crossover at \( k = 0.22 \) r.l.u. and \( \omega = 2.2 \). The vibrational modes with energy between 2.2 and 5.0 are thus diffusons.

To further affirm this classification of modes, we studied their level spacing distribution (LSD). LSD, with its foundation in the random matrix theory (RMT), is known to exhibit Wigner-Dyson statistics for diffusons and Poisson statistics for locons\(^{18}\). We calculated level spacings distribution using spectral unfolding, in which the original spectrum is mapped into an ordered set of numbers with uniform density of states. We find that the LSD for modes with \( 2.2 < \epsilon < 5.0 \) obeys Wigner-Dyson statistics whereas that for modes with \( \epsilon > 5.0 \) obeys Poisson statistics with slight deviation near zero spacing. This supports our classification of these modes as diffusons and locons respectively.

To explore mixing among phonon modes due to disorder, we introduce an energy correlation function \( f(\epsilon, \epsilon') \) as an overlap between the modes of the ordered system (\( \langle |o_{n}^{O}| \rangle \)) with those of the disordered system (\( \langle |o_{m}^{D}| \rangle \)):

\[
f(\epsilon, \epsilon') = \Sigma_{m,n} \langle |o_{m}^{D}| \rangle \langle |o_{n}^{O}| \rangle^{2} \delta(\epsilon - \epsilon_{m})\delta(\epsilon' - \epsilon_{n}).
\] (5)

It is based on the representation of modes of a disordered configuration as a linear combination of normal modes of a fully ordered system. The contour plots of \( f(\epsilon, \epsilon') \) (Fig. 3) clearly show that the acoustic modes of a nano-ordered system in the IR-crossover region emerge from mixing of acoustic and optical modes of the ordered system. At the fixed degree of disorder, this mixing becomes stronger with the number of nano-ordered regions. Secondly, diffusion modes in the optical region of the spectrum of a nano-ordered system arise mainly from mixing among optical modes with different wave vector. We find that the effects of disorder become stronger as the number (size) of nano-ordered regions increases (decreases).

To understand the nature of diffusons, we show in Fig. 3 the \( k \)-dependence of \( S_{\omega}(k) \) for \( \omega \approx 4.292 \pm 0.034 \) corresponding to peaks of \( S \) at the \( \Gamma \) point for a given configuration. It shows that the probability of finding a long wavelength optical mode decreases as the number of nano-ordered regions increases, as many of these degrees of freedom precipitate into the acoustic branches due to strong mixing. Correspondingly, the uncertainty in momentum \( \hbar k \), which is given by the full width at half maximum (FWHM) of a peak in spectral-density also

FIG. 2: For the configuration with 14 NORs: (a) IPR as a function of energy and (b) acoustic mode frequency and its inverse decay time as a function of wavevector, point of their crossover is indicated by a circle.

FIG. 3: Energy correlation between the modes of ordered system and that of a configuration having (a) 8 nano-ordered regions and (b) 14 nano-ordered regions. The straight line shows perfect correlation or NO mixing.
In summary, we find that chemical disorder on a 2-D lattice results in phonon modes of type: propagons, diffusons and locons. At the fixed degree of disorder, reduction in the size of nano-ordered regions results in increase (decrease) in the width (height) of peaks corresponding to long wavelength optical modes as a function of \( k \). This correlates with corresponding increase in the mixing between optical and acoustic modes. While the length-scale of chemical ordering needs to be large enough (a few nano-metre) for observing optical phonon modes with a definite momentum, it also has to be small to give adequate mixing with acoustic modes responsible for the “waterfall phonons”.

We thank Chandrabhas Narayan, Ranjith and Srikanth Sastry for useful discussions. UVW acknowledges a DuPont young faculty award and PG acknowledges CSIR, India for a research scholarship.

---

[1] S. Seal and M.-I. Barton, MRS Bulletin 29, 9 (2004).
[2] L. E. Cross, Ferroelectrics 76, 241 (1987).
[3] F. Chu, I. M. Reaney and N. Setter, J. App. Phys., 77, 1671 (1995).
[4] R. F. Service, Science 275, 1878 (1997).
[5] R. Pirc and R. Blinc, Phys. Rev. B 60, 13470 (1999).
[6] V. Westphal, W. Kleemann and M. D. Glinchuk, Phys. Rev. Lett. 68, 847 (2000).
[7] W. Cochran, Adv. Phys. 10, 401 (1961).
[8] P. W. Anderson, Fizika Dielektrikov (ed. G. I. Skanavi), Akad. Nauk USSR, Moscow (1960).
[9] P. M. Gehring, S.-E. Park, and G. Shirane, Phys Rev. Lett. 84, 5216 (2000).
[10] P. M. Gehring, S.-E. Park, and G. Shirane, Phys. Rev. B 63, 224109 (2001).
[11] J. Hlinka et al., Phys Rev. Lett. 91, 107602 (2003).
[12] N. Setter and L. E. Cross, J. Appl. Phys. 51, 4356 (1980).
[13] H.B. Krause, J.M. Cowley and J. Wheatley, Acta. Cryst. A35 1015 (1979).
[14] C. Perrin et al., J. Phys. Condens. Matter, 13 10231 (2001).
[15] H.Z. Jin et al., J. App. Phys. 89 5048 (2001).
[16] H. Quian and L.A. Bursill, Int. J. of Mod. Phys. 10, 2027 (1996).
[17] A. F. Ioffe and A. R. Regel, Prog. Semicond. 4, 237 (1960).
[18] P. B. Allen et al., Phil. Mag. B 79, 1715 (1999).
[19] S. N. Taraskin and S. R. Elliot, Phys. Rev. B 61, 12031 (2000).
[20] X. Gonze, Phys. Rev. B 55, 10337 (1997).
[21] H. Ehrenreich and L. M. Schwartz, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31, p. 149.
[22] H. Krakauer et al., J. Phys: Cond. Matt. 11, 3779 (1999).
[23] M. Glinchuk, A. Morozovska and E. Eliseev, Integrated Ferroelectrics 64, 17 (2004).