The Thermodynamic Stability of Two Dimensional Crystals with an Extended Coupling Scheme

D. J. Priour, Jr

Department of Physics, University of Missouri, Kansas City, Missouri 64110, USA

Dated: July 19, 2011

We calculate mean square deviations for crystals in one and two dimensions. For the two dimensional lattices, we consider several distinct geometries (i.e. square, triangular, and honeycomb), and find the same essential phenomena for each lattice structure. We investigate the stability of long-range crystalline order for a variety of coupling schemes, including short-range exponentially decaying inter-atomic potentials and long-range interactions with a power law dependence $r^{-\alpha}$. For the latter in the 1D case, we find a critical value $\alpha_{1d} = 1.615 \pm 0.005$ for the power law decay exponent below which crystalline order is intact, and above which thermal fluctuations destroy long-range order when $T > 0$. The corresponding critical value for two dimensional lattices with displacements confined to the plane is $\alpha_{2d} = 3.15 \pm 0.025$. If motion perpendicular to the crystal plane is permitted, thermally induced distortions diverge rapidly (i.e. linearly) in dual layer systems with local stiffness provided by an extended coupling scheme, even if the interaction is long ranged, decaying as a power law in the separation between lattice sites.

PACS numbers: 62.25.Jk, 62.23.Kn, 63.22.Np

I. INTRODUCTION AND THEORETICAL TECHNIQUES

Crystals are regular periodic physical systems with the atomic constituents organized in periodic arrays, where the periodicity is a characteristic of the crystal in its equilibrium configuration and a manifestation of long-range positional order. However, the effect of thermal fluctuations must be taken into consideration at finite temperatures where thermally excited lattice vibrations may degrade or destroy crystalline order. An early theoretical treatment developed by Lindemann examined the effect of lattice vibrations in a framework which neglected the correlations of atomic motions, but which nonetheless provides a reasonable description (on an order of magnitude basis) for the melting of three dimensional solids.

A salient component of the Lindemann analysis is the Lindemann criterion where the melting of a solid is considered to have taken place when mean square deviations from equilibrium exceed a tenth of a lattice constant. X-ray diffraction data, which may provide a direct measure of long-range order in a crystal lattice (and hence a means to determine temperatures where crystalline order is lost) finds reasonable agreement with the Lindemann criterion. The accord is manifest in the finding that Bragg peaks corresponding to broken translational symmetry vanish when mean square fluctuations from equilibrium (also determined from an analysis of X-ray diffraction data) are in the vicinity of a tenth of a lattice constant, as specified in the Lindemann result.

A factor of significance for the effectiveness of the Lindemann criterion is the tendency for atoms in three dimensional crystals to have a large number of neighbors [e.g. a dozen nearest neighbors in the face of face centered cubic (fcc) lattices]. Hence, mean field treatments in the spirit of Weiss molecular mean field theory are more likely to provide a reasonable theoretical description since statistical fluctuations tend to suppressed somewhat by averaging when a relatively large number of neighbors are present.

On the other hand, it should be understood that apart from the number of nearest neighbors, dimensionality is a very important parameter which may affect the thermodynamic characteristics and integrity of a crystal lattice to a large degree. Nano-scale engineering often takes place in systems of low dimensionality such as carbon nanotubes where the length may exceed the width by several orders of magnitude; nanotubes tend to be regarded as one dimensional systems. Graphene sheets, covalently bonded single layer honeycomb lattices of carbon atoms, may be considered genuine monolayers, and hence possess strongly two dimensional character. The thermodynamic stability of a system is strongly dependent on its dimensionality with statistical fluctuations becoming more important for two dimensional systems, and very important for essentially 1D structures such as nanotubes.

An important theoretical result known as the Mermin-Wagner theorem predicts that as the bulk limit is approached, thermal fluctuations destroy long-range crystalline order in the context of 1D lattices. However, this result does not preclude the stabilization of positional order for $T > 0$ if the interaction between atomic members is long-ranged (e.g. decaying as a power law in the separation between positions in the crystal lattice). In this work, it is our program to examine conditions which preserve long range order in low dimensional systems at finite temperatures.

In one dimension, the deleterious effect of thermal fluctuations is felt most severely, and ultimately only short-range order exists if the interatomic interaction is finite in range. In three dimensions, long-range positional order is intact for finite temperatures below the melting temperature $T_m$. Two dimensional solids are often re-
garded as an intermediate case where thermal fluctuations are strong enough to destroy long-range order as the size of the system is increased, but only in a very gradual manner. Although crystalline order in 2D systems does not survive in the thermodynamic limit if the interaction is confined to nearest neighbors or is otherwise finite in range, a long-range coupling with power law decay may stabilize long-range positional order. In fact, even for one dimensional solids, we find a critical decay exponent \( \alpha_{1D}^c = 1.615 \pm 0.005 \) below which crystalline order remains stable for \( T > 0 \), whereas long-range order is only gradually lost in the bulk for power law decays where \( \alpha > \alpha_c \). Similarly, the corresponding exponent in 2D is \( \alpha_{2D}^c = 3.15 \pm 0.025 \), where long range crystalline order is preserved for \( \alpha < \alpha_{2D}^c \), whereas thermal fluctuations destroy positional order if \( \alpha > \alpha_{2D}^c \). Within the bounds of numerical error, we obtain the same value for the threshold exponent \( \alpha_{2D}^c \) for distinct lattice geometries including square lattices, triangular lattices, and honeycomb lattices.

We examine various types of coupling schemes, including very short-ranged interactions where atoms interact with only a few nearest neighbors and perhaps also next-nearest neighbors. We also consider extended schemes where there is a finite coupling to all neighbors, but where the interaction is still short-ranged, with a rapid decay profile, such as that of an inter-atomic potential with an exponential dependence \( V \propto e^{-\gamma r} \) where \( \gamma^{-1} \) is the finite length scale corresponding to the coupling scheme. Finally, we also consider a long-ranged algebraically decaying coupling of the form \( V(r) = r^{-\alpha} \) where \( \alpha \) may assume different values, though for the energy per atom to be finite in the bulk limit, the exponent must exceed threshold values which depend on dimensionality of the lattice. For single dimensional systems, one must have \( \alpha > \alpha_{1D}^c = 1 \) and \( \alpha > \alpha_{2D}^c = 2 \) for two dimensional crystals.

We report on a calculation of the atomic root mean square deviation \( \delta_{\text{RMS}} \) about positions of equilibrium in 1D and 2D crystals. In section I, we discuss theoretical methods used to calculate the partition function and hence calculate salient thermodynamic quantities by decoupling the vibrational states used to gauge the integrity of long-range crystalline order such as \( \delta_{\text{RMS}} \). In section II, we examine one dimensional systems, finding positional order to be destroyed except in a long-range coupling scheme, (i.e. a power law dependence where the decay exponent \( \alpha \) must lie between \( \alpha_{1D}^c = 1 \) and an upper bound exponent \( \alpha_{1D}^c = 1.615 \pm 0.005 \)). In section III, we perform a similar analysis for two dimensional square lattices, where we generalize to an extended scheme, and find a gradual destruction of crystalline order with increasing system size \( L \) for short-ranged couplings. However, we find that a power law decay profile where \( \alpha < \alpha_{2D}^c = 3.15 \pm 0.025 \) is sufficient to maintain positional order at finite temperatures. In addition to the square lattice, in Section IV we also examine triangular and honeycomb lattices, finding the ability of a long-range interaction between atoms to preserve crystalline order is not affected by the specific type of lattice geometry under consideration, and the threshold exponents in all three cases are identical within the bounds of error in the calculations. Finally, in section V, we consider motion transverse to the plane of the crystal lattice for locally stiff dual layer systems where even if interaction between particles is taken to be long-ranged, we find the perpendicular motions rapidly compromise long-range order as the size of the system is increased.

A salient component of our treatment is the explicit accounting for atomic motions in discrete systems. The harmonic approximation, which neglects anharmonic terms in the potential set up by geometric effects has been tested directly in the context of Monte Carlo simulations and found to be accurate to within one part in \( 10^3 \) for the systems considered.

Since our interest is in equilibrium thermodynamic characteristics of the system, we begin with the lattice potential

\[
V = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{n_i} V(r_{ij}),(1)
\]

where \( n_i \) is the number of neighbors corresponding to each atom in the system indexed with the label \( i \), and \( N \) is the total number of particles contained in the crystal lattice. The factor of \( 1/2 \) in the lattice potential expression is present to compensate for double counting of the energy associated with individual “bonds” between atomic pairs \( i \) and \( j \).

For small deviations from equilibrium positions, a “harmonic approximation” is possible, and one finds instead

\[
V = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{n_i} K_{ij} (l_{ij} - l_{ij}^{0})^2, (2)
\]

the first nonzero term of a Taylor expansion of \( V(r_{ij}) \) where \( l_{ij} \approx l_{ij}^{0} \), and \( K_{ij} \) is the second derivative of the potential \( V(r_{ij}) \) at \( r_{ij} = l_{ij}^{0} \). In the results we report on here, we restrict attention to temperatures below those which would cause melting in the bulk (determined by the Lindemann criterion), where the harmonic approximation would tend to fail well. A primary issue of interest is whether there is any finite temperature range where long-range positional order is intact, and our calculations are in the context of temperatures not of the magnitude that would disrupt the bonding topology and create dislocations, but thermal regimes considerably below the temperature range which might begin to rupture bonds between neighbors. For covalent solids such as two dimensional sheets of graphene and carbon nanotubes where energies stored in covalent bonds are far in excess of \( k_B T \) at 300K, even room temperature may be considered a “low” temperature in the sense of being considerably below temperature scales where thermal fluctuations
would perturb the local bonding scheme in a significant way.

In one dimension, the bonds are collinear, and the potential will remain quadratic as the energies of all bonds between atoms are summed. However, in two dimensional geometries, restoring forces to oppose displacements from equilibrium will be exerted in different directions along distinct bond axes between an interacting pair of atoms. As a consequence, it will be necessary to make an additional harmonic approximation in order to obtain a quadratic Hamiltonian and subsequently exploit translational invariance for the regular lattices we examine.

In general, a bond length \( l_{ij} \) between atoms \( i \) and \( j \) will appear as

\[
 l_{ij} = \sqrt{\left( \Delta_{ij}^{0x} + \delta_{x}^{i} - \delta_{x}^{j} \right)^{2} + \left( \Delta_{ij}^{0y} + \delta_{y}^{i} - \delta_{y}^{j} \right)^{2} + \left( \Delta_{ij}^{0z} + \delta_{z}^{i} - \delta_{z}^{j} \right)^{2}}
\]

(3)

where \( \Delta_{ij}^{0x} \equiv (x_{i}^{0} - x_{j}^{0}), \Delta_{ij}^{0y} \equiv (y_{i}^{0} - y_{j}^{0}), \) and \( \Delta_{ij}^{0z} \equiv (z_{i}^{0} - z_{j}^{0}). \) Thus, the potential energy stored in the bonds depends only on the difference of coordinates such as, e.g., \( \Delta_{ij}^{0x} \) for the equilibrium \( x \) coordinate differences and \( \delta_{x}^{i} - \delta_{x}^{j} \) for differences constructed from the corresponding shifts from equilibrium. If the latter are sufficiently small in relation to the former, it is appropriate to expand about \( \Delta_{ij}^{0x}, \Delta_{ij}^{0y}, \Delta_{ij}^{0z} \) and to quadratic order one will have \( (l_{ij} - l_{ij}^{0})^{2} \approx \left[ \Delta_{ij} \cdot (\delta_{i} - \delta_{j}) \right]^{2} \) where \( \Delta_{ij} \) is a unit vector formed by subtracting the position vectors \( x_{i} \) and \( x_{j} \) corresponding to the atom \( i \) and its neighbor \( j \), such that \( \Delta_{ij} = (x_{i}^{0} - x_{j}^{0})/\|x_{i}^{0} - x_{j}^{0}\| \). Hence, the atomic potential may be written to quadratic order in \( \delta_{i} \) and \( \delta_{j} \), and one has in particular

\[
 V_{Har} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{n_{i}} \frac{K_{ij}}{2} \left[ \Delta_{i} \cdot (\delta_{i} - \delta_{j}) \right]^{2}
\]

(4)

It will be necessary to solve an eigenvalue problem to decouple the vibrational modes. However, with Fourier analysis, the problem may be reduced to the task of diagonalizing a \( 2 \times 2 \) matrix, a \( 4 \times 4 \) matrix in the case of a lattice with a honeycomb geometry, or at most a \( 6 \times 6 \) matrix for the case of the locally stiff dual-layer system, even in cases where the coupling scheme is extended to encompass many neighbors for each atomic member. We will consider systems in one dimension where we show that long-range crystalline order may be stabilized in the case of slowly decaying power law potentials, but not for localized exponentially decaying coupling schemes. We also examine two dimensional lattice geometries, and find similar phenomena; again, a long-range power law decay is needed to preserve crystalline order at finite temperatures.

Finally, we are careful to restrict motion to collinear displacements in the context of 1D systems and inplane motions in the case of the locally stiff dual-layer system. The lattices are very easily disturbed by transverse displacements, and we find that relaxing the collinear and coplanar restrictions in 1D and 2D yields mean square fluctuations which diverge rapidly with increasing system size \( N \). As we find with explicit calculation in section V, this rapid (i.e., at a linear) growth in \( N \) occurs even if the interaction between atoms is a long ranged power law decay in locally stiff dual layer crystal geometries.

We use the results for the eigenvalues for the vibrational modes to calculate thermodynamic properties related to crystalline order such as the thermally averaged mean square fluctuations about equilibrium per site, \( \delta_{\text{RMS}} \). As noted elsewhere and summarized here, the mean square displacements about equilibrium may be calculated in terms of the eigenvalues for the vibrational states.

In terms of the vibrational modes, the lattice energy may be written as

\[
 \mathcal{H}_{\text{Har}} = \frac{1}{2} \sum_{\alpha=1}^{M} \lambda_{\alpha} c_{\alpha}^{2}
\]

(5)

with \( M \) the total number of particles contained in the lattice. The connection between the vibrational states and the mean square fluctuations is

\[
 \langle \delta_{\text{RMS}} \rangle^{2} = \frac{1}{M} \sum_{i=1}^{M} \left( \langle \delta_{i}^{x} \rangle^{2} + \langle \delta_{i}^{y} \rangle^{2} + \langle \delta_{i}^{z} \rangle^{2} \right)
\]

(6)

With the eigenvectors indexed with the label \( \alpha \) and using, e.g., \( \delta_{i}^{x} = \sum_{\alpha=1}^{M} c_{\alpha} v_{i}^{x} \), to express the displacements in terms of the eigenvectors, one finds for a specific system configuration

\[
 \delta^{2} = \frac{1}{M} \sum_{i=1}^{M} \sum_{\alpha=1}^{M} \sum_{\alpha' =1}^{M} c_{\alpha} c_{\alpha'} \left( v_{i}^{x} v_{i}^{x} + v_{i}^{y} v_{i}^{y} + v_{i}^{z} v_{i}^{z} \right)
\]

(7)

In the thermal average, the factor \( c_{\alpha} c_{\alpha'} \) will be as often positive as negative, and hence only in the case \( \alpha = \alpha' \) will there be a net contribution to the thermal average \( \langle \delta_{\text{RMS}} \rangle^{2} \). If the vectors are taken to be normalized, one finds

\[
 \langle \delta_{\text{RMS}} \rangle^{2} = \frac{1}{M} \sum_{\alpha=1}^{M} \langle c_{\alpha}^{2} \rangle
\]

(8)

With the lattice energy expressed in this way, the partition function becomes a product of Gaussian integrals,

\[
 Z = \prod_{\alpha=1}^{3M} \int_{-\infty}^{\infty} e^{-\beta \lambda_{\alpha} c_{\alpha}^{2}/2} dc_{\alpha} = \prod_{\alpha=1}^{3M} \left( \frac{2\pi \tau}{\lambda_{\alpha}} \right)^{1/2}
\]

(9)

where \( \tau \equiv k_{B} T \). Finally, a thermal derivative of \( Z \) leads to

\[
 \langle \delta_{\text{RMS}} \rangle^{2} = \frac{d}{d\tau} \ln(Z) = \sum_{\alpha=1}^{3M} \lambda_{\alpha}^{-1} \tau
\]

(10)
Hence, for the mean square deviation, we have

$$\langle \delta_{\text{RMS}} \rangle = \tau^{1/2} \sqrt{\sum_{a=1}^{3M} \delta_{\text{RMS}}^n}$$

The term in the radical is not temperature dependent, but is instead determined by characteristics of the lattice geometry and the bonding scheme between atomic members. In this work, we calculate $\delta_{\text{RMS}}^n$, a mean square RMS deviation normalized with respect to temperature. Zero eigenvalues are artifacts of the periodic boundary conditions, correspond to global translations of the lattice, and are excluded from the sum.

## II. SYSTEMS IN ONE DIMENSION

In the 1D systems we consider, only longitudinal displacements are examined; similarly, for the two dimensional geometries, lattice vibrations are considered to be confined to the two dimensional plane with no transverse motions considered. Periodic boundary conditions are implemented in both the one and two dimensional cases. An important characteristic of systems in one dimension is the fact that all bonds are collinear, and hence there is no purely geometric source of anharmonic effects. The lattice potential energy will have the form

$$V = \sum_{i=1}^{n} \sum_{m=1}^{n} K_m (\delta_i - \delta_{i+m})^2$$

(12)

Since only longitudinal motions are considered, the label “$\alpha$” that would normally appear as a subscript on the “$\delta$” symbols is suppressed. The sum recorded in Eq. (12) is configured to avoid the redundant summation over bonds, and the counting “$1/2$” factor is not required. To maximize the number of neighbors coupled to any particular atom while avoiding multiple couplings to the same atom via the periodicity condition, we set $n = (N - 1)/2$ and we always consider an odd number of atomic members.

It is convenient to operate in terms of Fourier components, where we have $\delta_i = \sum_k e^{ikl} \delta_k$; on substitution, the expression for the lattice energy has the form

$$E = 2 \sum_{k_x} \left[ \sum_{m=1}^{n} K_m (1 - \cos mk_x) \right] |\delta_{k_x}|^2,$$

(13)

which has been diagonalized with the use of Fourier components $\delta_k$. The eigenvalues are given by $\lambda_{k_x} = 2 \sum_{m=1}^{n} K_m (1 - \cos km)$, and the normalized thermally induced shift $\delta_{\text{RMS}}$ has the form

$$\delta_{\text{RMS}}^n = \left( \sum_{k_x} \lambda_{k_x}^{-1} \right)^{1/2}$$

(14)

We first examine a localized potential which in the 1D context would certainly be expected to yield a divergent mean square fluctuation $\delta_{\text{RMS}}$ with increasing system size $N$. As a companion result to gain complementary insight, we also calculate the density of states corresponding to the system. One merit of obtaining the vibrational density of states is the fact that it may be computed in the thermodynamic limit without encountering divergences with the aid of Monte Carlo sampling. On the other hand, the divergence or convergence of the mean square deviations will be signaled by specific signatures in the low eigenvalue regime of the density of states without the need for an extrapolation to the thermodynamic limit.

In the case where interactions are confined to nearest neighbors, the eigenvalues $\lambda_{k_x}$ have the simple form $2K_0 (1 - \cos k_x x)$. The corresponding thermally averaged $\delta_{\text{RMS}}^n$ values in the case of finite systems are shown in the graph in Fig. 1 and there is a steady rise with in the RMS fluctuations with increasing $n$. The expansion of the mean square deviations from equilibrium is sub-linear, but it may be shown that the increase continues indefinitely (i.e., diverges in the thermodynamic limit) by graphing instead $\langle \delta_{\text{RMS}}^2 \rangle$, as in the inset of Fig. 1. The dependence on $N$ quickly reverts to an asymptotically linear increase with $N$, and to a good approximation $\delta_{\text{RMS}}^2 = N^{1/2}$ for moderate to large systems.

We next extend the coupling scheme to many neighbors where the coupling decays at an exponential rate, as might be found at least on a qualitative level for a covalently bonded system where the rapidly decaying overlap of the orbitals of atomic neighbors (and hence the magnitude of the exchange coupling) has an asymptotically exponential decay as the separation between the pair of atoms becomes sufficiently large. The lattice energy will have the form

$$V_{\text{exp}} = \sum_{i=1}^{N} \sum_{m=1}^{n} K_0 e^{-\gamma m} (\delta_i - \delta_{i+m})^2$$

(15)

Hence in terms of Fourier components, the total lattice
potential becomes

$$V_{\exp} = \sum_k \left( 2K_0 \sum_{m=1}^{n} e^{-\gamma m} [1 - \cos mk] \right)$$  \hspace{1cm} (16)$$

Again, operating in terms of Fourier components decouples the modes, and the appropriate eigenvalues $\lambda_k$ are given by

$$\lambda_k = 2 \sum_{m=1}^{n} e^{-\gamma m} [1 - \cos mk]$$  \hspace{1cm} (17)$$

where the prefactor $K_0$ has been suppressed. In addition, the label “x” on the wave vector has also been suppressed for the sake of convenience. Although the coupling scheme is extended to many neighbors, the potential is in an important sense still a local interaction due to its rapid decay, where the appropriate length scale is the inverse decay rate $\gamma^{-1}$. By appealing to the formula for a geometric sum, $r + r^2 + \ldots + r^n = (r - r^{n+1})/(1 - r)$ (where $r$ is taken to be complex and $|r| < 1$) and using the fact that $\cos mk = \frac{1}{2}(e^{imk} + e^{-imk})$, one may obtain an explicit expression for $\lambda_k$ which does not require the intermediate summation. Applying the geometric series formula for a finite series yields

$$\lambda_k = 2e^{-\gamma} \left( \frac{1 - e^{-\gamma n}}{1 - e^{-\gamma}} \right)$$  $$e^{-\gamma} \left( e^{ik} \left[ \frac{1}{1 - e^{-\gamma + ik}} \right] + e^{-ik} \left[ \frac{1}{1 - e^{-\gamma - ik}} \right] \right)$$  \hspace{1cm} (18)$$

Combining the last two fractional terms gives

$$\lambda_k = 2 \left( \frac{1 - e^{-\gamma n}}{e^{\gamma} - 1} \right) \left[ \frac{\cos k + e^{-\gamma(n+1)} \cos nk}{\cosh \gamma - \cos k} \right]$$  \hspace{1cm} (19)$$

a tidier and computationally convenient expression to use in calculating the RMS displacements $\delta_{\text{RMS}}$.  

As $n$ becomes large, terms proportional to $e^{-\gamma n}$ quickly become suppressed by the rapid exponential decay. Hence, for $n \gg \gamma^{-1}$, one will obtain

$$\lambda_k = \frac{2}{e^{\gamma} - 1} + \frac{e^{-\gamma} - \cos(k)}{\cosh(\gamma) - \cos(k)}$$  \hspace{1cm} (20)$$

The results are shown in Fig. 3 for the scaling of $\delta_{\text{RMS}}$ with respect to the size $N$ of the system. To keep the results for different values of $\gamma$ on the same footing, we use the prefactor $K_0$ as a normalization of the coupling with $K_0 = e^{\gamma}$. A similar procedure is also used in calculations involving exponentially decaying extended couplings in 2D. In this manner, the convergence to the results for the case where only nearest neighbors are involved in the coupling scheme is easier to see.

In the main part of the graph, the square of the RMS deviation is graphed with respect to system size $N$ for a broad range of system sizes. The curves corresponding to the different decay constants are asymptotically linear in the system size although the slopes decrease with decreasing $\gamma$ as the coupling becomes longer in range. The inset of the graph shows a closer view of $\delta_{\text{RMS}}$. Each of the curves rises steadily for sufficiently large $N$, notwithstanding non-monotonicities for small to moderate $N$ in the case $\gamma = 0.25$ where the decay of the interaction is relatively slow. In latter case, there is competition between thermal fluctuations and an increase in lattice rigidity which occurs as the linear crystal grows, providing atoms with more neighbors. Eventually, however, $N$ exceeds the length scale $\gamma^{-1}$ of the coupling between atoms, and the balance shifts in favor of thermal fluctuations. The latter increase in importance with increasing $N$ and thus eventually destroy long-range crystalline order.

We also examine the eigenvalue density of states for different decay rates $\gamma$. With the range of the potential being set by $\gamma^{-1}$, larger values of $\gamma$ would correspond to a more rapid decay and a shorter range of the interaction between neighbors. In calculating the density of states, we use a Monte Carlo sampling process where the values of $k$ are not quantized, permitting one to genuinely achieve the bulk limit for the purpose of obtaining the density of states. To obtain a smooth curve a large number of eigenvalues (i.e. $2.5 \times 10^8$ for the histograms corresponding to the exponentially decaying coupling scheme) are sampled. The formula given in the continuum limit in Eq. (20) is the appropriate expression to use for $\lambda_k$ in the Monte Carlo sampling process.

The normalized density of states for a range of decay constants $\gamma$ appears in Fig. 3. Panel (a) is a standard plot with the density of states on the vertical axis, while to facilitate the viewing of the DOS curves, the logarithm of the DOS curves are shown in panel (b). Even for relatively long-range cases such as $\gamma = 0.25$, the density of states retains the “U”-shaped profile of the nearest neighbor case. The latter corresponds effectively to $\gamma = \infty$, and is shown in red in the graphs. For convenience in comparing results, we again choose $K_0 = e^{\gamma}$ in calculating the DOS curves. The convergence to the $\gamma = \infty$ case with increasing $\gamma$ is evident for the case $\gamma = 2.0$, where close agreement with the DOS calculated for the nearest neighbor case is evident in panel (b) of Fig. 1. In the latter, the ordinate is chosen to be $\log_{10}(\text{DOS})$ to help show the structure of the density of states curves more clearly.

Finally, we examine a genuinely long-range interatomic potential with a power law decay profile. The lattice potential energy will have the form

$$E = \sum_{l=1}^{N} \sum_{m=1}^{n} K_0 m^{-\alpha} (\delta_{l+m} - \delta_l)^2$$  \hspace{1cm} (21)$$

where $\alpha$ is the decay exponent of the power law interaction ($\alpha > 1$), and again $n = (N - 1)/2$. In terms of
the DOS curves. 2
is a graph of
Hence, the modes are now decoupled with eigenvalues
Hence, the modes are now decoupled with eigenvalues

\[ E = \sum_k \sum_{m=1}^n 2K_0 m^{-\alpha} (1 - \cos mk) |\delta_k|^2 \]  

\[ \alpha = 1 \] (where the lattice energy may diverge with increasing system size) below which long range crystalline order is stable with respect to thermal fluctuations in one dimensional lattices.

To identify \( \alpha^{1D}_c \), we calculate the normalized mean square fluctuations \( \delta_{\text{RMS}}^n \) with respect to system size \( n \), producing log-log graphs. The highest value of \( \alpha \) where the mean square deviations converge is identified as \( \alpha^{1D}_c \), the upper limit for the decay exponent in the extended power law decay scheme where long-range crystalline order is still supported at finite temperatures.

The mean square deviations, useful thermodynamic quantities with which to diagnose the presence or absence of long-range crystalline order, are shown in Fig. 4 and Fig. 5 (with the abscissa shown as a base ten logarithm over five decades of system sizes \( N \)). In Fig. 4, \( \delta_{\text{RMS}}^n \) curves are shown for a relatively wide range of \( \alpha \) values. Over the broad range of systems on the horizontal axis, five orders of magnitude, the mean square displacements rise monotonically for \( \alpha = 2.0 \) and \( \alpha = 1.75 \), while \( \delta_{\text{RMS}}^n \) decreases steadily for \( \alpha = 1.5 \) and \( \alpha = 1.25 \). The curves suggest a decay exponent \( \alpha_c \) in the vicinity of \( \alpha_c = 1.6 \) as a boundary between crystals where long-range order is unstable at finite temperatures, and one dimensional solid where crystalline order is retained for \( T > 0 \). The inset is the corresponding log-log graph of the mean square fluctuations plotted for the same \( \alpha \) values as in the main graph, which is a semi-logarithmic plot.

In Fig. 4, RMS deviation curves are shown for a tighter span of power law decay exponents (ranging from \( \alpha = 1.60 \) to \( \alpha = 1.65 \)) to identify with greater accuracy the numerical value of \( \alpha_c \). To facilitate the determination of the exponent separating crystals with long-range order and those disrupted by thermal fluctuations, we place dark circles over the maxima of the \( \delta_{\text{RMS}}^n \) curves. For \( \alpha > 1.625 \), the maxima are located at the edge of the plot, consistent with a steady increase (and likely divergence in the bulk limit) of the RMS curves. On the other hand, for \( \alpha < 1.6125 \), the thermally averaged RMS deviations are non-monotonic, reaching a maximum for finite values of \( N \) and then declining, presumably toward a stable bulk value. We identify the boundary as \( \alpha_c = 1.615 \pm 0.005 \). It should be emphasized that while long-range order is not supported for decay exponents in excess of \( \alpha_c \), the divergence of \( \delta_{\text{RMS}}^n \) with increasing system size is nonetheless quite slow, sublinear in \( \log_{10}(N) \), whereas a strictly logarithmically diverging mean square deviation would instead rise at a more rapid linear rate.

To obtain information complementary to the RMS fluctuations, we again calculate the eigenvalue density of states. We also use Monte Carlo sampling where wave numbers are chosen at random, with uniform probability, to calculate the vibrational density of states with the results shown in Fig. 5. The double sum in Eq. (22) requires careful consideration, in that one must be certain that enough terms have been included in the inner sum that a convergent result is obtained. To be certain convergence

\[ \sum_{m=1}^n \sum_k 2K_0 m^{-\alpha} (1 - \cos mk) |\delta_k|^2 \]
FIG. 4: (Color Online) $\delta_{\text{RMS}}^n$ is plotted on a semi-logarithmic (all logs are base ten) scale in the main draft for selected values of $\alpha$ for one dimensional systems. The inset is a log-log graph of the mean square deviations for the same values of $\alpha$ as in the main graph.

FIG. 5: (Color Online) $\delta_{\text{RMS}}^n$ is plotted on a semi-logarithmic scale for a relatively tight range of $\alpha$ values. The large dark circles indicate maxima in the mean square deviation curves; it is concluded that $\alpha_c = 1.615 \pm 0.005$.

FIG. 6: (Color Online) Eigenvalue Density of States (DOS) for the one dimensional lattice with a power law decay where the decay exponent $\alpha$ varies from $\alpha = 1.5$ in panel (a) to $\alpha = 2.5$ in panel (d).

FIG. 7: (Color Online) Three distinct lattice geometries are shown. Panel (a) is a portion of a square lattice, panel (b) represents the triangular lattice, and panel (c) shows the honeycomb lattice with inequivalent sites represented with distinct colors.

III. TWO DIMENSIONAL CRYSTALS

For the case of a two dimensional system, the analysis is in many respects parallel to that applied for the one dimensional lattices. However, the additional dimension makes available richer choices for the lattice geometry. We examine various coupling schemes for three types of lattices; the square lattice, the triangular lattice, and the honeycomb lattice. In Fig. 7 panel (a) represents the square lattice, the triangular lattice is depicted in panel (b), and the honeycomb lattice appears in panel (c). A peculiarity of the honeycomb lattice is the presence of inequivalent sites, and this characteristic is highlighted in panel (c) of Fig. 7 where different colors are used in labeling the sites. Although the geometries we examine have different characteristics, the essential qualitative characteristics and the most salient physics are found to share much in common.

We first consider the square lattice, and we initially take into account only interactions between nearest neighbors where at the present level of approximation the
lattice lacks rigidity. The lattice energy is

$$E = \frac{K}{2} \sum_{i,j=0}^{N-1} \left[ (\delta_{x,i+1,j} - \delta_{x,i,j})^2 + (\delta_{y,i+1,j} - \delta_{y,i,j})^2 \right]$$

(23)

We express the displacements in terms of Fourier components with, e.g.,

$$\delta_{x,i,j} = \sum_k \delta_{k} e^{i(k_{x,i} + k_{y,j})},$$

with $I$ being the imaginary unit. In terms of $\delta_{k}^x$ and $\delta_{k}^y$, the energy has the form

$$E = \frac{k}{2} \sum_k \left[ (1 - \cos k_x)|\delta_{k}^x|^2 + (1 - \cos k_y)|\delta_{k}^y|^2 \right];$$

(24)

in this manner the degrees of freedom are decoupled. Inspection of Eq. (23) reveals that the eigenvalues are $2N$ fold degenerate and identical to the eigenvalues obtained for the case of the one dimensional crystal where only interactions between nearest neighbors were considered. Since the eigenvalues are the same as those in the 1D case with interactions only between nearest neighbors, crystalline order is readily disrupted by thermal fluctuations. Hence, $(\delta_{\text{RMS}}^n)^2$ will scale with $N$ just as was the case for the 1D counterpart.

If one takes into account coupling to next-nearest neighbors as well, then the lattice energy in real space is

$$E = \frac{K}{2} \sum_{i,j=0}^{N-1} \left( \frac{2 - \cos k_x}{\cos k_x \cos k_y} \cdot \sin k_x \sin k_y \right)$$

$$+ \frac{2 - \cos k_y}{\cos k_x \cos k_y} \cdot \sin k_x \sin k_y$$

(25)

Operating in terms of Fourier components, one diagonalizes the matrix

$$\begin{pmatrix}
2 - \cos k_x & \sin k_x \sin k_y \\
- \cos k_x \cos k_y & 2 - \cos k_y
\end{pmatrix}$$

(26)

The eigenvalues are given by

$$\lambda_{\pm} = (4 - \cos k_x \cos k_y - 2 \cos k_x \cos k_y)$$

$$\pm \sqrt{(\cos k_x - \cos k_y)^2 + 4 \sin^2 k_x \sin^2 k_y}$$

(27)

(28)

The results for the mean square deviations $\delta_{\text{RMS}}^n$ appear in Fig. 8. One may also calculate the vibrational DOS, and the results appear in panel (a) of Fig. 8. The introduction of next-nearest neighbor interactions is very effective in reducing the deleterious effect of thermal fluctuations on long-range crystalline order, though there is still a weak divergence in $\delta_{\text{RMS}}^n$ in the bulk limit. The square $(\delta_{\text{RMS}}^n)^2$ quickly assumes an asymptotically linear form with respect to $\log_{10} N$. The much slower increase of the RMS deviations with $N$ is reflected in the DOS profile, where instead of exhibiting a sharp cusp in the low eigenvalue regime, the DOS curve terminates smoothly. However, the fact that the DOS tends to a finite value as the eigenvalue vanishes is still enough to cause a divergence in the mean square displacements from equilibrium.

We next examine a general case where there are interactions with many neighbors. In real space, the energy stored in the lattice has the form

$$E = \frac{1}{2} \sum_{i,j=-n}^{n} \frac{1}{2} \sum_{l,m=-n}^{n} K(r_{lm}) (\delta_{l,m} - \delta_{ij})^2$$

(29)

where the inner "$1/2$" factor compensates for multiple counting of bond energies and the choice $n = (N - 1)/2$ allows each atomic member to interact with all of the atoms contained in crystal while avoiding multiple interactions with the same particle. Since $\Delta_{lm} = [l, m]$, the appropriate unit vector directed between particles given the labels "$i + l, j + m$" and "$ij$" is $\hat{\Delta}_{lm} = [l, m]/\sqrt{l^2 + m^2}$. Again, we may decouple the vibrational modes by expressing the coordinate shifts in terms of Fourier components. The lattice potential energy may then be written as

$$E = \frac{1}{2} \sum_{i,j=0}^{N-1} \sum_{l,m=-n}^{n} \frac{K(r_{lm})}{2rr_{lm}} \left[ (\delta_{l,m} - \delta_{ij})^2 \right]$$

(30)

with the "$1/2$" factor present to compensate for redundant bond counting. The range radius $r_{lm}$ is defined with $r_{lm} \equiv \sqrt{l^2 + m^2}$, with the full vector given by $r_{lm} = l\hat{x} + m\hat{y}$. In terms of Fourier components, one
will have
\[ E = \frac{1}{2} \sum_{k_i} \sum_{r_{lm}}^{n} \frac{K(r_{lm})}{r_{lm}^2} [1 - \cos(k \cdot r_{lm})] \] (31)
\[ \times \left( \sum_{m=-n}^{n} \sum_{l,m=-n}^{n} K(r_{lm})r_{lm}^2 [1 - \cos(k \cdot r_{lm})] \right)^2 \] (32)
which may also be written as
\[ \frac{1}{2} \sum_{l,m=-n}^{n} K(r_{lm}) \delta_{lm}^2 [1 - \cos(k \cdot r_{lm})] \left[ \Delta_{lm} \Delta_{lm}^* \right] \] (33)
a representation which will prove more compact for more complicated systems such as the honeycomb lattice crystals with more than one layer in the direction transverse to the crystal plane, examined in Section V.

We first turn to the case of an exponentially decaying coupling scheme, and we calculate the $\delta_{RMS}$ to the crystal plane, examined in Section V.

We first turn to the case of an exponentially decaying coupling scheme, and we calculate the $\delta_{RMS}$ to the crystal plane, examined in Section V. The results for the thermally averaged means square displacements are shown in Fig. 9 for a range of different decay constants $\gamma$. The computational burden of calculating the auxiliary sum will grow with $N$, but one aspect of the exponential decay that is of assistance in the calculations is the fact that the sum may be safely truncated when the distance between interacting atoms becomes several times greater than the range of the short-ranged coupling (i.e. terms beyond beyond $m$ and $l$ pairs such that $\sqrt{l^2 + m^2} \gg \gamma^{-1}$) need not be included. In particular, we obtain results which are very well converged if we discard terms beyond 20 decay lengths $\gamma^{-1}$. Ultimately, thermally induced deviations from equilibrium destroy long-range order, and the RMS deviations diverge slowly $\delta_{RMS}^2$ again scales linearly with $\log_{10}(N)$, but the rate of divergence decreases with decreasing $\gamma$. In particular, as the range $\gamma^{-1}$ of the inter-atomic coupling is increased, the slope of the graph of $\delta_{RMS}^2$ with respect to $\log_{10}(N)$ decreases, although the RMS deviations eventually still diverge in the thermodynamic limit.

The DOS is also calculated, with results appearing in Fig. 10 for a range of $\gamma$ values. We use Monte Carlo sampling to choose $k_x$ and $k_y$ from a continuum range, and thereby operate in the thermodynamic limit for the purpose of calculating the DOS curves. At least $10^6$ eigenvalues are sampled in generating the DOS curves. The low eigenvalue region of the DOS graph is very similar to the corresponding regime of the density of states where only interactions with nearest and next-nearest neighbors are included.

Next, we examine the much slower power law decays $K_{ij} = K r_{ij}^{-\alpha}$ in the inter-atomic separation $r_{ij}$ where the exponent $\alpha$ controls the rate of the decay, long-ranged in the sense that there is not a length scale to set the range of the coupling. Again, we first calculate the mean square displacements with respect to the size of the system, and then we examine the density of states for the eigenvalues. The $\delta_{RMS}$ results are shown in Fig. 11.

Computational subtleties similar to those encountered for the case of the one dimensional solid in with a long-ranged coupling scheme must be carefully navigated since the higher dimensionality ($d = 2$) will cause the computational burden to grow even more rapidly (nominally as $L^2$ if interactions with all neighbors are included) with system size. Again, we use Monte Carlo sampling to se-
select wavevectors and accumulate eigenvalues to build up the vibrational DOS. The auxiliary sum over dummy indices l and m giving the eigenvalue would in principle contain an infinite number of terms (in the bulk limit, each atom in the crystal would have an infinite number of neighbors), but we truncate the sum at a finite range. The presence of sinusoidal terms in the sum, as in the corresponding 1D case, provides an oscillatory element and will hasten the convergence of the sum, thereby reducing the computational burden. We check convergence with respect to the truncation range by calculating the DOS with successive doublings of the truncation length \( N_\alpha \) until the DOS profile ceases to change with additional doublings of the system size. The results for the vibrational DOS appear in Fig. 12. One notes that the convergence with respect to the truncation radius is least rapid for \( \alpha = 2.5 \). However, the graphs are relatively well converged for \( \alpha = \alpha_{2D}^c \) and higher values of the decay exponent. When \( \alpha \) is in the vicinity of \( \alpha_{2D}^c \), there is very little support in the low eigenvalue regime. On the other hand, with increasing \( \alpha \) the interaction decays more rapidly, and ultimately the histogram amplitude in the zero eigenvalue limit rises to a finite value, contributing to a divergence in the mean square fluctuations with increasing system size.

### IV. ALTERNATE TWO DIMENSIONAL GEOMETRIES

The treatment in the case of the triangular and honeycomb lattices is very similar to the approach used in the case of the square lattice. Interestingly, the triangular lattice is rigid with only a nearest neighbor interaction in the context of the harmonic approximation, and the mere inclusion of nearest neighbors is enough to set up quasi-long range order where thermally induced fluctuations about equilibrium diverge very slowly [i.e. \( (\delta_{\text{RMS}})^2 \) increases as the logarithm of the system size just as in short-ranged extended interactions for the square lattice]. For the triangular lattice, the lattice energy in real space has the form

\[
E = \frac{4}{N} \sum_{i,j=0}^{N-1} \left( \left[ \hat{x} \cdot \left( \delta_{i+1,j} - \delta_{ij} \right) \right]^2 + \left( \left[ \frac{1}{2} \hat{x} + \frac{\sqrt{3}}{2} \hat{y} \right] \cdot \left( \delta_{i+1,j+1} - \delta_{ij} \right) \right]^2 + \left( \left[ \frac{1}{2} \hat{x} - \frac{\sqrt{3}}{2} \hat{y} \right] \cdot \left( \delta_{i,j+1} - \delta_{ij} \right) \right]^2 \right) \tag{34}
\]

and the eigenvalues for the decoupled vibrational modes are obtained by diagonalizing the \( 2 \times 2 \) matrix

\[
\begin{pmatrix}
3 - 2 \cos k_x - \frac{1}{2} \cos k_y & 2 \sin k_x \\
2 \sin k_x & 3 - 2 \cos k_y - \frac{1}{2} \cos k_x
\end{pmatrix}
\]

yielding

\[
\lambda_\pm = \left[ 3 - \cos k_x - \cos k_y - \cos(k_y - k_x) \right] \pm \sqrt{\cos^2 k_x + \cos^2 k_y + \cos^2(k_y - k_x) - \cos k_x \cos k_y - \cos k_y \cos(k_y - k_x) - \cos k_x \cos(k_y - k_x)} \tag{36}
\]

The results for the mean square fluctuations as well as the vibrational DOS are given in Fig. 13.

We generalize the nearest-neighbor case to an extended scheme where each atomic member may interact with

![FIG. 11: (Color Online) Mean square deviations for an interaction decaying as a power law for decay exponents \( \alpha \) near the threshold \( \alpha_{2D}^c \). The inset shows a broader view, while the main graph is a closer view of the transition from converging to diverging \( \delta_{\text{RMS}} \) curves.](image1)

![FIG. 12: (Color Online) The vibrational density of states for the two dimensional square lattice with a power law decay interaction. DOS curves for various values of the decay parameter \( \alpha \) are shown, with traces for different values of the truncation length \( N_\alpha \) on the same plot.](image2)
many neighbors. In real space, the lattice potential energy may be written as

\[ E = \frac{1}{2} \sum_{i,j=0}^{N} \sum_{l,m=-n}^{n} \frac{1}{2} K(r_{lm}) \hat{\Delta}_{lm}^{-1}(\hat{\epsilon}_{i+1,j+m} - \hat{\epsilon}_{ij}), \]  

(37)

where the components of the unit vector \(\hat{\Delta}_{lm}\) are \(\hat{\Delta}_{lm}^{x} = (l + m/2)/r_{lm}\) and \(\hat{\Delta}_{lm}^{y} = \sqrt{3}m/2r_{lm}\), where \(r_{lm} = (l^2 + m^2 + lm)^{1/2}\) is the distance separating interacting pairs in the triangular lattice geometry. After expressing the displacements in terms of Fourier components, one calculates the eigenvalues of the 2 x 2 matrix

\[ \frac{1}{2} \sum_{l,m=-n}^{n} g_{lm} \begin{bmatrix} \hat{\Delta}_{lm}^{x} & \hat{\Delta}_{lm}^{y} \\ \hat{\Delta}_{lm}^{y} & \hat{\Delta}_{lm}^{x} \end{bmatrix}, \]  

(38)

where \(g_{lm} = [1 - \cos(k_{x}l + k_{y}m)]K(r_{lm})\). As in the case of the square lattice, we consider for the triangular lattices an exponentially decaying coupling scheme, and the results are shown in Fig. 14 for over four decades of system sizes. Again, the quantity \((\delta_{\text{RMS}}^{2})\) increases linearly as \(\beta \log_{10} N\) with the slope \(\beta\) decreasing with decreasing decay rate \(\gamma\) (and hence increasing range of the coupling).

We also prepare graphs of the vibrational density of states, shown in the four graphs in Fig. 15 for a range of values of the decay constant \(\gamma\). The wide separation between the RMS curves corresponding to \(\gamma = 2.0\) and \(\gamma = 1.0\), \(\gamma = 0.75\), and \(\gamma = 0.5\) is mirrored in the DOS curves where for the smaller decay rates the eigenvalue histogram curve intersects the ordinate with very low amplitudes. On the other hand, for the more rapid decay

\[ \log_{10}(N) \]

FIG. 13: (Color Online) The mean square deviation for the triangular lattice with nearest neighbor couplings. The main graph is a semi-logarithmic plot of \(\delta_{\text{RMS}}\), while inset (a) shows the vibrational density of states. A graph of the raw \(\delta_{\text{RMS}}^{2}\) appears in panel (b).

\[ \log_{10}(N) \]

FIG. 14: (Color Online) Normalized mean square curves and eigenvalue density of states for the square lattice with an exponential coupling scheme. The main plot shows \((\delta_{\text{RMS}}^{2})\) with respect to the base ten logarithm of the system size \(N\), while inset (a) is the corresponding graph for \(\delta_{\text{RMS}}^{2}\). Inset (b) shows the density states curve for the triangular lattice for \(2.5 \times 10^{8}\) eigenvalues sampled in the bulk limit via Monte Carlo.

\[ \log_{10}(N) \]

FIG. 15: (Color Online) Density of states curves for \(\gamma = 2.0\), \(\gamma = 1.0\), \(\gamma = 0.75\), and \(\gamma = 0.50\) in panels (a), (b), (c), and (d) respectively for the triangular lattice with an exponentially decaying coupling scheme.

where \(\gamma = 2.0\), the amplitude in the regime of low eigenvalues is much higher, and the DOS graph resembles that of the nearest neighbor case to a much greater degree than DOS profiles corresponding to lower decay rates of the exponential coupling. As for the square lattice geometry, we examine a long-ranged power law interaction in the context of triangular lattices. The mean square deviations from equilibrium are graphed in Fig. 10 with the inset of the plot showing a closer view of the \((\delta_{\text{RMS}}^{2})\) curves. A salient question is
if lattices with geometries which differ from those of the square lattice will exhibit long-range crystalline order for the same range of decay exponents $\alpha$ as in the context of the square lattice. We find up to the bounds of error $\alpha_{c}^{2D} = 3.15 \pm 0.025$ calculated for the triangular lattice to be identical to the threshold exponent for the square lattice.

We show the corresponding eigenvalue histograms for the power law decay for the decay exponents $\alpha = 5.0$, $\alpha = 4.0$, $\alpha = 3.5$, and $\alpha = 3.125$ in panels (a), (b), (c), and (d) respectively of Fig. 17. While the eigenvalue histograms plotted in the panel (a) and panel (b) correspond to decay exponents significantly higher than $\alpha_{c}^{2D}$, the DOS curve in panel (c), is plotted for a decay exponent only slightly above the threshold value, and the histogram in panel (d) of Fig. corresponds to a value of $\alpha$ just below (though very nearly equal) to $\alpha_{c}^{2D}$. Whereas the DOS curves in panel (a) and (b) clearly tend to a finite value as the eigenvalue approaches zero, the amplitude for the slower decay $\alpha = 3.125$ and tends to zero in the the limit that the eigenvalue is very small; for the case $\alpha = 3.5$, the amplitude reaches a finite but very small value in the zero eigenvalue limit. A DOS amplitude tending to zero in the low eigenvalue limit, as seen for $\alpha = 3.125$ is consistent with the preservation of long-range crystalline order indicated in the convergence of the mean square deviations graphed in Fig. 16.

We examine the honeycomb lattice, which differs from the square in triangular lattices in that it possesses two inequivalent sites (labeled “A” and “B” for convenience). We again appeal to translational invariance, operating in terms of Fourier components, to decouple the vibrational modes for the honeycomb lattice. The relationship of sites of type “A” and “B” to nearest neighbors is illustrated in Fig. 20.

Following this labeling convention, the lattice energy in real space has the form

$$E = \frac{4K}{\pi} \sum_{i,j=0}^{N-1} \left\{ \left[ \left( \frac{\sqrt{3}}{2} \hat{x} + \frac{1}{2} \hat{y} \right) \cdot \left( \delta_{ij}^{A} - \delta_{ij-1}^{A} \right) \right]^2 + \left[ -\hat{y} \left( \delta_{ij}^{A} - \delta_{ij}^{B} \right) \right]^2 \right\} \right.$$ (39)

where it is sufficient to sum over the three bonds surrounding the atoms labeled “A” with no factor of $\frac{1}{2}$ needed to compensate for double counting. In Fourier
In addition to Fourier decomposition, the diagonalization of a $4 \times 4$ matrix will be necessary to completely decouple the vibrational modes appropriate to the honeycomb lattice with the nearest neighbor coupling scheme; the matrix in question is

$$
E = \frac{k}{2} \sum_{k} \left[ \frac{3}{2} \left( |\delta_{k}^{A}|^2 + |\delta_{k}^{B}|^2 + |\delta_{k}^{Ax}|^2 + |\delta_{k}^{By}|^2 \right) 
- \frac{1}{4} \left( 1 + e^{-ikx} \right) e^{iky} \left( \delta_{k}^{Ax} \delta_{k}^{By} + \delta_{k}^{Ax} \delta_{k}^{By} \right) 
- \frac{1}{4} \left( 1 + e^{ikx} \right) e^{-iky} \left( \delta_{k}^{Ax} \delta_{k}^{By} + \delta_{k}^{Ax} \delta_{k}^{By} \right) 
+ \frac{\sqrt{2}}{4} \left( e^{-ikx} - 1 \right) e^{-iky} \left( \delta_{k}^{Ax} \delta_{k}^{By} + \delta_{k}^{Ax} \delta_{k}^{By} \right) 
- \frac{\sqrt{2}}{4} \left( e^{-ikx} - 1 \right) e^{-iky} \left( \delta_{k}^{Ax} \delta_{k}^{By} + \delta_{k}^{Ax} \delta_{k}^{By} \right) \right] 
\right]
$$

where $\hat{A}$ and $\hat{B}$, and $\hat{B}^\dagger$ is the Hermitian conjugate of $\hat{B}$. The sub-matrices $\hat{A}$ and $\hat{B}$ are given by

$$
\hat{A} = \begin{bmatrix} \frac{3}{2} & 0 & 0 \\ 0 & \frac{3}{2} & 0 \\ 0 & 0 & \frac{3}{2} \end{bmatrix}
$$

and

$$
\hat{B} = e^{iky} \begin{bmatrix} -\frac{3}{4} \left( 1 + e^{-ikx} \right) \frac{\sqrt{2}}{4} \left( e^{-ikx} - 1 \right) - e^{-iky} - \frac{1}{4} \left( 1 + e^{-ikx} \right) \end{bmatrix}
$$

However, to obtain a crystal which is locally stiff, one must examine an extended scheme which includes each atomic member interactions with many neighbors. In real space, the lattice energy may be expressed as

$$
E = \sum_{n}^{N} \sum_{j=0} \left[ \frac{1}{2} K(x_{lm}) \left( \Delta_{lm}^{x} \Delta_{lm}^{x} + \Delta_{lm}^{y} \Delta_{lm}^{y} \right) \right] 
+ \sum_{n}^{N} \sum_{j=m} \left[ \frac{1}{2} K(r_{lm}^{ab}) \left( \Delta_{lm}^{x} \Delta_{lm}^{x} + \Delta_{lm}^{y} \Delta_{lm}^{y} \right) \right]
$$

where the first and second terms in the sum take into account interactions between atoms labeled “A” and “B”, respectively; the identical form of “A-A” and “B-B” interaction terms is due to the fact that the “A” and “B” species both define triangular lattices, as illustrated in Fig. We take the lattice constant to be unity, and the components of the unit vector $\Delta_{lm}^{x}$ appropriate to the triangular sublattices are $\Delta_{lm}^{x} = \sqrt{3} (l + m/2)/r_{lm}$ and $\Delta_{lm}^{y} = (3 m/2)/r_{lm}$, where $r_{lm} = (3[l^2 + m^2 + lm])^{1/2}$.
(but does not halt) the rate of divergence of the mean square fluctuations. The large separation between the RMS curves corresponding to \( \gamma = 2.0 \) and the slower decays \( \gamma = 1.0 \), \( \gamma = 0.75 \), and \( \gamma = 0.50 \) is consistent with changes in the density of states curves where the histogram amplitude in the low eigenvalue regime is sharply diminished as \( \gamma \) decreases from \( \gamma = 2.0 \) to \( \gamma = 1.0 \).

In the case of a power law decay, results for the mean square deviations are shown in the semi-logarithmic graphs in Fig. 23 where the systems sizes considered span two decades, with a closer view for a more restricted range of the decay exponent \( \alpha \) in the main graph; the inset is a graph of RMS curves for a broader set of \( \alpha \) values. As in the cases of the square and triangular lattices, the threshold exponent \( \alpha^\text{2D} \) is determined by examining whether the RMS curves converge or diverge for very large system sizes. In agreement with the square and triangular geometries, we find \( \alpha^\text{2D} = 3.15 \pm 0.025 \) for the critical decay exponent.

The eigenvalue histogram curves shown in Fig. 23 are consistent with the behavior of the mean square deviation curves given in Fig. 22. For the more rapid decays \( \alpha = 4.0 \) and \( \alpha = 4.5 \), the amplitude of the density of states is finite, which eventually contributes to a divergence in \( \delta^\text{RMS} \). The divergence in the mean square fluctuations is much slower for \( \alpha = 3.5 \), a characteristic which is echoed in the eigenvalue histogram in panel (c) of Fig. 23, where in the zero eigenvalue limit the histogram amplitude is finite but very small. Finally, for \( \alpha = 3.125 \), just below \( \alpha^\text{c} \), the density of states curve tends to zero in the low eigenvalue limit.

V. TRANSVERSE DISPLACEMENTS IN AN EXTENDED SCHEME

In each of the preceding cases discussed in this work, thermally induced deviations of the lattice sites have been confined either to motion within the lattice plane in the context of two dimensional systems, or collinear movements for the lattice in 1D. However, we also consider displacements perpendicular to the lattice for two dimensional systems. To provide local stiffness of covalent two dimensional lattices realized in nature where the finite thickness would provide rigidity with respect to...
transverse displacements tending to push atoms above or below the plane of the crystal, we examine a dual layer geometry where an extended scheme provides a local stiffness.

In fact, to provide as much stability as possible, we consider a long-range coupling scheme in the interaction between atoms within a layer as well as between layers decreases as a power law (with the decay exponent designated \( \alpha \)) in the separation between atomic species. The potential energy stored in the lattice is similar in abstract form to the corresponding expression for the honeycomb lattices, and is given by

\[
E = \sum_{i,j=0}^{N} \sum_{l,m=-n}^{n} \left( \frac{1}{2} K(r_{lm}^s) \hat{\Delta}_{lm}^s (\hat{\delta}_{1l+m,j}^A - \hat{\delta}_{1l+m,j}^B) + \frac{1}{2} K(r_{lm}^{ab}) \hat{\Delta}_{lm}^{ab} (\hat{\delta}_{1l+m,j}^A - \hat{\delta}_{1l+m,j}^B) \right) \tag{47}
\]

in a real space representation, where the unit vectors corresponding the intraplanar couplings \( \hat{\Delta}_{lm}^s \) have \( x \) and \( y \) components given by

\[
\hat{\Delta}_{lm}^x = \frac{l}{r_{lm}^s}; \quad \hat{\Delta}_{lm}^y = \frac{m}{r_{lm}^s},
\]

where the separation between interacting sites within a plane is \( r_{lm}^s = \sqrt{l^2 + m^2} \). The components of the unit vector \( \hat{\Delta}_{lm}^{ab} \) are identical to those of the planar case with the exception of a nonzero \( z \) component \( \hat{\Delta}_{lm}^{z(ab)} = 1/r_{lm}^{ab} \) where the distance between sites in the two distinct lattice planes is \( r_{lm}^{ab} = \sqrt{m^2 + l^2 + 1} \). Operating in terms of Fourier components reduces the decoupling of the vibrational modes to the diagonalization of a \( 6 \times 6 \) matrix of the form where \( \hat{A} \) and \( \hat{B} \) are \( 3 \times 3 \) sub-matrices, with \( \hat{B}^* \) the Hermitian conjugate of \( \hat{B} \). The sub-matrices have the form

\[
\hat{A} = \sum_{l,m=-n}^{n} \begin{bmatrix}
    d_{lm}^{xx(ab)} & d_{lm}^{xy(ab)} & d_{lm}^{xz(ab)} \\
    d_{lm}^{yx(ab)} & d_{lm}^{yy(ab)} & d_{lm}^{yz(ab)} \\
    d_{lm}^{zx(ab)} & d_{lm}^{zy(ab)} & d_{lm}^{zz(ab)}
\end{bmatrix}
\]

\[
\hat{B} = \sum_{l,m=-n}^{n} e^{i(kx l + ky m)} \begin{bmatrix}
    d_{lm}^{xx(ab)} & d_{lm}^{xy(ab)} & d_{lm}^{xz(ab)} \\
    d_{lm}^{yx(ab)} & d_{lm}^{yy(ab)} & d_{lm}^{yz(ab)} \\
    d_{lm}^{zx(ab)} & d_{lm}^{zy(ab)} & d_{lm}^{zz(ab)}
\end{bmatrix}
\]

Results for the mean square deviation \( \delta_{\text{RMS}}^\alpha \) are shown in Fig. 23 for a variety of decay exponents ranging from a weak decay \( \alpha = -2.5 \) to a considerably more rapid decay with the separation distance \( \alpha = -6.0 \). A salient feature in each of the RMS curves shown in the graph is an asymptotic linear growth with the size \( N \) of the system, though the slope of the linear diverge in system size decreases with decreasing \( \alpha \). Broadly speaking, there are two regimes for each value of \( \alpha \), and somewhat abbreviated for the more rapidly decaying coupling where \( \alpha = -6 \). The latter is closer to what one would find in covalently bonded (but non-polar) systems such as graphene where Van der Waals interactions decreasing with the sixth power of the inter-atomic separation constitute the main source of long-range attraction between particles. Hence, London interactions would not prevent atomic displacements transverse to the lattice plane from destroying crystalline order.

VI. CONCLUSIONS

We have examined the effect of thermally induced lattice vibrations on long range order in one and two dimensional crystals. In the case of crystals in one dimension, long-range positional order is (as expected) disrupted by thermal fluctuations with the \( \delta_{\text{RMS}}^\alpha \) scaling as \( N^{1/2} \). For inherently long-ranged interactions scaling as power laws in the distance between interacting atoms, the divergence is much slower for \( \alpha > \alpha_c^{1D} = 1.615 \), while crystalline order is intact even at finite temperatures if \( \alpha < \alpha_c^{1D} \).
For two dimensional crystals, we find the same essential phenomena with respect to thermodynamic stability of the crystal for square, triangular, and honeycomb lattices. For the latter two, thermal fluctuations destroy long-range crystalline order at finite temperatures, but the divergence in $\delta_{\text{RMS}}^n$ occurs very slowly with increasing system size. On the other hand, RMS deviations decay rapidly for simple square lattices where only nearest neighbor couplings are active. However, an extended coupling scheme to both nearest and next-nearest neighbors considerably mitigates the effect of thermal fluctuations on crystalline order, and the resulting slow divergence is quantitatively similar to that seen in the triangular and honeycomb lattices where the coupling is confined entirely to nearest-neighbors.

When we extend the coupling to many neighbors, but still implement a short-ranged coupling (e.g. an exponential decay with the range set by the inverse decay rate $\gamma^{-1}$), we find qualitatively the same results as for the square lattice with couplings both to nearest and next-nearest neighbors, as well as the triangular and hexagonal lattices in atomic members only interact with nearest neighbors with $(\delta_{\text{RMS}}^n)^2$ scaling linearly with $\log_{10}(N)$. However, the slope of the linear dependence becomes smaller as $\gamma$ is decreased, as a longer-ranged coupling is more effective at suppressing the effects of thermal fluctuations. As in the case of systems in 1D, a longer range coupling in the form of a power law can maintain long-range crystalline order for $T > 0$ if the decay exponent does not exceed $\alpha_{c}^{2D} = 3.15$.

Allowing thermally induced fluctuations perpendicular to the lattice causes a rapid divergence (i.e. linear) of the RMS deviations with the system size, even if the lattice geometry is dual-layered in an extended scheme to provide local stiffness. The growth of $\delta_{\text{rms}}$ is asymptotically linear even if the coupling between sites is long-ranged, decaying as a power law. Hence, long-ranged London interactions would not be enough by themselves to preserve positional order in a covalently bonded locally rigid two dimensional lattice.

Acknowledgments

Useful conversations with Yogesh Joglekar are gratefully acknowledged.

1. F. Lindemann, Z. Phys. 11, 609 (1910).
2. Klaus Sokolowski-Tinten, Christian Blome, Juris Blums, Andrea Cavalleri, Clemens Dietrich, Alexander Tarasevitch, Ingo Uschmann, Eckhard Förster, Martin Kammler, Michael Horn-von-Hoegen, and Dietrich von der Linde, Nature 422, 287-289 (2003).
3. Guoyin Shen, Vitali B. Prakapenka, Mark L. Rivers, and Stephen R. Sutton, Phys. Rev. Lett., 92, 185701 (2004).
4. N. D. Mermin and H. Wagner, Phys. Rev. Lett., 17, 1133 (1966).
5. N. D. Mermin, Phys. Rev. 176, 250 (1968).
6. D. J. Priour, Jr. and J. L. Losey, cond-mat 1002.3965 (2010).