Symmetry-Adapted Molecular Modeling of Nanostructures and Biomembranes

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Abstract

Tremendous advances in nanoscience during the past decades have drawn a new horizon for the future of science. Many biological and structural elements such as DNA, bio-membranes, nanotubes, nanowires and thin films have been studied carefully in the past decades. In this work we target to speed up the computational methods by incorporating the structural symmetries that nanostructures have. In particular, we use the Objective Structures (OS) framework to speed up molecular dynamics (MD), lattice dynamics (phonon analysis) and multiscale methods. OS framework is a generalization of the standard idea for crystal lattices of assuming periodicity of atomic positions with a large supercell. OS not only considers the translational periodicity of the structure, but also other symmetries such as rotational and screw symmetries. In addition to the computational efficiency afforded by Objective Structures, OS provides us with more flexibility in the shape of the unit cell and the form of the external deformation and loading, comparing to using the translational periodicity. This is because the deformation and loading should be consistent in all cells and not all deformations keep the periodicity of the structures. For instance, bending and twisting cannot be modeled with methods using the structure's periodicity. Using OS framework we then carefully studied carbon nanotubes under non-equilibrium deformations. We also studied the failure mechanism of pristine and twisted nanotubes under tensile loading. We found a range of failure mechanisms, including the formation of Stone-Wales defects, the opening of voids, and the motion of atoms out of the cross-section. We also used the OS framework to make concrete analogies between crystalline phonons and normal modes of vibration in non-crystalline but highly symmetric nanostructures.

Keywords: Symmetry-adapted analysis, Objective structures, Molecular dynamics, Phonon analysis, Multiscale modeling, Nanotubes

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Introduction

1

Mindboggling advances in the nanotechnology have attracted the scientific community to study nono- and micro-scale structures and biomaterials. These studies span from experimental aspects by means of high-tech microscopes such as STM and AFM, to theoretical and numerical aspects due to availability and increase in the computational power of computers. The cost of the experiments has increased the role of analytical and computational methods. But sometimes the large number of degrees of freedom (DOF) in the computational methods makes them computationally infeasible. We can reduce the number of DOF by exploiting the structural symmetries. In this work we will develop symmetry-adapted methods by working within the framework of objective structures (OS).

OS generalizes the notion of a crystal or periodicity by using ideas from frameindifference. In chapter 2 we give a concrete definition of objective structures. In brief, [Jam06] and following works have shown that many highly symmetric but noncrystalline nanostructures have close analogies to crystals. These analogies have led to some important practical methods: e.g., a generalization of periodic boundary conditions for classical molecular dynamics and tight binding to enable the analysis of chiral nanostructures as well as the ability to apply torsional loads [ZAD11, ZJD09b, ZJD09a, ZDS10, DJ07, NZJD10, DJ10, DJ11, AD11, ADE12, AD12]. All of these exploit the fact that the symmetries of the nanostructure, together with frame-indifference, imply that the first derivative of the potential energy has certain symmetries. This symmetry in the first and second derivatives is a generalization of the fact that forces on image atoms and the components of the Hessian matrix are identical in a periodic crystal, respectively.

This work deals with three symmetry-adapted molecular methods. First, we apply the notion of OS to the molecular dynamics method (MD) and systematically study the structural failure and mechanical response of chiral single-walled carbon nanotubes. This is explained in chapter 3. We make a specific contribution in this part, namely we extend the formulation of non-equilibrium symmetry-adapted MD by adding thermostat [Hoo85] to simulate the effect of a heat bath and barostat [PR81] to simulate the effect of an applied far-field stress and torque. These enable MD calculations of systems with specified temperature, stress and torque rather than specified energy and shape. We show that the use of these thermostats and barostats in the appropriate manner does not affect the fundamental property of OS, namely that applying the equations of MD to the simulated atom automatically implies that all images also satisfy the equation of MD with no fictitious forces.

Second, we develop the symmetry-adapted phonon analysis method. Phonons, i.e. normal modes, are extremely important to understand the properties of crystals. For instance, phonon analysis provides insight into thermodynamic properties and mechanical stability [Dov93, BH98, ETS06, EST06]. In chapter 4, we use the framework of OS introduced by James [Jam06] to extend the notion of phonon analysis to noncrystalline but symmetric nanostructures. Our strategy is to use an intermediate linear transformation from real-space to an intermediate space in which the Hessian matrix of second derivatives is block-circulant. The block-circulant nature of the Hessian enables us to then follow the procedure to obtain phonons in crystals: namely, we use the Discrete Fourier Transform from this intermediate space to obtain a blockdiagonal matrix that is readily diagonalizable. We formulate this for general OS and then apply it to study carbon nanotubes of various chiralities that are subjected to axial elongation and torsional deformation. In addition to the computational efficiency afforded by OS in providing the transformations to almost-diagonalize the Hessian, the framework provides an important conceptual simplification to interpret the phonon curves. Our finding of characteristic oscillations in the phonon curves motivates a simple one-dimensional geometric nonlocal model of energy transport in generic OS. The model shows the interesting interplay between energy transport along axial and helical directions.

Third, in chapter 5, we use the notion of OS and develop a novel multiscale technique for molecular modeling of bio-membranes and engineering materials such as graphene sheets and nanotubes. Our method is similar to the quasi-continuum method (QC) [TOP96, KO01] which is developed for crystals. QC relies on the Cauchy-Born rule [Eri08, AAQKK09, KQKA09] to relate the atomic positions to the continuum fields through the local deformation gradient. We extend the QC method by replacing the Cauchy-Born rule with OS framework. This enables us to model non-crystalline molecules and materials. This is the project that I am currently working on. We have developed the model and numerically tested it for simple problems, that is we modeled a multiscale membrane constructed by a simple Bravais lattice whose atoms interact with Lennard-Jones potential and compared the results to the full atomistic calculation. We need to add more complex potentials to be able to get more realistic results. We should also add internal atomic shifts to our model to be able to simulate multi-lattices, that is lattices with a collection of interpenetrating simple Bravais lattices.

Objective Structures (OS)

2

2.1 Objective Structures Formulation

James [Jam06] defined an objective atomic structure as a finite or infinite set of atoms in which every atom sees the same environment up to translation and rotation. Similarly, an objective molecular structure is defined as a structure with a number of identical *molecules*, each molecule consisting of a number of atoms, arranged such that *corresponding* atoms in every molecule see the same environment up to translation and rotation. We note that the molecules in an objective molecular structure need not correspond to standard physical molecules as usually understood. Bravais (multi) lattices are special cases of objective atomic (molecular) structures in which each atom (molecule) has the same environment up to translation and the rotation is trivial.

Following recent works that build on James' original formulation, e.g. [DEJ, DJ11, DJ10, AD11, ADE12, AD12], we can define OS equivalently in the language of group theory. The group theoretic approach enables practical calculations. Let $G = \{g_0, g_1, \dots, g_N\}$ be a set of isometries indexed by a multi-index. Each element

of G has the form $g_j = (Q_j | c_j)$ where $Q_j \in O(3)$ is orthogonal and $c_j \in \mathbb{R}^3$ is a vector.

The action of an isometry on a point $\boldsymbol{x} \in \mathbb{R}^3$ is

$$g_j(\boldsymbol{x}) = \boldsymbol{Q}_j \boldsymbol{x} + \boldsymbol{c}_j \tag{2.1}$$

Composition of mappings then provides:

$$g_i(g_j(\boldsymbol{x})) = \boldsymbol{Q}_i \left(\boldsymbol{Q}_j \boldsymbol{x} + \boldsymbol{c}_j \right) + \boldsymbol{c}_i = \boldsymbol{Q}_i \boldsymbol{Q}_j \boldsymbol{x} + \boldsymbol{Q}_i \boldsymbol{c}_j + \boldsymbol{c}_i$$

This motivates a definition for multiplication of isometries:

$$g_i g_j = (\boldsymbol{Q}_i \boldsymbol{Q}_j | \boldsymbol{Q}_i \boldsymbol{c}_j + \boldsymbol{c}_i)$$
(2.2)

From this definition, it follows that the identity element is $g_{\mathbf{0}} := (\mathbf{I}|\mathbf{0})$ and the inverse of g_{i} is defined by $g_{i}^{-1} := (\mathbf{Q}_{i}^{T}| - \mathbf{Q}_{i}^{T}\mathbf{c}_{i}).$

If the set G is additionally a group with respect to the multiplication operation above, then placing an atom at each of the points given by the action of elements of G on a given point \boldsymbol{x}_0 gives an objective atomic structure. In addition, placing an atom of species k at each of the points given by the action of elements of G on a given set of points $\boldsymbol{x}_{0,k}$ gives an objective molecular structure.

In this paper, we will consider OS described by groups of the form

$$G = \{g_1^{i_1}g_2^{i_2}g_3^{i_3} ; (i_1, i_2, i_3) \in \mathbb{Z}^3\}$$
(2.3)

Here, $g_1 = (\bar{\mathbf{Q}}_1 | \bar{\mathbf{c}}_1)$, $g_2 = (\bar{\mathbf{Q}}_2 | \bar{\mathbf{c}}_2)$ and $g_3 = (\bar{\mathbf{Q}}_3 | \bar{\mathbf{c}}_3)$ are the generators of the group. We assume that they commute, i.e. $g_1g_2 = g_2g_1$ and so on. This immediately implies that G itself is Abelian. As shown in [DEJ], G of this form does not describe all possible OS; however, as also shown there, those OS that cannot directly be described can nevertheless be described by such a G by enlarging the unit cell and neglecting certain intra-unit cell symmetries. Denoting the atomic positions in the unit cell by $\boldsymbol{x}_{(0,0,0),k} := \mathbf{x}_{0,k}, k = 1, \dots, M$, the OS is described by

$$\mathbf{x}_{i,k} := \boldsymbol{x}_{(i_1, i_2, i_3), k} = g_1^{i_1} g_2^{i_2} g_3^{i_3}(\mathbf{x}_{\mathbf{0}, k}) = \boldsymbol{Q}_i \mathbf{x}_{\mathbf{0}, k} + \boldsymbol{c}_i \quad ; \quad \boldsymbol{i} = (i_1, i_2, i_3) \in \mathbb{Z}^3$$
(2.4)

Using (2.2), we have that

$$Q_{i} = \bar{Q}_{1}^{i_{1}} \bar{Q}_{2}^{i_{2}} \bar{Q}_{3}^{i_{3}}$$

$$c_{i} = \bar{Q}_{1}^{i_{1}} \bar{Q}_{2}^{i_{2}} \left(\sum_{p=0}^{p=i_{3}-1} \bar{Q}_{3}^{p} \bar{c}_{3} \right) + \bar{Q}_{1}^{i_{1}} \left(\sum_{p=0}^{p=i_{2}-1} \bar{Q}_{2}^{p} \bar{c}_{2} \right) + \left(\sum_{p=0}^{p=i_{1}-1} \bar{Q}_{1}^{p} \bar{c}_{1} \right)$$
(2.5)

for positive exponents i_1, i_2, i_3 . Negative exponents are defined through the inverse.

An important property of OS is that elements of G map images of the unit cell $\mathbf{x}_{0,k}$ to each other. For instance, consider the i and j images of the unit cell:

$$\mathbf{x}_{i,k} = g_1^{i_1} g_2^{i_2} g_3^{i_3}(\mathbf{x}_{\mathbf{0},k}) = \left(g_1^{i_1-j_1} g_2^{i_2-j_2} g_3^{i_3-j_3}\right) \left(g_1^{j_1} g_2^{j_2} g_3^{j_3}\right) (\mathbf{x}_{\mathbf{0},k}) \\ = \left(g_1^{i_1-j_1} g_2^{i_2-j_2} g_3^{i_3-j_3}\right) (\mathbf{x}_{\mathbf{j},k})$$
(2.6)

These relations follow directly from the closure and commuting properties of the Abelian group G.

Consider the orthogonal part of $g_1^{i_1-j_1}g_2^{i_2-j_2}g_3^{i_3-j_3}$: $(\mathbf{Q}_{i-j}|\mathbf{c}_{i-j}) = g_1^{i_1-j_1}g_2^{i_2-j_2}g_3^{i_3-j_3} = (g_1^{i_1}g_2^{i_2}g_3^{i_3})(g_1^{-j_1}g_2^{-j_2}g_3^{-j_3})$ $= (\mathbf{Q}_i|\mathbf{c}_i)(\mathbf{Q}_j|\mathbf{c}_j)^{-1} = (\mathbf{Q}_i\mathbf{Q}_j^T| - \mathbf{Q}_i\mathbf{Q}_j^T\mathbf{c}_j + \mathbf{c}_i)$

This provides the important relation:

$$\boldsymbol{Q}_{\boldsymbol{i}}\boldsymbol{Q}_{\boldsymbol{j}}^{T} = \boldsymbol{Q}_{\boldsymbol{i}-\boldsymbol{j}} \tag{2.7}$$

2.2 Crystal Lattices and Carbon Nanotubes as Objective Structures

Two important examples of OS are crystal multilattices and carbon nanotubes. We describe them using the general OS framework above.

To describe a crystal multilattice as an OS, we simply set $\bar{Q}_1 = I, \bar{Q}_2 = I, \bar{Q}_3 = I$. The vectors $\bar{c}_1, \bar{c}_2, \bar{c}_3$ are the lattice vectors.

Carbon nanotubes require only two generators. Therefore, we set g_3 to the identity. Consider a carbon nanotube with chiral indices (m, n) and axis e centered at the origin. Following [DEJ], we have the following relation between the group generators and the geometry of the carbon nanotube when we use a 2-atom unit cell:

$$g_{1} = (\mathbf{R}_{\theta_{1}}|\mathbf{0}), \quad \mathbf{R}_{\theta_{1}}\mathbf{e} = \mathbf{e}, \quad 0 < \theta_{1} = \frac{2\pi\min\left(|p|, |q|\right)}{\operatorname{GCD}(n, m)} \le 2\pi$$
$$g_{2} = (\mathbf{R}_{\theta_{2}}|\kappa_{2}\mathbf{e}), \quad \mathbf{R}_{\theta_{2}}\mathbf{e} = \mathbf{e}, \quad \theta_{2} = \pi \frac{p(2n+m) + q(n+2m)}{n^{2} + m^{2} + nm}, \quad \kappa_{2} = \frac{3l_{0}\operatorname{GCD}(m, n)}{2\sqrt{n^{2} + m^{2} + nm}}$$
(2.8)

 \mathbf{R}_{θ} is a rotation matrix with axis coinciding with \mathbf{e} and rotation angle θ . The quantity $l_0 = 0.142$ nm is the bond length of the graphene sheet before rolling. The integers p and q satisfy pm - qn = GCD(m, n), where GCD(m, n) is the greatest common divisor of m and n.

The radius of the nanotube is $r = \frac{l_0}{2\pi}\sqrt{3(n^2 + m^2 + nm)}$ and the positions of the atoms in the unit cell are:

$$\boldsymbol{x}_{(0,0),1} = r \boldsymbol{e}_1$$
$$\boldsymbol{x}_{(0,0),2} = r \cos\left[\frac{\pi(n+m)}{n^2 + m^2 + nm}\right] \boldsymbol{e}_1 + r \sin\left[\frac{\pi(n+m)}{n^2 + m^2 + nm}\right] \boldsymbol{e}_2 + \frac{l_0(m-n)}{2\sqrt{n^2 + m^2 + nm}} \boldsymbol{e}_2$$
(2.9)

where $(\boldsymbol{e}, \boldsymbol{e}_1, \boldsymbol{e}_2)$ are orthonormal.

Note that if m and n are relatively prime, i.e. GCD(m, n) = 1, then $\theta_1 = 0$ and g_1 reduces to the identity.

The generator g_1 is a rotation isometry, and g_2 is a screw isometry. The parameters $\kappa_2, \theta_1, \theta_2$ depend on the chiral indices (m, n) of the nanotube. In this description, the unit cell has 2 atoms at positions $\boldsymbol{x}_{(0,0),0}$ and $\boldsymbol{x}_{(0,0),1}$. We note the important special case that when the chiral indices m and n of the nanotube are relatively prime, g_1 reduces to the identity.

The 2-atom unit cell of (2.8) greatly limits the possible atomic motions for the calculations that we wish to perform. As in standard periodic calculations, small unit cells can greatly constrain the possible deformations. For real problems, a unit cell with more atoms can be useful. To this end, we first define an enlarged unit cell consisting of the atoms generated by $g_1^p g_2^q(\boldsymbol{x}_{(0,0),k})$, where k = 1, 2 and the indices p and q run over integers $p_1 \leq p \leq p_2$ and $q_1 \leq q \leq q_2$. The unit cell now consists of $2(p_2 - p_1 + 1)(q_2 - q_1 + 1)$ atoms. To generate the nanotube, we then define the group $H = \{h_1^i h_2^j; (i, j) \in \mathbb{Z}^2\}$ with $h_1 = g_1^{p_2 - p_1 + 1}$ and $h_1 = g_1^{p_2 - p_1 + 1}$. Note that H is a subgroup of G. The action of elements of H on the enlarged unit cell define precisely the same nanotube as using G on the 2-atom unit cell. However, since the atoms in the enlarged unit cell are not constrained to each other by symmetry, they can explore a larger space of deformations.

Two examples of FDs that can be generated from such a procedure are shown in Fig. Figure 2.1.

We note certain features of the OS isometry group approach. First, OS above enables facile MD calculations of nanotubes that are chiral whereas periodic boundary conditions would require extremely long unit cells Further, periodicity would constrain the deformation and possibly suppress certain failure modes; while OS also does this due to the choice of FD, extremely different FDs can be chosen (e.g. Fig. Figure 2.1) to test for artifacts of this choice. Furthermore, OS enables a transparent approach to the application of external loads that cause twisting and extension; the choices for h_1, h_2 can be thought of as corresponding to an unloaded nanotube, and changing θ_2 would correspond to imposed twist, while changing κ_2 would correspond to imposed extension. Finally, imposed twist can cause a complete lack of translational symmetry in the nanotube and would require, in principle, infinitely long unit



Figure 2.1: Two fundamental domains with 164 atoms for (8,6) nanotube. Top: a helical FD with $i_1 = 0, i_2 = 0, j_1 = 0, j_2 = 81$; bottom: a cylindrical FD with $i_1 = 0, i_2 = 1, j_1 = 0, j_2 = 40$. Blue atoms belong to the FD and green atoms to the images under the subgroup.

cells with periodic MD, but can be easily and efficiently handled with OS.

2.3 Consequences of Frame Indifference on the Potential Energy and its Derivatives

By frame-indifference, the potential energy of the OS, $\phi(\boldsymbol{x}_{0,k}, \ldots, \boldsymbol{x}_{i,k}, \ldots)$ where $k = 1, \ldots, M$ and $\boldsymbol{i} = (i_1, i_2, i_3) \in \mathbb{Z}^3$, is invariant under rigid translations and rotations of the entire structure, assuming that external fields are either absent or also similarly transform. We apply the specific rigid translation and rotation associated to elements of G, i.e., consider the transformation $g_{-\boldsymbol{i}} := g_1^{-i_1}g_2^{-i_2}g_3^{-i_3}$.

$$\phi \left(\mathbf{x}_{\mathbf{0},k}, \dots, \mathbf{x}_{\mathbf{i},k}, \dots, \mathbf{x}_{\mathbf{j},l}, \dots \right) = \phi \left(g_{-\mathbf{i}} \mathbf{x}_{\mathbf{0},k}, \dots, g_{-\mathbf{i}} \mathbf{x}_{\mathbf{i},k}, \dots, g_{-\mathbf{i}} \mathbf{x}_{\mathbf{j},l}, \dots \right)$$
$$= \phi \left(\mathbf{x}_{-\mathbf{i},k}, \dots, \mathbf{x}_{\mathbf{0},k}, \dots, \mathbf{x}_{\mathbf{j}-\mathbf{i},l}, \dots \right)$$
(2.10)

The key observation that enabled Objective Molecular Dynamics [DJ07, DJ10] is as follows. The force on atom (i, k) is $f_{i,k} = -\frac{\partial \phi}{\partial \mathbf{x}_{i,k}}$. Starting from the potential energy in (2.10), we perturb atom (i, k) along the coordinate direction e^{α} and atom (j, l) along the coordinate direction e^{β} . Formally, we can write:

$$\phi \left(\mathbf{x}_{\mathbf{0},m}, \dots, \mathbf{x}_{i,k} + \epsilon_1 e^{\alpha}, \dots, \mathbf{x}_{j,l} + \epsilon_2 e^{\beta}, \dots \right)$$

= $\phi \left(g_{-i} \mathbf{x}_{\mathbf{0},m}, \dots, g_{-i} (\mathbf{x}_{i,k} + \epsilon_1 e^{\alpha}), \dots, g_{-i} (\mathbf{x}_{j,l} + \epsilon_2 e^{\beta}), \dots \right)$
= $\phi \left(\mathbf{x}_{-i,m}, \dots, \mathbf{x}_{\mathbf{0},k} + \epsilon_1 \mathbf{Q}_i^T e^{\alpha}, \dots, \mathbf{x}_{j-i,l} + \epsilon_2 \mathbf{Q}_i^T e^{\beta}, \dots \right)$
= $\phi \left(\mathbf{x}_{\mathbf{0},k} + \epsilon_1 \mathbf{Q}_i^T e^{\alpha}, \dots, \mathbf{x}_{n,m}, \dots, \mathbf{x}_{j-i,l} + \epsilon_2 \mathbf{Q}_i^T e^{\beta}, \dots \right)$ (2.11)

The calculation is justified as follows: from the first to the third line, we follow precisely (2.10), and in the last step we simply rearrange the arguments because the energy does not not depend on the labeling of the atoms.

Setting $\epsilon_2 = 0$ identically and taking the limit of $\epsilon_1 \to 0$:

$$\frac{\partial \phi}{\partial x_{i,k}^{\alpha}} = \sum_{\gamma=1}^{3} Q_{i}^{\alpha\gamma} \frac{\partial \phi}{\partial x_{\mathbf{0},k}^{\gamma}} \Leftrightarrow \mathbf{f}_{i,k} = \mathbf{Q}_{i} \mathbf{f}_{\mathbf{0},k}$$
(2.12)

This transformation law for the force acting on an atom in the unit cell and its images enables the analog of periodic molecular dynamics in general OS [DJ07, DJ10].

James [Jam06] also noted a similar transformation law for elements of the second derivative (Hessian) matrix \boldsymbol{H} . Taking the limit consecutively of $\epsilon_1 \to 0$ and $\epsilon_2 \to 0$:

$$\frac{\partial^2 \phi}{\partial x_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} \partial x_{\boldsymbol{j},\boldsymbol{l}}^{\beta}} = \sum_{\gamma,\eta} Q_{\boldsymbol{i}}^{\alpha\gamma} \frac{\partial^2 \phi}{\partial x_{\boldsymbol{0},\boldsymbol{k}}^{\gamma} \partial x_{\boldsymbol{j}-\boldsymbol{i},\boldsymbol{l}}^{\eta}} Q_{\boldsymbol{i}}^{\beta\eta} \Leftrightarrow \boldsymbol{H}_{(\boldsymbol{i},\boldsymbol{k})(\boldsymbol{j},\boldsymbol{l})} = \boldsymbol{Q}_{\boldsymbol{i}} \boldsymbol{H}_{(\boldsymbol{0},\boldsymbol{k})(\boldsymbol{j}-\boldsymbol{i},\boldsymbol{l})} \boldsymbol{Q}_{\boldsymbol{i}}^{T} \qquad (2.13)$$

Note that for a periodic crystal $Q_i = I$ for all i, therefore providing the standard relation that H is block circulant.

The key physical content of (2.13) is that interactions between any pair of atoms in the structure can be mapped to the interactions between atoms in the unit cell and atoms in some other image cell.

Symmetry-adapted Non-equilibrium Molecular Dynamics of Nanotubes

3

3.1 Introduction

Molecular dynamics (MD) is a key tool to understand the atomic-level mechanisms of the deformation of carbon nanotubes. However, the large number of atoms in a nanotube requires the simulation of only a small subset of the entire system to be computationally feasible. While crystals have a natural translational symmetry that enables the application of periodic boundary conditions to a small number of atoms, the translational symmetry in nanotubes can require simulation of a large number of atoms. Hence we apply the framework of Objective Structures (OS) [Jam06]. OS provides a symmetry-adapted approach to the modeling of complex nanostructures. In the case of chiral nanotubes, it provides a generalization of periodic boundary conditions that takes into account both translational and rotational symmetries simultaneously. The resulting Objective boundary conditions enable simulation of chiral nanotubes with a small set of atoms. In addition, OS provides a method to apply bending [NZJD10] and torsional loads to nanotubes [DJ07] as well as nonequilibrium extensional strain rates [DJ10]; it has been proved there that in these methods, each atom in the system obeys exactly the equations of MD without any spurious forces.

In this work we make add thermostat and barostat to the formulation of Objective MD. As currently formulated, OS generalizes periodic boundary conditions. An extremely useful tool in equilibrium periodic molecular dynamics is the use of thermostats [Hoo85] to simulate the effect of a heat bath and barostats [PR81] to simulate the effect of an applied far-field stress. These enable MD calculations of systems with specified temperature and stress rather than specified energy and shape. Based on the Berendsen barostat, we present a generalization to the equilibrium OS setting; in particular we obtain a formula to apply a given axial force along the nanotubes rather than specify the strain rate as previously done [DJ10]. Additionally, we show that the use of these thermostats and barostats in the appropriate manner does not affect the fundamental property of OS, namely that applying the equations of MD to the simulated atom automatically implies that all images also satisfy the equation of MD with no fictitious forces.

3.2 Objective MD at constant temperature and axial force

Objective molecular dynamics (OMD) is a generalization of periodic MD [DJ07] that uses objective images, rather than periodic ones, to compute the forces on atoms. In [DJ10], it was shown that one could satisfy the equations of MD even if the elements of the OS isometry group were certain explicit functions of time. In the particular case that the generator $h_2 = (\mathbf{R}_{\theta_2} | \kappa_2 \mathbf{e})$ is such that $\kappa_2(t) = at + b$ with a, b constants, each atom moves according to the laws of MD while the nanotube undergoes axial elongation. The relation between an atom in molecule i and the corresponding atom in molecule 0 is then

$$\begin{aligned} \boldsymbol{x}_{i,k}(t) &= \boldsymbol{Q}_i \boldsymbol{x}_{0,k}(t) + \boldsymbol{a}_i t + \boldsymbol{b}_i \\ \dot{\boldsymbol{x}}_{i,k}(t) &= \boldsymbol{Q}_i \dot{\boldsymbol{x}}_{0,k}(t) + \boldsymbol{a}_i \\ \ddot{\boldsymbol{x}}_{i,k}(t) &= \boldsymbol{Q}_i \ddot{\boldsymbol{x}}_{0,k}(t) \end{aligned}$$
(3.1)

where $g_i = (\mathbf{Q}_i | \mathbf{c}_i(t) := \mathbf{a}_i t + \mathbf{b}_i)$ is the group element that maps molecule 0 to molecule *i*, and $\mathbf{a}_i, \mathbf{b}_i$ are related to *a*, *b* above.

The potential energy $\phi({\mathbf{x}_{i,k}}) : \mathbb{R}^{6MN} \to \mathbb{R}$, exhibits two fundamental invariances. The first is frame-indifference: $\phi({\mathbf{x}_{i,k}}) = \phi({\mathbf{Q}\mathbf{x}_{i,k}+\mathbf{c}})$ for all \mathbf{Q} orthogonal and \mathbf{c} . The second is permutation invariance, i.e., the labeling of the atoms is not important. These properties enable a simple proof that in an OS, even with the isometry group being affine functions of time, every atom satisfies the equations of MD [DJ10]. In addition, the force on an image atom is related to the force on the atom in the FD through

$$\boldsymbol{F}_{i,k} := -\frac{\partial \phi}{\partial \mathbf{x}_{i,k}} = -\mathbf{Q}_i \frac{\partial \phi}{\partial \mathbf{x}_{0,k}} =: \boldsymbol{Q}_i \boldsymbol{F}_{0,k}$$
(3.2)

using the chain rule.

We now consider the effect of adding barostats or thermostats to maintain a given temperature or axial force, following the ideas for periodic MD [$BPvG^+84$]. We note that time-dependent isometry groups correspond to non-equilibrium settings whereas thermostats and barostats are equilibrium ideas. Thus, in what follows, we restrict the group elements to be constant in time; barostats and thermostats provide desired initial conditions for the non-equilibrium calculations.

For isothermal and isobaric simulations, Berendsen [BPvG⁺84] coupled the system to external baths with fixed reference temperature \tilde{T} and fixed reference stress tensor $\widetilde{\boldsymbol{\sigma}}$. His modified equation of motion is

$$\dot{\boldsymbol{v}}_{0,k} = \frac{\boldsymbol{F}_{0,k}}{m_k} + \gamma \left(\frac{\widetilde{T}}{T} - 1\right) \dot{\boldsymbol{x}}_{0,k}$$

$$\dot{\boldsymbol{x}}_{0,k} = \boldsymbol{v}_{0,k} + \beta \left(\widetilde{\boldsymbol{\sigma}} - \boldsymbol{\sigma}\right) \cdot \boldsymbol{x}_{0,k}$$
(3.3)

where $\boldsymbol{\sigma}$ is the virial stress tensor, T is the averaged temperature and scaling constants β and γ represent the coupling of pressure and thermal baths to the system. We modify $(3.3)_2$ to specify the axial force in the \boldsymbol{e} direction:

$$\dot{\boldsymbol{x}}_{0,k} = \boldsymbol{v}_{0,k} + \beta \left(\widetilde{\boldsymbol{R}} - \boldsymbol{R} \right) \cdot \boldsymbol{x}_{0,k}, \text{ where } \boldsymbol{R} = R\boldsymbol{e} \otimes \boldsymbol{e}, \widetilde{\boldsymbol{R}} = \widetilde{R}\boldsymbol{e} \otimes \boldsymbol{e}$$
(3.4)

where \widetilde{R} is the specified axial force and R is the virial force in z direction.

The virial force is work-conjugate to the specific length of the nanotube and we obtain it from the derivative of the free energy with respect to length. We write an expression for the virial force along the axial direction e of the OS following [CFEW08]. The axial force is defined as the derivative of the free energy with respect to the corresponding length dimension L. We begin by introducing scaled atomic positions $\{s_i\}$, and the matrix H, where $\det(H) = \Omega$ is the volume of the fundamental domain and atomic positions $x_i = H \cdot s_i$. The free energy of the canonical ensemble is then:

$$\psi = -k_B T \ln \left\{ \frac{\Omega^N}{\Lambda^{3N} N!} \int d^{3N} \boldsymbol{s}_i \exp\left[-\frac{U(\{\boldsymbol{s}_i\}, \boldsymbol{H})}{k_B T}\right] \right\}$$
(3.5)

where k_B is Boltzmann's constant, T is the temperature, $\Lambda = \hbar (2\pi m k_B T)^{-1/2}$ and \hbar is Planck's constant. Note that both Ω and U depend on L. Then,

$$\frac{\partial \psi}{\partial L} = \frac{\Omega^N \int \exp\left[-\frac{U(\{\boldsymbol{s}_i\}, \boldsymbol{H})}{k_B T}\right] \frac{\partial U}{\partial L} d^{3N} \boldsymbol{s}_i - k_B T N \Omega^{N-1} \frac{\partial \Omega}{\partial L} \int \exp\left[-\frac{U(\{\boldsymbol{s}_i\}, \boldsymbol{H})}{k_B T}\right] d^{3N} \boldsymbol{s}_i}{\Omega^N \int \exp\left[-\frac{U(\{\boldsymbol{s}_i\}, \boldsymbol{H})}{k_B T}\right] d^{3N} \boldsymbol{s}_i}$$
(3.6)

This is similar to the idea behind virial pressure [LB06] and virial stress [CFEW08]. The virial force R is averaged over time/ensemble and FD:

$$R = \frac{-1}{L} \left\langle \frac{1}{2} \sum_{i=-N}^{N-1} \sum_{k=1}^{M} \sum_{\substack{j=-N\\(j,l)\neq(i,k)}}^{N-1} \sum_{l=1}^{M} F_{(i,k)(j,l)} x_{(i,k)(j,l)} + \sum_{i=-N}^{N-1} \sum_{k=1}^{M} m_k (v_{i,k})^2 \right\rangle$$
(3.7)

where $\langle ... \rangle$ represents time-averaging, L the length of the system in the axial direction, $v_{i,k}$ the axial component of the velocity of the (i, k) atom. The axial components of the force and separation vectors between atoms (i, k) and (j, l) are $F_{(i,k)(j,l)}$ and $x_{(i,k)(j,l)}$ respectively. Using the fact that images of the FD see the same environment up to a translation and rotation, this can be simplified to:

$$R = \frac{-1}{L_0} \left\langle \frac{1}{2} \sum_{j=-N'}^{N'} \sum_{\substack{k=1\\(j,l)\neq(i,k)}}^{M} \sum_{l=1}^{M} F_{(0,k)(j,l)} x_{(0,k)(j,l)} + \sum_{k=1}^{M} m_k (v_{0,k})^2 \right\rangle$$
(3.8)

Here, L_0 is the axial length of the FD, and atoms in the FD interact with their images as far as the molecules $\pm N'$. We have not considered long-range forces such as due to electromagnetic phenomena.

Now, we show that the modified equations of motion $(3.3_1, 3.4)$ hold for all atoms. For atoms in the image cells, the velocity $\dot{\boldsymbol{v}}_{i,k}$ is given by

$$\dot{\boldsymbol{v}}_{i,k} = \boldsymbol{Q}_i \cdot \dot{\boldsymbol{v}}_{0,k} = \boldsymbol{Q}_i \cdot \frac{\boldsymbol{F}_{0,k}}{m_k} + \gamma \left(\frac{\widetilde{T}}{T} - 1\right) \boldsymbol{Q}_i \cdot \dot{\boldsymbol{x}}_{0,k} = \frac{\boldsymbol{F}_{i,k}}{m_k} + \gamma \left(\frac{\widetilde{T}}{T} - 1\right) \dot{\boldsymbol{x}}_{i,k} \quad (3.9)$$

Similarly, we can write the analog of (3.4) for atom (i, k):

$$\dot{\boldsymbol{x}}_{i,k} = \boldsymbol{Q}_i \cdot \dot{\boldsymbol{x}}_{0,k} = \boldsymbol{Q}_i \cdot \boldsymbol{v}_{0,k} + \beta \boldsymbol{Q}_i \cdot \left(\widetilde{\boldsymbol{R}} - \boldsymbol{R} \right) \cdot \boldsymbol{x}_{0,k} = \boldsymbol{Q}_i \cdot \boldsymbol{v}_{0,k} + \beta \boldsymbol{Q}_i \cdot \left(\widetilde{\boldsymbol{R}} - \boldsymbol{R} \right) \cdot \boldsymbol{Q}_i^T \boldsymbol{Q}_i \cdot \boldsymbol{x}_{0,k}$$
(3.10)

Using that $\widetilde{R} - R = (\widetilde{R} - R) e \otimes e$, where e is the axis of the nanotube and of the

orthogonal tensor \boldsymbol{Q} , we have that $\boldsymbol{Q}_i \cdot (\widetilde{\boldsymbol{R}} - \boldsymbol{R}) \cdot \boldsymbol{Q}_i^T = \widetilde{\boldsymbol{R}} - \boldsymbol{R}$. Hence,

$$\dot{\boldsymbol{x}}_{i,k} = \boldsymbol{Q}_i \cdot \boldsymbol{v}_{0,k} + \beta \left(\widetilde{\boldsymbol{R}} - \boldsymbol{R} \right) \cdot \left(\boldsymbol{Q}_i \cdot \boldsymbol{x}_{0,k} + \boldsymbol{b}_i - \boldsymbol{b}_i \right) = \boldsymbol{v}_{i,k} + \beta \left(\widetilde{\boldsymbol{R}} - \boldsymbol{R} \right) \cdot \left(\boldsymbol{x}_{i,k} - \boldsymbol{b}_i \right)$$
(3.11)

where \boldsymbol{b}_i is the translation vector of i^{th} group generator, g_i (3.1). Comparing (3.9, 3.11) with (3.3₁, 3.4), we conclude that all atoms satisfy the modified equation of motion.

The velocity-Verlet time integration of the modified equations is

$$\boldsymbol{v}_{0,k}\left(t+\frac{\Delta t}{2}\right) = \boldsymbol{v}_{0,k}(t) + \left[\frac{\boldsymbol{F}_{0,k}(t)}{m_{k}} + \gamma\left(\frac{\widetilde{T}}{T(t)} - 1\right)\boldsymbol{v}_{0,k}(t)\right]\frac{\Delta t}{2}$$
$$\boldsymbol{x}_{0,k}(t+\Delta t) = \left[1 + \beta\Delta t\left(\widetilde{\boldsymbol{R}} - \boldsymbol{R}\right)\right] \cdot \boldsymbol{x}_{0,k}(t) + \boldsymbol{v}_{0,k}\left(t + \frac{\Delta t}{2}\right)\Delta t \qquad (3.12)$$
$$\boldsymbol{v}_{0,k}\left(t+\Delta t\right) = \frac{2}{2 - \gamma\left(\frac{\widetilde{T}}{T(t+\frac{\Delta t}{2})} - 1\right)\Delta t}\left[\boldsymbol{v}_{0,k}\left(t+\frac{\Delta t}{2}\right) + \frac{\boldsymbol{F}_{0,k}(t+\Delta t)}{m_{k}}\frac{\Delta t}{2}\right]$$

3.3 Non-equilibrium objective molecular dynamics of single-walled carbon nanotubes

In this section, we report the results of extensive non-equilibrium objective molecular dynamics calculations that examine the effect of temperature, strain rate, chirality, and pre-stretch/pre-compression, with particular focus on the failure modes. We used the Tersoff potential [Ter88] to model the atomic interactions. The FD is constructed using subgroups as described above, and we verify our calculations by testing with different choices of FD.

The procedure that we use for all our calculations is as follows. First, we use the temperature and axial force control as formulated above to relax the nanotubes to the prescribed initial temperature and initial axial force. This is to reach an equilibrium configuration and no external strain rate is applied during this phase. Rather, the length of the nanotube evolves under the barostat. Next, we remove both the thermostat and barostat and a constant strain rate is applied. The system evolves under the influence of the external strain rate. As we update the atomic positions following the Verlet algorithm, we also update the group elements as they change due to the imposed strain rate. This in turn changes the positions of the image atoms that are generated under the action of the group elements. Consequently, the calculation of force on atoms in the FD is coupled to the imposed strain rate.

3.3.1 Effect of Temperature, Strain Rate and Chirality

Fig. Figure 3.1a shows failure strain surfaces as a function of chirality and strain rate, with different surfaces corresponding to different initial temperatures. A general trend that we notice is that chirality plays a stronger role at higher strain rates but its influence decreases at the lower strain rates. We also notice that the failure strain at temperatures of 1500K and 1000K are extremely small ($\sim 0.08\%$) at strain rates of $10^5 - 10^6 s^{-1}$ independent of the chirality. Strain rates below $10^5 s^{-1}$ require extremely long computational times on the order of several months, even with high-performance computing, and thus we do not have comprehensive data for these strain-rate regimes.

However, a limited set of calculations with (6,6) nanotubes shows that the failure strains begin to trend back upwards at 10^4 s⁻¹, Fig. Figure 3.1b. While the calculations at 10^3 s⁻¹ are still in progress, they show that the failure strain is bounded below by ~ 1%. Since the chirality does not strongly influence the behavior at the lower strain rates, we conjecture that this behavior is shared by other nanotubes. A number of previous studies at higher strain rates [DJ10, DHY06, JTF04, WCS03, DY04, ZA10, LCY10] have found that reducing strain rate lowers the failure strain, in contrast to the general expectation that lower strain rates and higher temperatures promote ductile behavior. While we also observe this trend, at the lowest rates that we have calculated this trend begins to reverse.

We observe three primary failure moodes of the nanotubes. The mostly widely ob-



Figure 3.1: Left: failure strain surfaces as a function of chirality and strain rate, with different surfaces corresponding to different initial temperatures; right: failure strain for (6,6) nanotubes down to 10^4s^{-1}

served mode was the formation of Stone-Wales defects in which a bond rotates within the surface of the nanotube, and subsequently, two pentagons and two heptagons are created (Fig. Figure 3.2a) leading to a dislocation dipole. While the Stone-Wales defect can lower the energy significantly, the high barrier for nucleation can require thermal activation and hence its formation can be temperature-dependent as well as strain-rate dependent. This mode of failure typically correlates with large plastic deformation or ductility and higher failure strains on Fig. Figure 3.1.

The second widely-observed mode can be considered as a microscopic version of brittle fracture. Essentially, the stretching of bonds leads to breakage of a single bond, typically quickly followed by the failure of neighboring bonds (Fig. Figure 3.2b).

The third failure mode is out-of-surface motion of atoms (figure Figure 3.2c). Bonds rotate out of the plane and the atom which has moved off the surface bonds with other atoms.

The failure mechanisms listed above refer to the initial stages of defect forma-

tion and growth. In the advanced stages, these mechanisms can be concurrent. For instance, as the number of Stone-Wales defects increases, this can lead to void formation and subsequent failure in a brittle sense; this is typical of the high failure strain calculations. Figs. Figure 3.3 shows some examples of these mechanisms operating in combination.



Figure 3.2: Failure modes: (a) Stone-Wales defect (b) brittle void formation (c) outof-surface motion. Blue indicates the simulated atoms in the FD, and other atoms are the images. For clarity, only the atoms on the front surface of the nanotubes are shown.

We have closely monitored the failure mechanisms of simulations with different temperatures, strain rates and chiralities and the results are summarized here.

We find that the out-of-plane bond rotation is the major cause of failure at high temperature (1250-1500K) and low strain rate (10^5-10^6s^{-1}) . From Fig. Figure 3.1, nanotubes at these conditions fail at very low strain. Although we observed Stone-Wales defects prior to the failure in a few of these calculations, they do not lead to failure that is instead driven by out-of-surface motion. In the other high temperature calculations (above 1000K), Stone-Wales activity is the primary mechanism of failure.



Figure 3.3: Concurrent failure modes: (a) Stone-Wales and brittle void formation (b) disassociated Stone-Wales and two brittle void formation (c) Stone-Wales and out-of-surface bond rotation (d) all three modes.

Possibly, this is due the higher temperature enabling passage of the Stone-Wales activation barrier.

In most cases at lower temperatures (300K and 500K), we observed Stone-Wales defects prior to failure. However, at the higher strain rates calculated $(10^7 \text{s}^{-1} \text{ and } 10^8 \text{s}^{-1})$, brittle fracture occurs before Stone-Wales defects and plays a more significant role in failure. At lower strain rates (10^5s^{-1}) , Stone-Wales defects usually nucle-

ate before brittle fracture and they play a significant role in failure. For instance, in some simulations, we observed multiple Stone-Wales defects simultaneously. We also observed that the Stone-Wales defects cause the opening and enlargement of voids. Interestingly, at intermediate strain rates $(10^{6}s^{-1})$, Stone-Wales defects were infrequently observed. Instead, brittle fracture and consequent void opening was more commonly observed and played the key role in failure. In general however, the trend was that Stone-Wales defects are observed more often at lower strain rates, possibly because the lower strain rates allow more time for the crossing of the Stone-Wales formation barrier.

Finally, we observe that chirality does not significantly change the failure mechanism but does influence the failure strain. When Stone-Wales defects or brittle fractures are the major cause of the failure, nanotubes with larger chiral angles fail at higher strain. However, when out-of-surface bond rotation is the dominant failure mechanism, there is little change in the failure strain with change in chirality. These out-of-surface bond rotation cases correspond to high temperature and low strain rate.

3.3.2 Effect of Pre-Stretch and Pre-Compression

In this section, we examine the the effect of imposing an initial axial force (-90nN to +55nN) for different initial temperatures and strain rates. We note that the structure constructed by (2.8) with the values of κ_2 and l_0 listed there corresponds to a nanotube that is axially compressed by a force of 30nN at 300K.

Figure Figure 3.4 shows the force-extension curves from a range of different conditions¹. The key finding is that pre-stretch negligibly affects the force-extension behavior and has only a minor role in the final failure. This observation is robust across a range of temperatures, initial stretches, and strain rates. The fact that the

¹ Displacement is defined as the change in length of a FD with reference length 0.7379nm.

nonlinear force-extension behavior is not affected by pre-stretch can enable the use of axial forces to reliably tune the linearized stiffness of carbon nanotube and hence achieve interesting wave propagation effects [DNJ04, DNJ⁺06]. In addition, Fig. Figure 3.4 also shows the softening of the force-extension curve with temperature.

Figure Figure 3.5 shows the evolution of temperature for different axial forces with initial temperature 300K. These curves show that temperature evolution is independent of initial axial force to within a few degrees Kelvin; additionally, some of the discrepancy in temperature evolution is due to the fact that our thermostatting is set to provide the same initial temperature irrespective of starting strain. We notice the very sharp increase in temperature close to the failure strain.



Figure 3.4: Left: Force-extension curves at 300K and 500K at strain rate $10^5 s^{-1}$ with different axial forces (in nN); right: Force-extension curves at 300K and 1000K at strain rate $10^7 s^{-1}$ with different axial forces (in nN).

In previous work [DJ10], it was conjectured that extreme cross-sectional distortions seen shortly before failure may be due to the initial axial stress arising from unrelieved thermal expansion. Our formulation of a barostat enables us to test this conjecture, and we find it false; the cross-sectional distortions are seen with initial compressive and axial forces as well as when the force is absent.



Figure 3.5: Temperature vs. displacement at initial temperature of 300K and strain rate of 10^{6} s⁻¹.

3.4 Conclusion

We have applied the OS framework to perform non-equilibrium MD calculations of carbon nanotubes extended at a constant strain rate. We have examined the effect of varying strain rate from $10^4 - 10^8 \text{s}^{-1}$, initial temperature from 300 - 1500K, and a range of chiralities. The OS framework enables simulation of carbon nanotubes with a small set of atoms enabling a larger set of computations at lower strain rates.

We have formulated an analog of a barostat to enable us to exert a specified axial force at equilibrium. The barostat preserves the important feature of OS that each atom follows exactly the same equations of motions and there are no uncontrolled spurious forces. This enabled us to test the effect of initial axial force on the failure of carbon nanotubes.

We have found that three modes dominate the failure behavior: first, the formation of Stone-Wales defects; second, the formations of voids and brittle failure; and third, the motion of atoms out of the surface of the nanotube. In addition, these failure modes were also observed to operate concurrently. We have found that
both chirality and initial axial stretch/compression play a relatively minor role in comparison to the influence of temperature and strain rate. The OS formulation, in combination with high-performance computing, enables us to access relatively low strain rates (for MD). While our findings at strain rates $10^8 - 10^5 s^{-1}$ agree qualitatively with other studies in that lowering strain rate reduces the failure strain, we are able to access the regime at $10^4 s^{-1}$. We observe the interesting reversal of this trend: the failure strains at $10^4 s^{-1}$ increase in comparison with $10^5 s^{-1}$. Calculations at $10^3 s^{-1}$ are ongoing.

Symmetry-Adapted Phonon Analysis

4.1 Introduction

Phonons, i.e. normal modes, are extremely important to understand the properties of crystals. For instance, phonon analysis provides insight into thermodynamic properties and mechanical stability [Dov93, BH98, ETS06, EST06]. In this chapter, we use the framework of Objective Structures (OS) to extend the notion of phonon analysis to noncrystalline but symmetric nanostructures.

In this chapter, we exploit in an essential way the symmetry in the second derivative of the potential energy, i.e. the Hessian matrix has various submatrices that are related to each other. While this was noted by James [Jam06], it has not been exploited in practical calculations. Here, we find that this property implies that a preliminary linear transformation renders the Hessian matrix block-circulant as in periodic crystals, thus enabling the use of standard Fourier techniques after the preliminary transformation. While a significant part of our analysis is general and applies broadly to all structures that belong to the family of OS, we also specialize the analysis to carbon nanotubes and other one-dimensional systems to do numerical calculations. Except where stated as a model system, we use the well-characterized Tersoff interatomic potential for carbon that provides a balance between bond-order accuracy and computational efficiency [Ter88].

We emphasize that many researchers have studied phonons in carbon nanotubes for over a decade now. For instance, an early example is [YKV95a]; a more recent review is [JDD08]. An important feature of all of these studies is that they directly use methods from periodic systems. This often requires the use of very large unit cells that require expensive calculations to compute the phonon analysis, and more importantly the computed information is extremely complex and difficult to analyze for new physics. Recent papers that exploit the symmetry of nanotubes are [GLW08, PL06c].

We go beyond these methods in some significant ways. First, our approach based on OS provides a tight link to deformation of the nanotubes. This is critical to go beyond exclusively axial-load-free and twisting-moment-free nanotubes; in fact, as recent work shows, the load- and moment- free structure of chiral nanotubes likely does *not* correspond to the assumed highly-symmetric configuration [VBSF⁺10, ZAD11, AD12]. Relaxing or applying such loads is readily accomplished using the OS framework [Jam06, DJ07]. Second, our analysis exposes the close analogies to periodic crystals; additionally, it is general and applicable to a wide variety of OS that go beyond carbon nanotubes.

4.2 Notation

 \mathbb{Z} denotes the set of all integers and \mathbb{Z}^3 the set of triples of all integers.

For a quantity \boldsymbol{A} , the Fourier transform is denoted by \boldsymbol{A} .

To avoid ambiguity, the summation convention is *not* used and sums are always indicated explicitly.

Throughout this chapter, M and N are used for the number of atoms per unit cell

and the number of unit cells in the OS respectively. Note that M is always finite but N can be infinite. The unit cells are labeled by multi-indices denoted by boldface, i.e. $\mathbf{i} = (i_1, i_2, i_3)$, and atoms within a given unit cell are labeled by regular non-bold indices. For example, the position of the k atom in the \mathbf{i} unit cell is denoted $\mathbf{x}_{i,k}$.

Bold lower case and upper case letters represent vectors and matrices, respectively. The rectangular Cartesian component and the exponent of a vector or matrix are shown respectively by Greek letters and lower case Latin letters as superscripts.

The subscripts of vectors and matrices are used to convey information about the structure of the quantity in addition to denoting components. We will often deal with matrices of size $3MN \times 3MN$ corresponding to an OS with 3MN degrees of freedom (DoFs). Such a matrix \boldsymbol{A} can be divided into $N \times N$ blocks, with each block further sub-divided into $M \times M$ sub-blocks of size 3×3 . Then, $\boldsymbol{A}_{(i,k)(j,l)}$ denotes a 3×3 sub-block, typically corresponding to the pair of atoms labeled by (\boldsymbol{i}, k) and (\boldsymbol{j}, l) . Also, $\boldsymbol{A}_{\boldsymbol{ij}}$ denotes a $3M \times 3M$ matrix, typically corresponding to atoms in the unit cells labeled \boldsymbol{i} and \boldsymbol{j} .

Similarly, for a vector \boldsymbol{b} of size $3MN \times 1$, writing \boldsymbol{b}_i denotes the \boldsymbol{i} -th block of \boldsymbol{b} of size $3M \times 1$ typically corresponding to the unit cell labeled by \boldsymbol{i} . Further, $\boldsymbol{b}_{i,k}$ denotes a sub-block of \boldsymbol{b}_i of size 3×1 , typically corresponding to the atom k in the unit cell labeled by \boldsymbol{i} .

For Fourier quantities, the correspondences for sub-blocks in vectors and matrices are not to unit cells but rather to wave numbers.

4.3 Normal Mode Analysis in Objective Structures

We first derive the standard linearized equations of motion in an OS. We then use the properties of the Hessian from the previous section to achieve a block-diagonalization of the Hessian such that each block is of size $3M \times 3M$. Each block is related to the frequency in Fourier space, but the transformation is not directly from real to

Fourier space but goes through an intermediate linear transform.

4.3.1 Linearized Equation of Motion around an Equilibrium Configuration

Let $\mathbf{\dot{x}} = {\mathbf{\dot{x}}_{i,k} ; k = 1, ..., M ; i \in \mathbb{Z}^3}$ be the equilibrium configuration. Consider a perturbation $\mathbf{u}_{i,k}$ about this configuration and use a Taylor expansion:

$$\phi(\mathring{\boldsymbol{x}} + \boldsymbol{u}) = \phi(\mathring{\boldsymbol{x}}) + \sum_{(\boldsymbol{i},\boldsymbol{k})} \sum_{\alpha=1}^{3} \frac{\partial \phi}{\partial x_{\boldsymbol{i},\boldsymbol{k}}^{\alpha}} \Big|_{\mathring{\boldsymbol{x}}} u_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} + \frac{1}{2} \sum_{(\boldsymbol{i},\boldsymbol{k})} \sum_{\alpha=1}^{3} \sum_{(\boldsymbol{j},\boldsymbol{l})} \sum_{\beta=1}^{3} \frac{\partial^{2} \phi}{\partial x_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} \partial x_{\boldsymbol{j},\boldsymbol{l}}^{\beta}} \Big|_{\mathring{\boldsymbol{x}}} u_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} u_{\boldsymbol{j},\boldsymbol{l}}^{\beta} + \dots$$

$$(4.1)$$

Since $\mathbf{\dot{x}}$ is an equilibrium configuration, the first derivative does not appear. Neglecting terms higher than quadratic:

$$\phi(\mathring{\boldsymbol{x}} + \boldsymbol{u}) = \phi(\mathring{\boldsymbol{x}}) + \frac{1}{2} \sum_{(\boldsymbol{i},\boldsymbol{k})} \sum_{\alpha=1}^{3} \sum_{(\boldsymbol{j},l)} \sum_{\beta=1}^{3} \frac{\partial^{2}\phi}{\partial x_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} \partial x_{\boldsymbol{j},l}^{\beta}} \bigg|_{\mathring{\boldsymbol{x}}} u_{\boldsymbol{i},\boldsymbol{k}}^{\alpha} u_{\boldsymbol{j},l}^{\beta}$$
(4.2)

Taking the limit of $\boldsymbol{u} \to \boldsymbol{0}$, the force on the atom (\boldsymbol{i}, k) is:

$$m_k \ddot{u}_{\boldsymbol{i},k}^{\alpha} = f_{\boldsymbol{i},k}^{\alpha} := -\frac{\partial \phi}{\partial x_{\boldsymbol{i},k}^{\alpha}} = -\sum_{(\boldsymbol{j},l)} \sum_{\beta=1}^3 \frac{\partial^2 \phi}{\partial x_{\boldsymbol{i},k}^{\alpha} \partial x_{\boldsymbol{j},l}^{\beta}} u_{\boldsymbol{j},l}^{\beta} = -\sum_{(\boldsymbol{j},l)} \sum_{\beta=1}^3 H_{(\boldsymbol{i},k)(\boldsymbol{j},l)}^{\alpha\beta} u_{\boldsymbol{j},l}^{\beta} \quad (4.3)$$

In compact matrix form,

$$\boldsymbol{M}\ddot{\boldsymbol{u}} = -\boldsymbol{H}\boldsymbol{u} \tag{4.4}$$

M and H are the $3MN \times 3MN$ mass and Hessian matrices respectively. Note that M is diagonal and trivially inverted. So define $\hat{H} := M^{-1}H$.

The linear form of (4.4) implies that solutions are exponentials, i.e., $\boldsymbol{u} = \hat{\boldsymbol{u}} \exp(-i\omega t)$ where ω is the angular frequency. Therefore, we seek to solve the eigenvalue problem:

$$\omega_p^2 \hat{\boldsymbol{u}}^p = \hat{\boldsymbol{H}} \hat{\boldsymbol{u}}^p \tag{4.5}$$

 ω_p^2 and $\hat{\boldsymbol{u}}^p$ are the eigenvalues and eigenvectors of $\hat{\boldsymbol{H}}$, with $p = 1, \dots, 3MN$. In generic finite structures, solving this eigenvalue problem can be computationally

demanding. In infinite periodic crystals, \boldsymbol{H} is block-circulant as noted above. Consequently, it can be block-diagonalized using the Fourier transform, thus converting the problem of solving a 3MN system into solving N systems of size 3M. Note that this is only formally true, because N is infinite in this case; in addition, the Fourier transform enables more than just computational saving as it provides important physical insights to organize the nominally infinite number of solutions. Therefore, instead of finding the eigenvalues of a $3MN \times 3MN$ matrix, we can calculate the eigenvalues of $3M \times 3M$ matrices N times (Appendix A). For an OS however, $\hat{\boldsymbol{H}}$ is not block-circulant. We deal with this in Section 4.3.2.

4.3.2 Block-diagonalization for an Objective Structure

As noted immediately above, the Hessian \hat{H} in an OS is not block-circulant; however, there is a close analogy in (2.13), i.e. $\hat{H}_{(p,k)(q,l)} = Q_p \hat{H}_{(0,k)(q-p,l)} Q_p^T$. As we show below, the linear transformation defined by the $3MN \times 3MN$ matrix

$$\boldsymbol{R}_{(\boldsymbol{p},k)(\boldsymbol{q},l)} = \boldsymbol{Q}_{\boldsymbol{p}} \delta_{\boldsymbol{p}\boldsymbol{q}} \delta_{kl} \tag{4.6}$$

takes us to the *Objective Space* in which \hat{H} is block-circulant. It is then possible to block-diagonalize \hat{H} using the DFT.

In the one-dimensional case \boldsymbol{R} has the form:

$$\boldsymbol{R} = \begin{bmatrix} [\boldsymbol{R}_{00}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{0}] \\ [\boldsymbol{0}] & [\boldsymbol{R}_{11}] & \cdots & [\boldsymbol{0}] \\ \vdots & \vdots & \ddots & \vdots \\ [\boldsymbol{0}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{R}_{(N-1)(N-1)}] \end{bmatrix}$$
(4.7)

We note that one-dimensional does not refer to real-space but rather to the number of slots in the multi-index that indexes the unit cells. Each submatrix \mathbf{R}_{pp} is a $3M \times 3M$ block-diagonal matrix

$$\boldsymbol{R}_{pp} = \begin{bmatrix} [\boldsymbol{Q}_{p}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{0}] \\ [\boldsymbol{0}] & [\boldsymbol{Q}_{p}] & \cdots & [\boldsymbol{0}] \\ \vdots & \vdots & \ddots & \vdots \\ [\boldsymbol{0}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{Q}_{p}] \end{bmatrix}$$
(4.8)

and each Q_j is a 3 × 3 orthogonal tensor. R is obviously orthogonal.

Defining $\hat{\boldsymbol{u}} = \boldsymbol{R}\hat{\boldsymbol{v}}$ and substituting this in (4.5), we get

$$\omega^2 \mathbf{R} \hat{\mathbf{v}} = \hat{\mathbf{H}} \mathbf{R} \hat{\mathbf{v}} \Rightarrow \omega^2 \hat{\mathbf{v}} = \mathbf{R}^T \hat{\mathbf{H}} \mathbf{R} \hat{\mathbf{v}} = \hat{\mathbf{D}} \hat{\mathbf{v}}$$
(4.9)

where $\hat{D} := R^T \hat{H} R$ is the transformed Hessian matrix. We now show that \hat{D} is block-circulant. Using (4.6), we have that:

$$\hat{\boldsymbol{D}}_{(\boldsymbol{p},k)(\boldsymbol{q},l)} = \boldsymbol{Q}_{\boldsymbol{p}}^T \hat{\boldsymbol{H}}_{(\boldsymbol{p},k)(\boldsymbol{q},l)} \boldsymbol{Q}_{\boldsymbol{q}}$$
(4.10)

Now, substitute (2.13) into (4.10):

$$\hat{\boldsymbol{D}}_{(\boldsymbol{p},k)(\boldsymbol{q},l)} = \boldsymbol{Q}_{\boldsymbol{p}}^{T} \boldsymbol{Q}_{\boldsymbol{p}} \hat{\boldsymbol{H}}_{(\boldsymbol{0},k)(\boldsymbol{q}-\boldsymbol{p},l)} \boldsymbol{Q}_{\boldsymbol{p}}^{T} \boldsymbol{Q}_{\boldsymbol{q}}$$

$$= \boldsymbol{Q}_{\boldsymbol{0}}^{T} \hat{\boldsymbol{H}}_{(\boldsymbol{0},k)(\boldsymbol{q}-\boldsymbol{p},l)} \boldsymbol{Q}_{\boldsymbol{q}-\boldsymbol{p}}$$

$$= \hat{\boldsymbol{D}}_{(\boldsymbol{0},k)(\boldsymbol{q}-\boldsymbol{p},l)}$$
(4.11)

where we have used (2.7) and $Q_0 = I$.

Therefore, \hat{D} is block-circulant and can be block-diagonalized by the DFT as described in Appendix A. Essentially, we use two successive linear transforms to solve

$$\omega^2 \tilde{\boldsymbol{v}} = \tilde{\boldsymbol{D}} \tilde{\boldsymbol{v}} \tag{4.12}$$

where $\tilde{\boldsymbol{D}}$ is block-diagonal and

$$\tilde{\boldsymbol{v}} = \boldsymbol{F} \hat{\boldsymbol{v}} = \boldsymbol{F} \boldsymbol{R}^T \hat{\boldsymbol{u}} \tag{4.13a}$$

$$\tilde{\boldsymbol{D}} = \boldsymbol{F} \hat{\boldsymbol{D}} \boldsymbol{F}^{-1} = \boldsymbol{F} \boldsymbol{R}^T \hat{\boldsymbol{H}} \boldsymbol{R} \boldsymbol{F}^{-1} = \boldsymbol{F} \boldsymbol{R}^T \boldsymbol{M}^{-1} \boldsymbol{H} \boldsymbol{R} \boldsymbol{F}^{-1}$$
(4.13b)

Since \tilde{D} is block-diagonal, we can simplify the dynamical equation (4.12) to read:

$$\left(\omega^{2}\right)^{\left[\boldsymbol{p}\right]}\tilde{\boldsymbol{v}}_{\boldsymbol{p}} = \tilde{\boldsymbol{D}}_{\boldsymbol{p}\boldsymbol{p}}\tilde{\boldsymbol{v}}_{\boldsymbol{p}} \tag{4.14}$$

where $(\omega^2)^{[p]}$ is the eigenvalue corresponding to the eigenvector \tilde{v}_p . From (A.7) and (4.11)

$$\tilde{\boldsymbol{D}}_{\boldsymbol{p}\boldsymbol{p}} = \sum_{\boldsymbol{r}} \exp\left[-i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{r}}\right] \hat{\boldsymbol{D}}_{\boldsymbol{0}\boldsymbol{r}}$$
$$= \sum_{\boldsymbol{r}} \exp\left[-i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{r}}\right] \hat{\boldsymbol{H}}_{\boldsymbol{0}\boldsymbol{r}} \boldsymbol{R}_{\boldsymbol{r}\boldsymbol{r}}$$
(4.15)

For the wave vector associated with \boldsymbol{p} , (4.14) gives 3M solutions analogous to the multiple branches in a phonon spectrum. We index these by ν . The displacement of the atom (\boldsymbol{q}, l) induced by the normal mode labeled by the wave-vector \boldsymbol{p} and the ν -th branch is obtained by solving for $\hat{\boldsymbol{u}}$ in (4.13a) and using (A.4) and (4.6):

$$\hat{\boldsymbol{u}}_{(\boldsymbol{q},l)}^{[\boldsymbol{p},\nu]} = \frac{1}{\sqrt{N}} \boldsymbol{Q}_{\boldsymbol{q}} \tilde{\boldsymbol{v}}_{(\boldsymbol{p},l)}^{[\nu]} \exp\left[-i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{q}}\right]$$
(4.16)

As can be seen from (4.13b), \mathbf{R} acts first on the Hessian matrix $\hat{\mathbf{H}}$ and "unwraps" the structure by transforming it to Objective Space. Subsequently, \mathbf{F} acts on the unwrapped periodic structure. Therefore both position vector \mathbf{y} and wave vector \mathbf{k} are defined in Objective Space. The quantities $\mathbf{k}_p \cdot \mathbf{y}_q$ can be obtained using the standard method for periodic systems outlined in Appendix A.

We summarize the key steps in our algorithm:

1. Calculate \hat{H}_{0r} , the Hessian matrix corresponding to interactions between any chosen unit cell, labeled **0**, and the neighboring cells. The size of \hat{H}_{0r} is $3M \times 3MN$.

- 2. Multiply each vertical block of \hat{H}_{0r} by the rotation matrix of that block, i.e. calculate $\hat{H}_{0r}R_{rr}$.
- 3. Calculate $\tilde{D}_{pp} = \sum_{r} \exp\left[-ik_{p} \cdot y_{r}\right] \hat{H}_{0r} R_{rr}$, the dynamical matrix associated with wave vector k_{p} .
- 4. Find the eigenvalues, $(\omega^2)^{[p,\nu]}$, and eigenvectors, $\tilde{v}_{p}^{[\nu]}$, of \tilde{D}_{pp} .
- 5. The normalized displacement of the atoms are $\hat{u}_{(q,l)}^{[p,\nu]} = \frac{1}{\sqrt{N}} Q_q \tilde{v}_{(p,l)}^{[\nu]} \exp \left[-ik_p \cdot y_q\right]$. The wave vector and the branch number respectively are labeled by p and ν .

4.4 A Numerical Example: Dispersion Curves of (6,6) Carbon Nanotubes

While the OS framework can be used for nanotubes with any chirality, in this section we focus on (6, 6) carbon nanotubes to illustrate some typical features of the phonon curves. This particular chirality also has a small translational unit cell that enables comparisons with standard periodic calculations.

We compare the effect of using four different unit cells.

- **Choice 1:** We use a periodic unit cell with 24 atoms, the smallest number required for periodicity. In OS terms, the group generators are g_1 = identity and a translation $g_2 = (\mathbf{I}|0.246 \text{nm } \mathbf{e})$. The phonon dispersion curves are plotted in Fig. Figure 4.1a.
- **Choice 2:** We use 24 atoms in the unit cell as in Choice 1, but in this case the images are related not by periodicity but by both translation (along e) and rotation (around e). The generators are g_1 = identity and a screw g_2 =

 $(\mathbf{R}_{\pi/3}|0.246$ nm $\mathbf{e})$. The phonon dispersion curves are plotted in Fig. Figure 4.1b.

- Choice 3: We use 12 atoms in the unit cell, with generators closely related to Choice
 2: g₁ = identity and a screw g₂ = (**R**_{π/6}|0.123nm e) The phonon dispersion curves are plotted in Fig. Figure 4.2.
- **Choice 4:** We make full use of the OS framework and use 2 atoms in the unit cell¹. The generators are $g_1 = (\mathbf{R}_{\pi/3}|\mathbf{0})$ and $g_2 = (\mathbf{R}_{\pi/6}|0.123 \text{nm } \mathbf{e})$. In Choices 1, 2, 3, the wavevector was one-dimensional because the structure was indexed by a single index (not a triple-valued multi-index). In this case, the wavevector is two dimensional, but takes only 6 discrete values in the direction corresponding to the rotation. This is because once we raise the rotation to the 6-th power, we start over; conceptually, this is similar to a finite ring of atoms that has a finite set of normal modes. The phonon dispersion curves are plotted in Fig. Figure 4.3.

Comparing the plots in Fig. Figure 4.1 shows, as expected, that there is a mapping between the plots obtained from Choices 1 and 2. Any eigenvalue in one is also present in the other, though typically at a different wavevector. Further, comparing Figs. Figure 4.1b and Figure 4.2, shows that if we unfold the curves of Fig Figure 4.1b we will recover Fig. Figure 4.2. Similarly, Fig. Figure 4.3 contains all the information, but in a much simpler description.

The OS description with 2 atoms per unit cell provides a useful perspective to examine the deformations. First, consider the case when the component of the wavevector in the discrete direction is 0. Each unit cell in the cross-section has the same displacement (in Objective Space) in the direction that corresponds to the

 $^{^{1}}$ OS constructed by non-commuting groups can describe carbon nanotubes with 1 atom per unit cell, but the complexity introduced by the non-commuting elements is formidable.



Figure 4.1: Dispersion curves of a (6, 6) carbon nanotube for (a) Choice 1 and (b) Choice 2. The wavevector is normalized by the length of the translation vector 0.246nm in g_2 . The large number of phonon curves that have equal and opposite slopes at the right edge of the plots (i.e. "folded over") are a signature of the large unit cell.



Figure 4.2: Dispersion curves of a (6, 6) carbon nanotubes using Choice 3. The wavevector is normalized by the length of the translation vector 0.123nm in g_2 . The band-folding shows that our unit cell still has unused symmetries.

discrete component of the wavevectors. Roughly, this corresponds to "cross-sections" that retain their "shape" and remain circular. The lowest three modes corresponding to $k_2 = 0$ and $k_1 \approx 0$ are plotted in Fig. Figure 4.4.

Next, consider the case when k_2 , the component of the wavevector in the discrete direction, is non-zero. In this case, the cross-sections no longer remain circular. Fig. Figure 4.5 shows examples of these modes. Notice the relation between k_2 and the symmetry of the cross-section.

Fig. Figure 4.6 shows an assortment of generic phonon modes at finite wavevectors.



Figure 4.3: Dispersion curves of a (6, 6) carbon nanotube using Choice 4 with 2 atoms in the unit cell. k_1 is the component of the wavevector in the continuous direction and normalized by 0.123 nm, and k_2 is the component in the discrete direction and normalized by the approximate perimeter P.



Figure 4.4: Phonon modes at $k_1 \approx 0$ and $k_2 = 0$ using Choice 4. (a) The undeformed reference nanotube. The colors of the atoms are only to enable visualization of the deformation. (b) The lowest branch corresponding to twisting. (c) The next-tolowest branch corresponding to axial elongation. (d) The third-from-lowest branch corresponding to a change in radius. In each of these deformations, the cross-section remains circular.

4.4.1 Density of States (DoS) of a (6,6) carbon nanotube

The density of states (DoS) of a system is an important thermodynamic quantity. It describes the number of modes or states available per unit energy (or frequency) at each energy level. The DoS can be calculated by making a histogram of the phonons frequencies of the system. Fig. Figure 4.7 shows the DoS of a (6,6) carbon nanotube constructed using Choices 1 and 4 for the unit cell. As expected, these curves are identical but the OS approach requires much less computational effort.

4.5 Long Wavelength and Rigid Body Modes for Carbon Nanotubes

In a 3D periodic crystal lattice, the lowest three eigenvalue branches tend linearly to 0 as $\mathbf{k} \to \mathbf{0}$. These *acoustic modes* correspond to uniform deformations with rigid body translation modes as the limit deformation. We find unusual contrasts with the crystal case when we apply this to carbon nanotubes. We find rigid body (zero energy) motions at both zero and finite wave vectors; in addition, we find that the long-wavelength deformation corresponding to uniform radial expansion costs finite



Figure 4.5: Some long-wavelength modes at finite k_1 and k_2 using Choice 4 (Fig. Figure 4.3). The symmetry of the cross-section corresponds to the value of the discrete component of the wavevector. (a) Mode from second branch at $k_1L_0/\pi = 1/6$ and $k_2P/\pi = 1/3$, similar to warping, (b) Mode from first branch at $L_0k_1/\pi = 1/3$ and $Pk_2/\pi = 2/3$, (c) Mode from first branch at $k_1L_0/\pi = 1/2$ and $Pk_2/\pi = 1$, (d) Mode from first branch at $L_0k_1/\pi = 2/3$ and $Pk_2/\pi = 4/3$, (e) Mode from first branch at $L_0k_1/\pi = 5/6$ and $Pk_2/\pi = 5/3$.

energy in real-space even in the limit of $\mathbf{k} \to \mathbf{0}$, thereby giving only two eigenvalue branches that tend to 0. The essential explanation for these observations is that long-wavelength is now defined with respect to objective space and not real space, whereas rigid-body modes are posed in real space for physical reasons.

We first outline this issue using as an example the choices of unit cell from Section 4.4. In Choice 1, four branches start from the origin, Fig. Figure 4.1a. These correspond to (i) axial stretch/translation with uniform motion along e, (ii)



Figure 4.6: An assortment of phonon modes at finite wavevectors. First figure is the reference state. The colors of the atoms have no significance and are only to enable easy visualization.



Figure 4.7: Density of states of a (6, 6) nanotube.

twist/rotation with uniformly tangential motion, and (iii) bending/translation in the plane normal to e. The bending mode is characterized by two degenerate branches with zero slope. The degeneracy is due the subspace of translations in the plane being two-dimensional [ADE13].

In Choice 2, Fig. Figure 4.1b, only two branches start from the origin. One corresponds to axial stretch / elongation, and the other one corresponds to twist / rotation. There is a branch that has zero frequency at $kL_0/\pi = 1/3$. This corresponds to the rigid translation modes in the plane normal to e, as we examine below.

Choice 3, Fig. Figure 4.2, is very similar to Choice 3, except that the branch with zero frequency at finite wavevector now goes to zero at $kL_0/\pi = 1/6$. We recall that that L_0 differs in Choices 2 and 3 precisely by a factor of 2, therefore this shift is simply because of unfolding the band diagram.

Choice 4, Fig. Figure 4.3, shows the rigid translation modes at $k_2P/\pi = 1/3$. In addition, for $k_2P/\pi = 0$, we see only two branches that go to 0 as the wavevector tends to zero; the lowest non-zero branch corresponds to uniform radial motion of the atoms. Because every unit cell has precisely the same deformation (in Objective space), this appears at $\mathbf{k} \to \mathbf{0}$. In addition, because the atoms within the unit cell do not move relative to each other, this corresponds to the acoustic modes that are zero energy at zero wavevector in crystals. The three higher branches at zero wavevector have the atoms in the unit cell moving with respect to each other, i.e. optic modes, and these are expected to have finite energy at zero wavevector.

4.5.1 Long Wavelength Modes in Objective Space

A long wavelength mode in Objective Space corresponds to $\mathbf{k} \to \mathbf{0}$. However, uniform deformations or their limiting rigid body translation / rotation modes, do not have as close a correspondence with long wavelengths as in crystal, because of the



Figure 4.8: A long-wavelength mode that corresponds to rigid rotation and therefore zero energy: (a) A schematic projection, viewed along the axis, of atomic positions and displacements in real space. All displacements are tangential. (b) In Objective space, all atoms displace uniformly, i.e., long wavelength.

intermediate transformation to Objective space. Consider a deformation induced by a normal mode, with the displacement in real space of atom (i, j) denoted by $u_{(i,j)}$. Denote the corresponding displacement in Objective space by $v_{(i,j)}$. For a normal mode with wavevector k_0 , if we set that the displacements in Objective space of corresponding atoms in every unit cell are the same, i.e. $\hat{v}_{(p,m)} = \hat{v}_{(q,m)}$ for every (p,m) and (q,m), then the DFT from Appendix A gives:

$$\tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} \exp\left[-i\boldsymbol{k}_{\boldsymbol{j}} \cdot \boldsymbol{y}_{\boldsymbol{p}}\right] = \tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} \exp\left[-i\boldsymbol{k}_{\boldsymbol{j}} \cdot \boldsymbol{y}_{\boldsymbol{q}}\right]$$
$$\Rightarrow \tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} = \exp\left[i\boldsymbol{k}_{\boldsymbol{j}} \cdot (\boldsymbol{y}_{\boldsymbol{p}} - \boldsymbol{y}_{\boldsymbol{q}})\right] \tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} \Rightarrow \boldsymbol{k}_{0} = \boldsymbol{0}$$
(4.17)

We consider two illustrative modes. Fig. Figure 4.8 shows schematically the position and displacements movement of atoms in real and Objective space for a rigid rotation mode. Assume that all atoms within the unit cell translate uniformly, i.e., this is an acoustic-like mode. It is long-wavelength in Objective space, and rigid body rotation in real space with zero energy in the limit.

Fig. Figure 4.9 shows schematically the position and displacements movement of atoms in real and Objective space for a uniform expansion mode. Assume that all atoms within the unit cell translate uniformly, i.e., this is an acoustic-like mode. In Objective space, this is long wavelength, but in real space this deformation costs finite



Figure 4.9: A long-wavelength mode that corresponds to uniform expansion rotation and therefore finite energy: (a) A schematic projection, viewed along the axis, of atomic positions and displacements in real space. All displacements are radial. (b) In Objective space, all atoms displace uniformly, i.e., long wavelength.

energy (proportional to the square of the amplitude) even in the long-wavelength limit.

4.5.2 Uniform Deformations and Rigid Body Translation in Real Space

We now consider setting up a uniform deformation, or rather the rigid body limiting translation, in real space and then analyze the wavevector at which it appears.

As above, denote the real-space displacement of atom (\boldsymbol{p}, m) by $\boldsymbol{u}_{(\boldsymbol{p},m)}$ induced by a normal mode, and denote the corresponding displacement in Objective space by $\boldsymbol{v}_{(\boldsymbol{p},m)}$. Consider a rigid body translation mode in real space, i.e., for any two atoms (\boldsymbol{p}, m) and (\boldsymbol{q}, n) , we have $\hat{\boldsymbol{u}}_{(\boldsymbol{p},m)} = \hat{\boldsymbol{u}}_{(\boldsymbol{q},n)}$. We now find the wave vector \boldsymbol{k}_{j} that corresponds to this deformation. Using (4.16):

$$\boldsymbol{Q}_{\boldsymbol{p}} \tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} \exp\left[-i\boldsymbol{k}_{\boldsymbol{j}} \cdot \boldsymbol{y}_{\boldsymbol{p}}\right] = \boldsymbol{Q}_{\boldsymbol{q}} \tilde{\boldsymbol{v}}_{(\boldsymbol{j},n)} \exp\left[-i\boldsymbol{k}_{\boldsymbol{j}} \cdot \boldsymbol{y}_{\boldsymbol{q}}\right] \Rightarrow$$
$$\boldsymbol{Q}_{\boldsymbol{p}-\boldsymbol{q}} \tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} = \exp\left[i\boldsymbol{k}_{\boldsymbol{j}} \cdot (\boldsymbol{y}_{\boldsymbol{p}} - \boldsymbol{y}_{\boldsymbol{q}})\right] \tilde{\boldsymbol{v}}_{(\boldsymbol{j},n)} \tag{4.18}$$

If $\boldsymbol{p} = \boldsymbol{q}$, then $\boldsymbol{Q}_{\boldsymbol{0}} = \boldsymbol{I}$ implying that $\tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} = \tilde{\boldsymbol{v}}_{(\boldsymbol{j},n)}$.

Now assume $r := p - q \neq 0$, implying $y_r = y_p - y_q$, giving the complex eigenvalue

problem:

$$\boldsymbol{Q}_{\boldsymbol{r}}\tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)} = \exp\left[i\boldsymbol{k}_{\boldsymbol{j}}\cdot\boldsymbol{y}_{\boldsymbol{r}}\right]\tilde{\boldsymbol{v}}_{(\boldsymbol{j},m)}$$
(4.19)

Recall that in nanotubes (section 2.2), the orthogonal part of the generators are coaxial and the axis further coincides with the nanotube axis e. Therefore,

$$\boldsymbol{Q}_{\boldsymbol{r}\equiv(r_1,r_2)} = \boldsymbol{R}_{\theta_1}^{r_1} \boldsymbol{R}_{\theta_2}^{r_2} = \boldsymbol{R}_{r_1\theta_1 + r_2\theta_2}$$
(4.20)

The eigenvalues of Q_r are therefore 1 and $e^{\pm i(r_1\theta_1+r_2\theta_2)}$, where θ_1 and θ_2 are the group parameters for the nanotube (section 2.2).

There are therefore three modes corresponding to rigid body translation:

- $\lambda_1 = e^{i\mathbf{k}_j \cdot \mathbf{y}_r} = 1$. Since this holds for all \mathbf{y}_r , the wavevector \mathbf{k}_j is zero. The eigenvector $\tilde{\mathbf{v}}_{(j,m)}$ will coincide with \mathbf{e} , and from (4.16) it follows that all the atoms will move axially. This mode is rigid translation in the axial direction.
- $\lambda_2 = e^{i \mathbf{k}_j \cdot \mathbf{y_r}} = e^{i(r_1 \theta_1 + r_2 \theta_2)}$. From (A.1,A.2), we have that $\frac{2\pi}{N_1} r_1 j_1 + \frac{2\pi}{N_2} r_2 j_2 = r_1 \theta_1 + r_2 \theta_2$ for all r_1 and r_2 . Therefore, $\frac{2\pi j_1}{N_1} = \theta_1$ and $\frac{2\pi j_2}{N_2} = \theta_2$. That is, the wavevector at which this rigid body translation occurs is $k_1 = \theta_1, k_2 = \theta_2$. The eigenvector $\tilde{\mathbf{v}}_{(j,m)}$ is orthogonal to the first eigenvector \mathbf{e} . In addition, using $\mathbf{Q}_r \tilde{\mathbf{v}}_{(j,m)} = e^{i\theta} \tilde{\mathbf{v}}_{(j,m)}$ into (4.16), we find that the nanotube will rigidly translate in the plane with normal \mathbf{e} .
- λ₃ = e^{ik_j·y_r} = e^{-i(r₁θ₁+r₂θ₂)}. As with λ₂, the wavevector at which this rigid body translation occurs is k₁ = −θ₁, k₂ = −θ₂. Since the wavevector is meaningful only up to sign, this is essentially the same. The eigenvector is also orthogonal to e and can be chosen normal to the second eigenvector.

The latter two modes above can alternately be considered as the limiting behavior of rigid rotations around axes that are perpendicular to e.



Figure 4.10: A rigid body translation with zero energy that corresponds to finitewavelength: (a) A schematic projection, viewed along the axis, of atomic positions and displacements in real space. (b) In Objective space, it is not long wavelength.

The phonon frequency of all of these modes is zero because rigid motions in realspace do not cost energy. Fig. Figure 4.10 demonstrates a schematic of a rigid body translation in real space that has finite wavelength in Objective space. Heuristically, the Objective transformation goes to a space that "unwraps" the structure.

4.6 Phonons and Stability

Phonon analysis provides important insights into the stability of crystals through identifying *soft modes*, i.e., non-rigid deformations that cost no energy [Dov93]. In addition, the phonon framework provides important insights and enables systematic identification of the appropriate larger unit cells at instabilities [ETS06, EST06]. As discussed in [ETS06], phonon analysis does *not* provide information about stability with respect to certain deformation modes; in particular, phonon stability does not test against *non-rank-one modes*. The analogy in linear continuum elasticity is that strong ellipticity tests only that waves speeds are real in all directions and all polarizations. In terms of the stiffness tensor, this does not test positive-definiteness of the stiffness against all tensors in the 6-dimensional strain space; rather it tests only against the subspace of strains that are symmetrized rank-one tensors. While phonons do test if solids are stable to uniform uniaxial extensions in every direction, they do not test if they are stable to superpositions of these, such as biaxial and triaxial stretch. Because the Fourier transform does not exist for the limit deformation, superposing modes and taking the limit is not equivalent to taking the limit and then superposing.

We also note that phonons test only the material stability but not against structural instabilities such as buckling [GMT93]. Structural instabilities are typically very sensitive to boundary conditions, e.g. the elementary Euler buckling loads. Testing the linear stability of an atomic structure against structural modes requires, in general, the brute-force solution of the full eigenproblem with a very large number of degrees of freedom.

In this section, we discuss two findings relevant to the role of phonons and stability. First, we discuss why there do not exist the analog of non-rank one modes in carbon nanotubes. That is, assuming that all phonon branches are positive, and in addition those branches that tend to 0 at long wavelength have positive slope (in the case of twisting and axial extension) or have positive second derivative (in the case of bending), then the nanotube is stable under any combination of these. In other words, a positive torsional modulus, extensional modulus, and bending modulus, do imply, unlike crystals, that they are stable under any combination of torsion-extension-bending. The second finding that we discuss is a numerical study of torsional buckling using two unit cells, one with 456 atoms and another with 24 atoms. As the former choice has much more freedom in deforming, we see torsional instabilities. With the latter choice, we find a signature of this instability in terms of zero phonon frequencies; in addition the eigenmode corresponding to the zero frequency predicts the nature of the instability. This also displays an important calculation that is enabled by the OS framework: torsion is simply not possible with periodic boundary conditions.

4.6.1 Stability Under a Combination of Long-wavelength Modes

The fact that there do not exist analogs of non-rank one modes in carbon nanotubes is made clear by the use of the OS framework. The OS description shows that nanotubes are one-dimensional in an essential way, in particular, the wavevector has only one continuous component. This enables a simple calculation to show that any superposition of twisting, extension and bending must be stable, if they are each individually stable.

First, we make a note about bending of nanotubes. As shown in [DEJ], a nanotube that bends does not remain an OS if the the group description has no generators that are translations. The difficulty with this situation is that atomic environments are no longer related, and in particular a theorem by James [Jam06] that equilibrium of single unit cell implies equilibrium of the OS is not valid. Therefore, in such a group description, it is not possible to define a bending modulus since this requires microscopic equilibrium to be meaningful. Alternately, any nanotube, even if chiral, can be described by a translational unit cell, though this cell may be very large. In this description that includes a translational generator, bending is well-defined. Essentially, it corresponds to the non-identical environments of atoms being replaced by a large unit cell in which atoms relax in possibly non-uniform ways. However, an important feature of this OS description is that bending now occurs at $\mathbf{k} \to \mathbf{0}$. The net result is that either the bending modulus cannot be defined, or if it can be defined then bending occurs at $\mathbf{k} \to \mathbf{0}$. This is important for our calculation below.

In a 2D Bravais lattice, phonon stability tests deformations of the form

$$\lim_{k_1 \to 0, k_2 = const.} \boldsymbol{A}_1(\boldsymbol{k}) e^{ik_1 x_1}, \text{ and } \lim_{k_2 \to 0, k_1 = const.} \boldsymbol{A}_2(\boldsymbol{k}) e^{ik_2 x_2}$$

Here A_1 and A_2 are arbitrary vectors; because of linearity, we can decompose them to correspond to polarizations of the appropriate normal modes that propagate in the same direction. Therefore, e.g., we are assured of the stability of any superposition of homogeneous shear and extension *only* when they are the limit of phonons that propagate in the same direction, if the component phonons are themselves stable. However, phonon stability cannot say anything about modes that involve deformations that are superpositions of phonons that propagate in different directions, i.e., a deformation of the form

$$\lim_{k_1\to 0,k_2\to 0,k_1/k_2=const.} \boldsymbol{A}_1(\boldsymbol{k})e^{ik_1x_1} + \boldsymbol{A}_2(\boldsymbol{k})e^{ik_2x_2}$$

For example, uniaxial stretch in each coordinate direction can be tested by the individual limits, while biaxial deformation requires the composite limit that cannot be achieved by superposing the individual limits.

In nanotubes, we only have a single continuous component of the wavevector. Therefore, all limits are with respect to only that component. If deformations of the form $\lim_{k\to 0} \mathbf{A}_j(k)e^{iky}$ are stable, where \mathbf{A}_j corresponds to axial stretch, twist, or bending, then it follows that deformations of the form $\lim_{k\to 0} \sum_j \mathbf{A}_j(k)e^{iky}$ are also stable simply by superposition. Physically, if we have positive bending stiffness, positive torsional stiffness, and positive extensional stiffness, the nanotube is stable to any combination of bending, torsion, and elongation.

4.6.2 Torsional Instabilities of Nanotubes

Soft-mode techniques to detect instabilities at the crystal-level have a long history in mechanics, as far back as [HM77]. Recently, they have been combined with bifurcation techniques to understand structural transformations in shape-memory alloys [ETS06]. They have also proved useful in understanding defect nucleation and propagation at the atomic scale, e.g. [MR08, LD11, DB06].

We numerically study the torsional instability of a (6, 6) carbon nanotube using both phonons and (zero temperature) atomistics. Phonons in principle test the stability of a large system efficiently, while atomistics requires us to use large unit cells if we are to capture complex instabilities. We find that phonon stability provides an accurate indicator of the onset of the instability as well as the initial post-instability deformation.

We use two different unit cells, one with 24 atoms and the other with 456 atoms. The smaller unit cell requires OS group generators given by $g_1 = (\mathbf{R}_{2\pi/3}|\mathbf{0})$ and $g_2 = (\mathbf{R}_{\pi}|0.75 \text{nm } \mathbf{e})$ and is shown in Fig. Figure 4.12. The larger unit cell requires a single translational generator, $g_1 = (\mathbf{I}|4.8 \text{nm } \mathbf{e})$.

For both choices, we apply a small increment of twisting moment, equilibrate, and repeat the process. For the smaller unit cell, we additionally test the phonon stability by computing the phonon frequencies at each load step. The twisting moment vs. twist angle and lowest eigenvalue vs. twist angle are plotted in Fig. Figure 4.11. In the atomistic simulations, the larger unit cell buckles at much lower twist angle (about $5^{\circ}/nm$) compared to $12^{\circ}/nm$ for the smaller unit cell. However, the phonon analysis of the smaller unit cell indicates that an eigenvalue becomes negative at about $5^{\circ}/nm$. This is consistent with the onset of buckling for the larger unit cell. Additionally, the eigenmode corresponding to the negative eigenvalue matches with buckling mode of the long tube computed directly from atomistics. The atomic deformation corresponding to the eigenmode is plotted in Fig. Figure 4.12, along with phonon spectra before and at the point of instability.

This calculation also provides a method to test for one possible route to failure for the OS analog of the Cauchy-Born rule. Specifically, loss of phonon stability is an indicator that the unit cell must be enlarged, i.e. affinely applied far-field boundary conditions do *not* give affine deformations of each unit cell [FT02].



Figure 4.11: Left: Twisting moment vs. twist angle using atomistics. Right: Lowest eigenvalue vs. twist angle for the smaller unit cell.



Figure 4.12: Phonon stability analysis. Top left: ten lowest modes for the untwisted nanotube. Top right: ten lowest modes just after the lowest eigenvalues becomes negative. The value of the discrete wavevector is $2/3\pi$. The twist angle at this state is about 5°/nm. The mode going to 0 in both plots corresponds to long-wavelength bending. Bottom: the eigenmode corresponding to the zero eigenvalue. This shows the deformation predicted by phonon analysis to have zero energy. Light blue atoms denote a single unit cell. The colors are only to aid visualization.

4.7 Energy Transport in Helical Objective Structures

Motivated by the features of the computed phonon curves in nanotubes, in this section we present a simplified geometric model that aims to capture the key physics of energy transport. The model is based on a balance between energy transport along a helical path and energy transport along an axial path. In an "unwrapped" helix, the former corresponds to transport through short-range interactions, i.e. the interactions are between neighbors that are nearby in terms of the labeling index, and the latter corresponds to long-range interactions, i.e. the interactions are between distant atoms in terms of the labeling index. Of course, in physical space, both these types of neighbors are at comparable distances, and interactions are therefore of comparable strength.

We begin by examining the phonon curves of nanotubes (m, n) where m and n are relatively prime. As noted in section 2.2, this implies that a single screw generator is sufficient to describe the nanotube with 2 atoms per unit cell. Figs. Figure 4.13 and Figure 4.14a show the dispersion curves of unloaded (11,9) and (7,6) nanotubes respectively. The rotation angles of the screw generator are $\theta_1 = \frac{271\pi}{301} \approx 0.9003\pi$ and $\theta_1 = \frac{39\pi}{127} \approx 0.307\pi$, respectively. As discussed in previous sections, two branches corresponding to torsion and axial elongation start from the origin, and one branch touches the k axis at precisely θ_1 . We mention that if we had used the periodic description for these nanotubes, we would require at least 1204 and 508 atoms in the unit cell for the (11,9) and (7,6) nanotubes respectively. Besides the significantly larger computational expense, it would imply that Figs. Figure 4.13 and Figure 4.14a contain 3612 and 1524 curves respectively! Physical interpretation would be impossible.

The key features of interest here are the "wiggles" in the phonon curves in Figs. Figure 4.13 and Figure 4.14a. There exist certain distinguished wavevectors at which



Figure 4.13: Dispersion curves of a (11, 9) carbon nanotube. FD contains 2 atoms.

the group velocity (i.e. slope of the dispersion curve) becomes zero in all branches. These wavevectors are primarily selected by geometry: Fig. Figure 4.14 compares the curves for a (7, 6) nanotube both with no load as well as with compressive axial force and nonzero twisting moment. In addition, the phonon curves depend on the specific interatomic potential, but we have found that the distinguished wavevectors have a very weak dependence. Similar wiggles, though not as prominent are also visible in Fig. Figure 4.3 for a (6, 6) nanotube. Since the group velocity gives the speed of energy transport, there is no energy transport at these distinguished wavevectors. These observations motivate a geometric model for the energy transport that neglects much of the complexity of the interatomic potential.



Figure 4.14: Dispersion curves of a (7,6) carbon nanotube. FD contains 2 atoms. (a) relaxed nanotube (b) compressed and twisted nanotube.

4.7.1 A Simplified One-Dimensional Nonlocal Model for Helical Objective Structures

The key idea is that when a helix is plotted in a space that uses the path length along the helix as the coordinate, there are short-range interactions that are due to neighbors along the helix in real space, and there are long-range interactions due to interactions between neighbors that lie above on the next loop in real space. Fig. Figure 4.15 shows a schematic of this geometric picture using a specific example. The goal is to write down the expression for energy transfer to the atoms with positive labels from the atoms with non-positive labels. Roughly, we want the energy flux crossing the surface represented by the dashed line. In real space, the roughly equal-strength bonds that cross the dividing surface are between atom pairs (0, 1), (0, 6), (-1, 5), (-2, 4), (-3, 3), (-4, 2), (-5, 1). In objective space, only the first of these bonds is "local" while the others are all "non-local".

The picture above for a generic nanotube with 2 generators is not essentially different. The Objective space picture is a set of parallel atomic chains, with infinite length in the direction corresponding to the powers of the screw generator, but a finite number of parallel chains with the number of of chains corresponding to the powers of the rotation generator. This can be considered as simply a single linear chain with an expanded unit cell.

For an OS Ω , we write down the total energy flux ψ from a subbody Ω^+ to $\Omega^- := \Omega \setminus \Omega^+$ over a time interval T:

$$\psi = \int_{t}^{t+T} \sum_{(\boldsymbol{p},m)\in\Omega^{+}} \sum_{(\boldsymbol{q},n)\in\Omega^{-}} \dot{\boldsymbol{u}}_{(\boldsymbol{p},m)} \cdot \boldsymbol{f}_{(\boldsymbol{p},m)(\boldsymbol{q},n)} dt$$
(4.21)

The superposed $\dot{\Box}$ represents the time derivative. The term $f_{(p,m)(q,n)}$ is the force between the atoms (p,m) and (q,n); while this is not always a uniquely-defined quantity in multibody potentials, in a linearized system this is simply $f_{(p,m)(q,n)} :=$



Figure 4.15: A schematic of the of the geometric model for energy transport (a) In real space (b) In Objective space. The energy flow to be analyzed takes place across the bold dashed line, i.e., how much energy do subunits $0, -1, -2, \ldots$ transfer to the subunits $1, 2, 3, \ldots$. The subunits can correspond to individual atoms or sets of atoms.

$\boldsymbol{H}_{(\boldsymbol{p},m)(\boldsymbol{q},n)}\left(\boldsymbol{u}_{(\boldsymbol{p},m)}-\boldsymbol{u}_{(\boldsymbol{q},n)} ight).$

We now compute the energy flux for a single phonon mode $u_{(p,m)} = Q_p \hat{u}_m \cos(\mathbf{k} \cdot \mathbf{y}_p - \omega t + \vartheta)$ where ϑ is a phase that eventually gets integrated out and disappears. We set the averaging interval to a single cycle, i.e., $T = 2\pi/\omega$. The energy flux is therefore

$$\psi = \omega \int_{t}^{t+T} \sum_{(\boldsymbol{p},m)\in\Omega^{+}} \sum_{(\boldsymbol{q},n)\in\Omega^{-}} \left[\boldsymbol{Q}_{\boldsymbol{p}} \hat{\boldsymbol{u}}_{m} \sin(\boldsymbol{k}\cdot\boldsymbol{y}_{\boldsymbol{p}} - \omega t + \vartheta) \cdot \boldsymbol{H}_{(\boldsymbol{p},m)(\boldsymbol{q},n)} \cdot \left(\boldsymbol{Q}_{\boldsymbol{p}} \hat{\boldsymbol{u}}_{m} \cos(\boldsymbol{k}\cdot\boldsymbol{y}_{\boldsymbol{p}} - \omega t + \vartheta) - \boldsymbol{Q}_{\boldsymbol{q}} \hat{\boldsymbol{u}}_{n} \cos(\boldsymbol{k}\cdot\boldsymbol{y}_{\boldsymbol{q}} - \omega t + \vartheta) \right) \right] dt \qquad (4.22)$$

Using (2.13), we have that

$$\psi = \frac{\omega}{2} \int_{t}^{t+T} \sum_{(\boldsymbol{p},m)\in\Omega^{+}} \sum_{(\boldsymbol{q},n)\in\Omega^{-}} \hat{\boldsymbol{u}}_{m} \cdot \boldsymbol{H}_{(\boldsymbol{0},m)(\boldsymbol{q}-\boldsymbol{p},n)} \hat{\boldsymbol{u}}_{m} \sin\left(2\boldsymbol{k}\cdot\boldsymbol{y}_{\boldsymbol{p}}-2\omega t+2\vartheta\right) dt$$
$$-\frac{\omega}{2} \int_{t}^{t+T} \sum_{(\boldsymbol{p},m)\in\Omega^{+}} \sum_{(\boldsymbol{q},n)\in\Omega^{-}} \hat{\boldsymbol{u}}_{m} \cdot \boldsymbol{H}_{(\boldsymbol{0},m)(\boldsymbol{q}-\boldsymbol{p},n)} \boldsymbol{Q}_{\boldsymbol{q}-\boldsymbol{p}} \hat{\boldsymbol{u}}_{n}$$
$$\times \left[\sin\left(\boldsymbol{k}\cdot(\boldsymbol{y}_{\boldsymbol{p}}+\boldsymbol{y}_{\boldsymbol{q}})-2\omega t+2\vartheta\right)-\sin\left(\boldsymbol{k}\cdot(\boldsymbol{y}_{\boldsymbol{p}}-\boldsymbol{y}_{\boldsymbol{q}})\right)\right] dt$$
(4.23)

Since the integrals are over a complete period $T = 2\pi/\omega$, all terms of the form $\sin(\ldots - 2\omega t \ldots)$ vanish. Using (4.10), this simplifies to:

$$\psi = \pi \sum_{(\boldsymbol{p},m)\in\Omega^+} \hat{\boldsymbol{u}}_m \cdot \sum_{(\boldsymbol{q},n)\in\Omega^-} \hat{\boldsymbol{D}}_{(\boldsymbol{0},m)(\boldsymbol{q}-\boldsymbol{p},n)} \sin\left(\boldsymbol{k}\cdot(\boldsymbol{y}_{\boldsymbol{p}}-\boldsymbol{y}_{\boldsymbol{q}})\right) \hat{\boldsymbol{u}}_n$$
(4.24)

Now consider a nanotube with two generators, i.e. a pure rotation generator with rotation angle $\theta_2 = 2\pi/N_2$, and a screw generator with the rotation component associated to an angle $-\pi < \theta_1 \leq \pi$. Consider the flow of energy across a surface that divides the OS into $\Omega^- = \{ \boldsymbol{q} : q_1 \leq 0 \}$ and $\Omega^+ = \{ \boldsymbol{q} : q_1 > 0 \}$, where the first slot in the multi-index corresponds to the screw and the second slot corresponds to the rotation. Then we can write:

$$\psi = -\pi \sum_{m,n} \hat{\boldsymbol{u}}_m \cdot \left[\sum_{q_2=0}^{N_2-1} \sum_{q_1 \ge 1} q_1 \hat{\boldsymbol{D}}_{(\boldsymbol{0},m)(\boldsymbol{q},n)} \sin(k_1 q_1 + k_2 q_2) \right] \hat{\boldsymbol{u}}_n$$
(4.25)

Note that the factor of q_1 appears in the sum because, in an OS, various atomic bonds are symmetry-related and therefore the sum need not run over these bonds.

The component k_2 of the wave vector corresponds to the pure rotation generator. Therefore, it takes only the discrete values $k_2 = 2\pi j/N_2, j = 0, \dots, N_2 - 1$.

At this point, the model is nominally exact. Our interest however is in a minimal model that captures the important features. In terms of energy transport, the wiggles in the phonon spectrum are of primary interest. We now make extremely harsh simplifying approximations on the nature of interactions, but retain the feature that interactions are non-local in Objective space. We see that this single feature is sufficient to understand the wiggles. We assume that (i) interactions are only nearest neighbor in real-space, and (ii) the magnitude of the interactions is the same for all near-neighbors. Under these assumptions, we search for the values of the wavevector at which $\psi = 0$.

Consider a (6, 6) nanotube ($N_2 = 6$ in this case). The bonds that connect Ω^+ and Ω^- under the assumptions above are (0, j)-(1, j) and $(0, j)-(1, (j + 5) \mod 6)$ for $j = 0 \dots 5$. These are all near-neighbors both in real and Objective space. Equation (4.25) specializes to:

$$6\left(\sin(k_1) + \sin(5k_2 + k_1)\right) = 0 \Rightarrow 2\sin(k_1 + 2.5k_2)\cos(2.5k_2) = 0 \tag{4.26}$$

Hence, for $k_2 = 2\pi j/6$, j = 0, ..., 5, the solution is $k_1 = \pi \left(r - \frac{5j}{6}\right)$, $r \in \mathbb{Z}$. These values match exactly with with the zero-slope points in Fig. Figure 4.3. In addition, there are no wiggles because all interactions are local in Objective space.

Now consider a (7, 6) nanotube. Here $N_2 = 1$ so there is only a single index. The nearest neighbors of the 0 unit cell are 6, 7, 13 and all of these are non-local in Objective space. Equation (4.25) specializes to:

$$6\sin(6k_1) + 7\sin(7k_1) + 13\sin(13k_1) = 0 \tag{4.27}$$

Numerically solving this gives the wave vectors $\pi \times \{0.000, 0.102, 0.154, 0.206, 0.307, 0.404, 0.463, 0.520, 0.614, 0.703, 0.771, 0.839, 0.921, 1.000\}$. This matches extremely well with Fig. Figure 4.14, with relative error of the order 10^{-7} .

We next consider a (11, 9), also with $N_2 = 1$. The nearest neighbors of the 0 unit cell are 9, 11, 20 and all of these are non-local in Objective space. Therefore,

$$9\sin(9k_1) + 11\sin(11k_1) + 20\sin(20k_1) = 0 \tag{4.28}$$



Figure 4.16: Energy transport in helices with different aspect ratios using model interatomic potentials. The red atoms are the near-neighbors of the blue atom in real-space. In the slender helix, there is no long-range interaction and it behaves like a 1D chain. The stubby helix has long-range interaction and has prominent wiggles in the phonon spectrum.

Numerically solving for the wavevectors of the wiggles, we find $\pi \times \{0.0, 0.066, 0.101, 0.134, 0.199, 0.260, 0.301, 0.342, 0.398, 0.452, 0.501, 0.552, 0.598, 0.643, 0.70, 0.762, 0.798, 0.836, 0.900, 0.967, 1.0\}$. This again matches extremely well with the full calculation in Fig. Figure 4.13, with relative error on the order of 10^{-8} .

Finally, we compute the phonon spectra for two nanotubes with different aspect ratios using model interatomic potentials, Fig. Figure 4.16. For the stubby helix, we find prominent wiggles as expected from our model that nonlocal interactions are important. For the slender helix, it behaves almost like a near-neighbor chain with no long-range interactions as we expect.

4.8 Anomalous phonon behavior of nanotubes: First-order influence of external load

4.8.1 Literature review

The low-dimensionality of nanotubes causes unusual features in the phonon curves due to geometric effects. In this section, we examine particularly the transverse acoustic (TA) phonon mode and its slope and curvature (second derivative) in the long wavelength limit.

Previous works have reported four acoustic modes of vibration for SWNT. There is consensus that two of the modes (longitudinal and twisting modes) have linear dispersion in the long wavelength limit. However, there has been discussion about the form of the other two TA modes which are doubly degenerate. E.g., several papers [YKV95b, STK⁺98, DE00, HBB⁺00, Hon01, MRT⁺02, SPH02, CYX⁺03, DMN⁺03] report linear dispersion for the TA modes. These authors do not analytically show that the TA modes should be linear, but argue that nanotubes do not have modes analogous to the out-of-plane "bending" mode of graphene, and thus, nanotubes must have linear long wavelength acoustic dispersion behavior. Among these works, two recent papers [SPH02, DMN⁺03] state that quadratic dependence is found in some other papers, but argue that this may be attributed to numerical errors.

In contrast, more recent papers [SPAS⁺99, Pop02, YLWH04, Gar04, PL06a, PL06b, ZPC08, TWS11] report a quadratic dependence of frequency on the wave number. The results presented in these papers are obtained by applying lattice dynamics methods to either tight-binding, ab-initio or empirical potential models. In still other papers [PDB00, Mah02, SA02, MJ04] analytical methods are used to argue that the TA mode should be quadratic. In particular, the papers[PDB00, Mah02, SA02] make an analogy between the phonon dispersion relation and the bending energy or sound velocity in a continuous thin tube. The paper [MJ04] develops a spring model and performs lengthy calculations for zig-zag and armchair nanotubes². Among these papers, the works[Pop02, Gar04, ZPC08, SA02, Mah02, PDB00] also mention that others have observed linear dependence of the TA dispersion relations.

² The conclusions of this study appear mixed. In the authors' words: "We have shown that flexure modes, those with $\omega \propto q^2$ at long wave length, exist in carbon nanotubes. We also find that the flexure modes cross over to linear dispersion at very small values of wave vector. We are unsure whether this cross over is a feature of our choice of spring constants, or is an actual feature of nanotubes."

However, these papers do not provide a reason for the discrepancy but rather only postulate that the use of unsuitable force constant parameters may lead to linear TA phonon dispersion.

In this part, we examine the question of the TA phonon dispersion through a combination of explicit calculations in model systems as well as numerical calculations.

4.8.2 Layered crystals and atomic sheet structures

Quadratic dependence on the wave vector for long wavelength TA phonons is well known in the context of layered crystals, such as graphite, and sheet structures, such as graphene. The first works in this area were by Komatsu[Kom51, Kom55] (1951) and Lifshitz[Lif52] (1952). Their work showed that the TA phonon mode, with wave vector parallel to the layers, is a "bending mode" and has quadratic dispersion. Other works concerned with bending modes in layered crystals include [Kom58, KW70, SA93, Zab01, SDO⁺11]. The dispersion relation results of these early investigations are summarized in the paper[KW70] as³

Transverse in-plane mode:
$$\omega_1^2 = \frac{C_{11} - C_{12}}{2\rho} \left(k_x^2 + k_y^2\right) + \frac{C_{44}}{\rho}k_z^2$$
 (4.29)

Longitudinal in-plane mode:
$$\omega_2^2 = \frac{C_{11}}{\rho} \left(k_x^2 + k_y^2 \right) + \frac{C_{44}}{\rho} k_z^2 \tag{4.30}$$

Out-of-plane (bending) mode:
$$\omega_3^2 = \frac{C_{44}}{\rho} \left(k_x^2 + k_y^2\right) + \frac{C_{33}}{\rho} k_z^2 + \Lambda^2 \left(k_x^2 + k_y^2\right)^2$$
(4.31)

Here, C_{11}, C_{12}, C_{33} and C_{44} are the elastic constants of the crystal, ρ is the density, k_x and k_y are the components of the wave vector parallel to the layer planes and k_z is the component of the wave vector perpendicular to the layers. The quantity

 $^{^{3}}$ Note, these equations correspond to the results of Lifshitz's work. Komatsu gives similar expressions except that he replaces the coefficients of the wave vector components by the squared sound velocities of graphite.
Λ characterizes the *bending rigidity* of layers and is determined mainly by intralayer forces. For layered crystals, the interlayer elastic constants C_{33} and C_{44} are usually negligible compared to Λ . This illustrates that the predominant contribution to the bending mode dispersion relation is due to the bending rigidity Λ .

It is important to note that Eqn. (4.31) holds for stress-free layers only. If the layer or sheet is subjected to non-zero in-plane stress then, according to Lifshitz, the dispersion of the bending mode is

$$\omega_3^2 = \frac{\sigma}{\rho} \left(k_x^2 + k_y^2 \right) \tag{4.32}$$

where σ is a measure of the stress in the layer. Thus, the TA bending mode dispersion relation of a stressed layer has a linear dependence on the long wavelength wave vector and has a slope proportional to the square-root of the stress. Making an analogy between layered crystals or sheets and nanotubes, one would then expect similar behavior of the TA phonon modes in nanotubes. In fact, this is exactly what we find in Section 4.8.4 from our numerical calculations.

4.8.3 Phonons in a Linear Atomic Chain

In this section, we examine a linear atomic chain as a model system that permits closed-form calculations. We show that the TA modes of a linear chain of atoms have linear dependence on the wave number when the chain is subjected to a nonzero axial force. Further, we show that the TA long wavelength phonon modes for a *force-free* chain correspond to bending, not shear.

Transverse acoustic phonon modes

For simplicity, we consider a linear chain of atoms which is free to deform in a twodimensional space. In the configuration of interest the position vector of atom j is $\mathbf{x}_j = x_j^{\alpha} \mathbf{e}_{\alpha} = aj\mathbf{e}_1$, where a is the lattice spacing of the chain, \mathbf{e}_1 is the axial direction of the chain, and $\alpha \in \{1, 2\}$. A standard argument leads to the eigenvalue equation for the phonon frequencies

$$\mathbf{D}_k \mathbf{v}_k = m \omega_k^2 \mathbf{v}_k \tag{4.33}$$

where m is the mass of each atom in the chain, k is the wave number (along the axial direction), ω_k is the phonon frequency, \mathbf{v}_k is the phonon polarization vector (eigenvector), and \mathbf{D}_k is the dynamical matrix given by

$$\mathbf{D}_k = \sum_j \mathbf{H}_{0j} \exp[-ikx_j^1] \tag{4.34}$$

Here, \mathbf{H}_{pq} is the Hessian of the chain's potential energy function $\phi = \phi(\{\mathbf{x}_j\})$. That is, $\mathbf{H}_{pq} = \partial^2 \phi / \partial \mathbf{x}_p \partial \mathbf{x}_q$. Due to the Euclidean invariance (objectivity) of the potential energy, we can—without loss of generality—take $\phi = \bar{\phi}(\{r_{pq}\})$ to be a function of the pair-distances $(r_{pq} \equiv ||\mathbf{x}_q - \mathbf{x}_p||)$ between atoms in the chain[TM11]. Then we find

$$\mathbf{H}_{0q} = \sum_{i \neq 0} \sum_{j \neq q} \frac{\partial^2 \bar{\phi}}{\partial r_{0i} \partial r_{qj}} \frac{\partial r_{0i}}{\partial \mathbf{x}_0} \frac{\partial r_{qj}}{\partial \mathbf{x}_q} + \sum_{i \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0i}} \frac{\partial^2 r_{0i}}{\partial \mathbf{x}_0 \partial \mathbf{x}_q} \\
= \sum_{i \neq 0} \sum_{j \neq q} \frac{\partial^2 \bar{\phi}}{\partial r_{0i} \partial r_{qj}} \frac{1}{r_{0i} r_{qj}} (\mathbf{x}_i - \mathbf{x}_0) \otimes (\mathbf{x}_j - \mathbf{x}_q) \\
+ \delta_{0q} \sum_{i \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0i}} \frac{1}{r_{0i}^3} \left[r_{0i}^2 \mathbf{I} - (\mathbf{x}_i - \mathbf{x}_0) \otimes (\mathbf{x}_i - \mathbf{x}_0) \right] \\
- (1 - \delta_{0q}) \frac{\partial \bar{\phi}}{\partial r_{0q}} \frac{1}{r_{0q}^3} \left[r_{0q}^2 \mathbf{I} - (\mathbf{x}_q - \mathbf{x}_0) \otimes (\mathbf{x}_q - \mathbf{x}_0) \right]$$
(4.35)

In the standard basis, this becomes

$$[H_{0q}]^{\alpha\beta} = \begin{bmatrix} \sum_{i\neq 0} \sum_{j\neq q} \frac{\partial^2 \bar{\phi}}{\partial r_{0i} \partial r_{qj}} \frac{i}{|i|} \frac{j-q}{|j-q|} & 0\\ 0 & \delta_{0q} \sum_{i\neq 0} \frac{\partial \bar{\phi}}{\partial r_{0i}} \frac{1}{|i|a} - (1-\delta_{0q}) \frac{\partial \bar{\phi}}{\partial r_{0q}} \frac{1}{|q|a} \end{bmatrix}$$
(4.36)

From this form of the Hessian, it is clear that the polarization vector for the TA phonon modes of the linear atomic chain is $\mathbf{v}_{TA} = [0, 1]^{T}$. Thus for this case, the TA

dispersion relation is found to be

$$\omega_{\mathrm{TA},k}^{2} = \frac{1}{m} \sum_{j} H_{0j}^{22} \exp\left[-ikja\right]$$

$$= \frac{1}{m} \sum_{j \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0j}} \frac{1}{|j|a} (1 - \exp\left[-ikja\right]).$$
(4.37)

Expanding the exponential in powers of (the small parameter) k and noting that $\partial \bar{\phi} / \partial r_{0j} = \partial \bar{\phi} / \partial r_{0-j}$, results in

$$\omega_{\mathrm{TA},k}^{2} = \left[\frac{1}{2m}\sum_{j\neq0}\frac{\partial\bar{\phi}}{\partial r_{0j}}|j|a\right]k^{2} + \left[\sum_{j\neq0}\frac{-1}{24m}\frac{\partial\bar{\phi}}{\partial r_{0j}}|j|^{3}a^{3}\right]k^{4} + \dots$$
(4.38)

Noting that $|j|a = r_{0j}$ and neglecting higher order terms we find

$$\omega_{\mathrm{TA},k}^{2} = \left[\frac{1}{2m}\sum_{j\neq0}\frac{\partial\bar{\phi}}{\partial r_{0j}}r_{0j}\right]k^{2} + \left[\frac{-1}{24m}\sum_{j\neq0}\frac{\partial\bar{\phi}}{\partial r_{0j}}r_{0j}^{3}\right]k^{4}$$
(4.39)

The virial axial force in a chain of atoms at zero temperature can be shown [AD11, AD12] to be $F = \frac{1}{2L} \sum_i \sum_j \frac{\partial \phi}{\partial r_{ij}} r_{ij} = \frac{1}{2a} \sum_j \frac{\partial \phi}{\partial r_{0j}} r_{0j}$. Thus, the linear part of the dispersion relation (ω versus k) is proportional to the square-root of the axial force in the chain. Next, we show that the second term in (4.39) is related to the bending stiffness of the chain.

Energy change corresponding to shear deformation

If γ is the shear parameter in the infinite chain, the displacement of the atoms is $u_j^1 = 0$ and $u_j^2 = \gamma x_j^1$. The separation between the atoms in the deformed chain will be

$$r_{jl} + \Delta r_{jl} = \left[r_{jl}^2 + (u_l^2 - u_j^2)^2 \right]^{1/2} = \left[r_{jl}^2 + \gamma^2 r_{jl}^2 \right]^{1/2} = r_{jl} \left[1 + \gamma^2 \right]^{1/2}$$
$$\approx r_{jl} \left[1 + \frac{\gamma^2}{2} + \frac{-\gamma^4}{4} + \cdots \right]$$
(4.40)

Therefore the change in distance between the atoms is $\Delta r_{jl} \approx \frac{\gamma^2}{2} r_{jl} = \frac{\gamma^2}{2} r_{0(j-l)}$. Expanding the potential energy density, $\tilde{\phi} = \bar{\phi}/2Na$, up to the first order in perturbation, gives an energy change of the form

$$\Delta \tilde{\phi} \approx \frac{1}{2Na} \sum_{j,l \neq j} \frac{\partial \bar{\phi}}{\partial r_{jl}} \Delta r_{jl} = \frac{\gamma^2}{4Na} \sum_{j,l \neq j} \frac{\partial \bar{\phi}}{\partial r_{0(l-j)}} r_{0(j-l)} = \frac{\gamma^2}{2a} \sum_{n \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0n}} r_{0n} = F \gamma^2 \quad (4.41)$$

where F is the virial axial force. As can be seen, the change in energy due to shear deformation is not related to the second term of (4.39).

Energy change corresponding to bending deformation

Now consider the chain subjected to bending. The atom with initial position $\mathbf{x}_j = ja\mathbf{e}_1$ will move to $\mathbf{y}_j = r[\sin(aj/r)\mathbf{e}_1 + \cos(aj/r)\mathbf{e}_2]$, where r is the radius of curvature. The arc length does not change during the bending. If $r_{jl} = (j-l)a$ is the separation between atoms j and l before the bending, after bending the separation will be

$$r_{jl} + \Delta r_{jl} = \left[(y_l^1 - y_j^1)^2 + (y_l^2 - y_j^2)^2 \right]^{1/2}$$

$$= \left[r^2 \left(\cos \frac{al}{r} - \cos \frac{aj}{r} \right)^2 + r^2 \left(\sin \frac{al}{r} - \sin \frac{aj}{r} \right)^2 \right]^{1/2}$$

$$= \sqrt{2}r \left[1 - \cos \frac{al}{r} \cos \frac{aj}{r} - \sin \frac{al}{r} \sin \frac{aj}{r} \right]^{1/2} = \sqrt{2}r \left[1 - \cos \frac{a(l-j)}{r} \right]^{1/2}$$

$$= 2r \sin \frac{r_{jl}}{2r}$$

$$\approx r_{jl} - \frac{r_{jl}^3}{24r^2}$$
(4.42)

This shows that

$$\Delta r_{jl} \approx -\frac{r_{jl}^3}{24r^2} \tag{4.43}$$

Expanding the potential energy density up to the first order in perturbation gives an energy change of the form

$$\Delta \tilde{\phi} = \frac{1}{2Na} \sum_{j,l \neq j} \frac{\partial \bar{\phi}}{\partial r_{jl}} \Delta r_{jl} = \frac{-1}{48Nr^2a} \sum_{j,l \neq j} \frac{\partial \bar{\phi}}{\partial r_{0(l-j)}} r_{0(j-l)}^3 = \frac{-1}{24r^2a} \sum_{n \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0n}} r_{0n}^3 \quad (4.44)$$

Hence, we find $\Delta \tilde{\phi} \approx \Lambda \frac{1}{r^2} = \Lambda \kappa^2$, where

$$\Lambda = \frac{-1}{24a} \sum_{n \neq 0} \frac{\partial \bar{\phi}}{\partial r_{0n}} r_{0n}^3 \tag{4.45}$$

is the bending stiffness and $\kappa = 1/r$ is the bending curvature. Thus, we have shown that the second term on the right hand side of (4.39) is related to the bending stiffness Λ . Consequently, the curvature of the force-free chain's TA dispersion relation is proportional to the square-root of its bending stiffness.

4.8.4 Numerical Calculations for Carbon Nanotubes

In this section, we use our symmetry-adapted phonon analysis method to numerically developed above to numerically demonstrate the connection between the TA dispersion relation and the axial force and bending stiffness of a SWNT. The distorted shape, i.e., the eigenmode, of the nanotube due to the transverse acoustic mode, near the long-wavelength limit of a (7, 6) nanotube is plotted in Fig. Figure 4.17. All calculations are performed using the Tersoff interatomic potential [Ter88].

Before we describe our results, we note that the paper [NAW97] shows, numerically, that bending modes with quadratic dispersion exist in quantum wires with rectangular cross section. The existence of only one continuous wave vector makes the wires similar to nanotubes. However, contrary to nanotubes, because of the rectangular cross section, the bending modes are no longer degenerate in wires. Our systematic symmetry-adapted phonon analysis method is able to deal with the de-



Figure 4.17: The distorted shape, i.e., the eigenmode, of the nanotube due to the transverse acoustic mode, near the long-wavelength limit of a (7, 6) nanotube.

generate behavior that occurs in nanotubes and clearly illustrates the quadratic dispersion of the TA phonon modes for a force-free tube.

First, we investigate the effect of axial relaxation on the density of states (DOS) and the form of the dispersion relation for the bending modes. Then we numerically show that the slope and curvature of the TA modes correspond to the axial force and bending rigidity, respectively.

Following the procedures outlined in this chapter, the dispersion curves and DOS for a relaxed (force-free) (7,6) SWNT are plotted in Fig. Figure 4.18. Adding axial force leads to one significant change of the dispersion curves and DOS. That is, the dispersion of low frequency TA modes changes from quadratic to linear in the long wavelength limit (as $k \rightarrow \theta$), where $\theta = 0.307\pi$ is the rotation angle of the (7,6) nanotube screw generator. A consequence of the low frequency dispersion curve near $k = \theta$ is that the DOS is singular near $\omega = 0$ for the force-free tube, while conversely, it is almost constant for tubes with non-zero force. This effect is illustrated in Fig. Figure 4.19, by plotting the long wavelength TA phonon dispersion relation near $k = \theta$ for tubes subjected to four different values of axial stress. Here, we define the axial stress as the axial force divided by the force-free circumference of the tube.



Figure 4.18: (Left) Dispersion curves and (right) DOS of zero-force axially relaxed (7,6) SWNT



Figure 4.19: The effect of axial stress on (left) the dispersion relation of the TA phonon modes and (right) the DOS of a (7,6) SWNT

The figure shows clear evidence that the long wavelength TA phonon dispersion behavior is related to the axial stress in the SWNT.

To show more conclusively that the slope and curvature of the long wavelength TA modes have the specific dependence postulated in this section, we compute (1) the bending modulus of SWNTs as a function of tube diameter, (2) the slope of the long wavelength TA phonon mode dispersion relation as a function of axial stress and tube diameter, and (3) the curvature of the long wavelength TA phonon mode dispersion relations for a force-free SWNT as a function tube diameter.

We compute the energy density versus curvature relation using zero-temperature objective molecular dynamics (based on [DJ07] which allows for the explicit control of curvature through a "bending group parameter") for armchair nanotubes with different diameters. In particular, we calculate the change in energy density, $\Delta \tilde{\phi} = \Delta \bar{\phi}/(\ell P)$, where ℓ is the objective cell length and P is the perimeter of the nanotube. For each radius, we calculate the bending stiffness Λ according to

$$\Delta \tilde{\phi} = \frac{1}{2} \Lambda \kappa^2 \quad \Rightarrow \quad \Lambda = \frac{2\Delta \phi}{\kappa^2}. \tag{4.46}$$

Figure 4.20 shows the variation of $\sqrt{\Lambda}$ versus the diameter. It is clear that the bending stiffness scales linearly with the square of the diameter.

Next, Fig. Figure 4.21(a) shows the (signed) square of the TA modes' slope (near $k = \theta$) as a function of axial stress for a variety of tube SWNT types. This slope was computed from our phonon dispersion calculations using a numerical differentiation algorithm. Finally, in Fig. Figure 4.21(b) we show the curvature, computed in a similar manner to the slope, for various nanotubes ranging from (6, 6) to (16, 16) as a function of the tube diameter.

From these figures we can infer the following important results:

• Fig. Figure 4.21(a) shows that the slope of the TA mode curve does not depend



Figure 4.20: The square root of bending stiffness (calculated by minimizing the energy of armchair nanotubes) versus the diameter of the nanotube. The points are from calculations and the line is a best-fit to the points.

on the specific nanotube. It is linearly related to the square root of the axial force.

• For various nanotubes of different diamters and chiralities, Fig. Figure 4.21(b) shows that the curvature of the TA mode curve scales linearly with the tube diameter, and Fig. Figure 4.20 in turn shows that square root of the bending



Figure 4.21: (a) Square of the slope of the TA mode vs. the axial stress. (b) Curvature of the TA mode vs. diameter for various nanotubes ranging from (6, 6) to (16, 16). The points are from calculations and the line is a best-fit to the points.

stiffness scales linearly with the tube diameter. Together, these imply that the curvature of the TA mode curve is directly related to the square root of the bending stiffness.

These plots therefore confirm our claim.

4.8.5 Simple Continuum Model and Discussion

First we consider the case of a rod that undergoes stretching deformations, but with a pre-stress. This gives us the expected conclusion that the pre-stress plays a role only in determining the equilibrium state around which linearization is conducted. Consider a rod of length L that is extend by an amount δ and with a pre-stress σ_0 . The energy of deformation is, to second order, given by

$$E \sim \sigma_0 \frac{\delta}{L} + \frac{1}{2} E_T \left(\frac{\delta}{L}\right)^2 + \dots$$
 (4.47)

Here E_T is the extensional modulus at the state of linearization. The natural frequencies from a normal mode analysis will be proportional to the square root of the coefficient of the quadratic term, i.e. $E_T^{\frac{1}{2}}$.

Now, to understand the current setting, we examine a beam that undergoes transverse deflections. Consider a beam of length L, and impose a bending deformation that causes a relative deflection Δ between the ends of the beam. A simple accounting of the geometric nonlinearity shows that there is an *extensional* strain of $\left(1 + \left(\frac{\Delta}{L}\right)^2\right)^{\frac{1}{2}} - 1$ which is simply $\frac{1}{2}\left(\frac{\Delta}{L}\right)^2$ to leading order. The energy of deformation is, to second order, given by

$$E \sim \frac{1}{2}\sigma_0 \left(\frac{\Delta}{L}\right)^2 + \dots$$
 (4.48)

The natural frequencies from a normal mode analysis will be proportional to the square root of the coefficient of the quadratic term, i.e. $\sigma_0^{\frac{1}{2}}$. When this term is

absent, higher-order effects such as bending control the curvature of the TA mode curve.

Therefore, this gives the unusual *direct* dependence of the normal mode frequencies on the axial force. As the above simple analysis shows, the key to this feature is the geometric nonlinearity of a slender structure.

As our calculations above have shown, the Density of States can also be tuned significantly by applying an axial force. Therefore, it is possible that properties such as heat transfer can be tuned by mechanical means.

Symmetry-Adapted Multiscale Modeling of Membranes

5

In chapters 3 and 4 we explained how to do full atomistic and molecular calculations using the structural symmetries. An essential difficulty in atomic and molecular modeling is that relevant system sizes of interest are very large. While accurate models of interactions between individual atoms and molecules are developed, the difficulty is that it is sometimes infeasible to solve these models on existing - or even conceived - computers. Multiscale methods are well-suited to such problems, that is near the regions in which atomic displacements are non-homogeneous we use full atomistic resolution and away from these regions we coarse-grain to retain only the effective influence. But existing molecular multiscale methods are suitable for crystals. In this chapter we develop a novel multiscale method for modeling not only crystalline structures but also other symmetric structures such as nanotubes, graphene and bio-membranes. In fact, our method is the generalization of the popular quasi-continuum method (QC) [TOP96, KO01].

5.1 Methodology

Quasi-continuum (QC) is a systematic methodology of minimizing the energy of a coarse-grained atomistic medium. QC enables us to find the equilibrium of an atomistic medium without considering every atom. Consider a system consisting of N atoms with short range interatomic interactions. Denote the site energy of the atom $i \in \{1, 2, \dots, N\}$ as E_i which is a function of the position and director vector of the atoms in a small neighborhood of atom i. We denote this neighborhood as Ω_i . Then the total potential energy of the system is

$$W = W(\{\boldsymbol{x}_i, \boldsymbol{n}_i\}) = \sum_{i=1}^{N} E_i(\{\boldsymbol{x}_j, \boldsymbol{n}_j | j \in \Omega_i\})$$
(5.1)

where \boldsymbol{x}_i and \boldsymbol{n}_i are the position and director vector of atom *i*, respectively. The director vectors are included in the energy to account for possible simulation of lipid bilayers. For most engineering materials we can simply neglect the dependence of energy on them.

The equilibrium configuration is found by minimizing (5.1) with respect to its arguments. This is computationally demanding. The aim of QC is to substantially reduce the number of degrees of freedom (DOF) from 3N (or 6N when considering the director vectors) such that the computation of the energy is accurately approximated without explicitly considering the site energy of every atom. This is done by choosing some atoms as the representative atoms. For simplicity we call them "repatoms" ¹. Repatoms are considered as the nodes of a FEM mesh. An example of a nonuniform mesh with quadrilateral elements is shown in Figure 5.1.

The density of repatoms varies in space and depends on how the system is de-

¹ Throughout this section, the repatom (nodal) values are distinguished from non-repatom values by a bar sign, $\bar{}$. For instance \bar{u}_r and u_i respectively show the repatom r and non-repatom i displacements.



Figure 5.1: Example of a nonuniform mesh. Large blue circles are the repatoms and small green circles are non-repatoms.

formed. In regions with uniform deformation, low density of repatoms is required because each atom sees the same environment. On the other hand, high density of repatoms is needed in regions with highly nonuniform deformation. From the atomistic perspective this is equivalent to choosing the repatoms in a way such that the atoms in every element see almost the same environment. Since these atoms have almost the same energy we can select few sample atoms in every element and approximate the total energy by

$$W^{h} = W^{h}(\{\bar{\boldsymbol{x}}_{r}, \bar{\boldsymbol{n}}_{i}\}) = \sum_{s=1}^{N_{S}} m_{s} E_{s}(\{\boldsymbol{x}_{j}^{h}, \boldsymbol{n}_{j}^{h} | j \in \Omega_{s}\})$$
(5.2)

where N_S is the total number of sample atoms and m_s is the number of atoms sampled by the sample atom s. If an element contains one sample atom then m_s would be equal to the number of atoms inside that element.

As mentioned, equation (5.2) assumes an almost same environment for atoms

in the neighborhood of every sample atom. This is a crucial criteria needed to be satisfied in numerical calculations. The regions which do not satisfy this criteria must be refined. In next sections we address this issue and provide the error bounds of the energy for membranes.

The number of DOF has been significantly reduced in eqn. (5.2) by keeping the DOF corresponding to the repatoms and removing the rest of them. The position and director vector of the removed atoms are interpolated by means of FEM shape functions

$$\boldsymbol{x}_{i}^{h} = \sum_{r=1}^{N_{rep}} N_{r}(\boldsymbol{X}_{i}) \bar{\boldsymbol{x}}_{r}$$
$$\boldsymbol{n}_{i}^{h} = \sum_{r=1}^{N_{rep}} N_{r}(\boldsymbol{X}_{i}) \bar{\boldsymbol{n}}_{r}$$
(5.3)

where X_i is the position of atom *i* in the undeformed configuration, N_{rep} is the number of repatoms and N_r is the shape function associated with repatom r^2 .

Equation (5.2) provides a substantial computational saving by replacing the summation over all atoms N in (5.1) with the summation over the sample atoms N_S which is typically several order of magnitudes smaller than N. The equilibrium configuration is then found by minimizing (5.2) with respect to the its arguments. To do so, we use conjugate gradient method [NW06] which requires the evaluation of the first

² Shape functions can either interpolate or approximate the repatom displacements. This is controlled by the form of the shape functions. The surface constructed by interpolatory shape functions passes through the repatom positions. Shape functions based on Lagrange polynomials and Hermit functions are two examples of interpolatory shape functions. On the other hand the limit surface constructed by (5.3) do not go through the repatoms if splines or other approximating shape functions are used. See appendix B for more information on the form of the shape functions and, in particular, how to construct them based on the splines.

derivative of energy. This can be obtained by using (5.3) and the chain rule

$$\frac{\partial W^{h}}{\partial \bar{\boldsymbol{x}}_{r}} = \sum_{s=1}^{N_{S}} m_{s} \left[\sum_{j \in \Omega_{s}} \frac{\partial E_{s}}{\partial \boldsymbol{x}_{j}^{h}} N_{r}(\boldsymbol{X}_{i}) \right] = 0$$
$$\frac{\partial W^{h}}{\partial \bar{\boldsymbol{n}}_{r}} = \sum_{s=1}^{N_{S}} m_{s} \left[\sum_{j \in \Omega_{s}} \frac{\partial E_{s}}{\partial \boldsymbol{n}_{j}^{h}} N_{r}(\boldsymbol{X}_{i}) \right] = 0$$
(5.4)

In appendix C we simplify equation (5.4) for pair and bond-order potentials.

We conclude this section by a remark on the sample atoms. They are the analogs of the numerical quadrature points in standard FEM. The number of sample atoms can be found by patch test analysis [ZTZ05]. Their number not only depends on the size and shape of the elements, but also on the material's constitutive equation. For instance it has been shown that first-order (one-point per triangular element) Gaussian quadrature is sufficient to obtain theoretical convergence rates and high accuracy for engineering materials [COS00, CO01]. On the other hand, Feng and Klug [FK06] argue that the evaluation of the energy with one quadrature point per element for lipid bilayers produces a non-positive-definite stiffness and results in zero-energy deformation modes. Their numerical analysis reveal that these issue is mitigated by using second-order Gaussian rule (three-point per triangular element). Arroyo and Belytschko [AB03] also used three Gauss points per element for the multiscale modeling of nanotubes. Our analysis of membranes meshed by quadrilateral elements reveals no significant difference between the energy evaluated by second-order (four-point) and third-order (nine-point) Gaussian quadratures.

5.2 Almost OS Membranes

As we have explained in the previous section the quasi-continuum framework assumes that the atoms in the neighborhood of every sample atom see almost the same environment. The mesh size around sample atoms which do not meet this requirement should be decreased. This requirement is always satisfied for crystals because the atomic displacements governed by linear shape functions satisfies the Cauchy-Born rule. But Cauchy-Born rule fails to describe the deformation of a crystalline membranes [AB02]. In this section we exploit the notion of objective structures and introduce an analog of Cauchy-Born for membranes. We will call them almost OS membranes. The important property of almost OS membranes is that the atoms lying in a small region see almost the same environment. Then in section 5.4 we explain how to systematically check if our structure is an almost OS membrane.

5.2.1 Defining the structure of membranes

We define the structure of a monolayer by a set of isometries $F = \{f_1^i f_2^j; (i, j) \in \mathbb{Z}^2\}$ applied to a point \boldsymbol{x}_0 where $f_1 = (\boldsymbol{Q}_1 | \boldsymbol{c}_1)$ and $f_2 = (\boldsymbol{Q}_2 | \boldsymbol{c}_2)$ are the generators of F, $\boldsymbol{Q}_m \in O(3)$ is an orthogonal tensor and $\boldsymbol{c}_m \in \mathbb{R}^3$ is a vector for $m \in \{1, 2\}$. The action of these isometries on a point $\boldsymbol{x} \in \mathbb{R}^3$ is

$$f_m(\boldsymbol{x}) = (\boldsymbol{Q}_m | \boldsymbol{c}_m)(\boldsymbol{x}) = \boldsymbol{Q}_m \boldsymbol{x} + \boldsymbol{c}_m \quad ; \quad m \in \{1, 2\}$$
(5.5)

from which we can define the power of the isometries f_m^i by

$$f_m^2(\boldsymbol{x}) = f_m(f_m(\boldsymbol{x})) = \boldsymbol{Q}_m^2 \boldsymbol{x} + (\boldsymbol{Q}_m + \boldsymbol{I})\boldsymbol{c}_m \Longrightarrow f_m^i(\boldsymbol{x}) = \boldsymbol{Q}_m^i \boldsymbol{x} + \left(\sum_{j=0}^{i-1} \boldsymbol{Q}_m^j\right)\boldsymbol{c}_m \quad (5.6)$$

and the composition of mapping by

$$f_{i}^{i} f_{2}^{j}(\boldsymbol{x}) = \boldsymbol{Q}_{1}^{i} \boldsymbol{Q}_{2}^{j} \boldsymbol{x} + \boldsymbol{Q}_{1}^{i} \left(\sum_{k=0}^{j-1} \boldsymbol{Q}_{2}^{k} \right) \boldsymbol{c}_{2} + \left(\sum_{k=0}^{i-1} \boldsymbol{Q}_{1}^{k} \right) \boldsymbol{c}_{1}$$
(5.7)

Let us first analyze each of the isometries individually. Consider a set of isometries $F_1 = \{f_1^i; i \in \mathbb{Z}\}$ where $f_1 = (\mathbf{Q}_1 | \mathbf{c}_1)$ as before and consider \mathbf{n}_1 to be the axis of \mathbf{Q}_1 , i.e. $\mathbf{Q}_1 \mathbf{n}_1 = \mathbf{n}_1$. F_1 generates either a helix, circle or line depending on \mathbf{Q}_1 and \mathbf{c}_1 . Clearly we will get a line along \mathbf{c}_1 if $\mathbf{Q}_1 = \mathbf{I}$. In order to better understand

the role of Q_1 and c_1 for the case $Q_1 \neq I$ we decompose $c_1 = q_1 + p_1$ such that $q_1 \parallel n_1$ and $p_1 \cdot n_1 = 0$. Since for any vector r, $(I - Q_1)r \cdot n_1 = 0$ we rewrite $p_1 = (I - Q_1)r_1$ where $r_1 \cdot n_1 = 0$. The existence of r_1 is guarantied by the invertibility of $I - Q_1 \neq 0$ on the plane perpendicular to n_1 . In other words f_1 has the form $f_1 = (Q_1 \mid (I - Q_1)r_1 + q_1)$. This is an important result because the role of each parameter is clearly distinguished and, as explained in the next paragraph, the calculation of the power of the isometry gets much easier. The term $(I - Q_1)r_1$ is pure bending and the term q_1 is pure translation. Strictly speaking, if $q_1 = 0$, $\{f_1^i(x_0); i \in \mathbb{Z}\}$ generates a circle with radius $|x_0 - r_1|$ centered at r_1 . Putting these terms together results in a helix with radius $|x_0 - r_1|$. The axis of the helix is along n_1 passing through r_1 .

To summarize the above paragraph, each isometry can be written as $f_m = (\mathbf{Q}_m | (\mathbf{I} - \mathbf{Q}_m)\mathbf{r}_m + \mathbf{q}_m)$, where $\mathbf{Q}_m \mathbf{q}_m = \mathbf{q}_m$ and $\mathbf{r}_m \cdot \mathbf{q}_m = 0$. This form provides much simplification in the calculation of the power of the isometry because it is easy to show

$$f_{m}^{i}(\boldsymbol{x}_{0}) = \boldsymbol{Q}_{m}^{i}(\boldsymbol{x}_{0} - \boldsymbol{r}_{m}) + \boldsymbol{r}_{m} + i\boldsymbol{q}_{m} = \boldsymbol{x}_{0} + (\boldsymbol{I} - \boldsymbol{Q}_{m}^{i})\hat{\boldsymbol{r}}_{m} + i\boldsymbol{q}_{m} \quad ; \quad m \in \{1, 2\} \quad ; \quad i \in \mathbb{Z}$$
(5.8)

where $\hat{\boldsymbol{r}}_m = \boldsymbol{r}_m - \boldsymbol{x}_0$.

Now that we have studied each individual isometry, let us get back to the monolayer case which requires to have both isometries. The atomic sites on the monolayer are defined to be the action of elements of F on \boldsymbol{x}_0 . In other words

$$\boldsymbol{x}_{i,j} = f_1^i f_2^j(\boldsymbol{x}_0) = \boldsymbol{x}_0 + \boldsymbol{Q}_1^i [(\boldsymbol{I} - \boldsymbol{Q}_2^j) \hat{\boldsymbol{r}}_2 - \hat{\boldsymbol{r}}_1 + j \boldsymbol{q}_2] + \hat{\boldsymbol{r}}_1 + i \boldsymbol{q}_1$$
(5.9)

5.2.2 OS and almost OS

The structure given by eqn. (5.9) is not an objective structure (OS) because F is not a group. Groups have certain properties. More precisely a set F is a group if it satisfies the following conditions

- 1. It should contain identity element id = (I|0),
- 2. Inverse: For each element $f_i \in F$ there exists $f_j \in F$ such that $f_i f_j = f_j f_i = id$,
- 3. Associativity: For all elements $f_1, f_2, f_3 \in F$, $f_1(f_2f_3) = (f_1f_2)f_3$,
- 4. Closure: For all f_1 and $f_2 \in F$, $f_1 f_2 \in F$.

Objective structures are characterized by groups. A structure is an OS if it can be defined by a group. A general result showed by James [Jam06] is that unbalanced forces on all molecules of an OS are equal and they have the same energy. This implies that every molecule of an OS is at equilibrium if only one molecule is at equilibrium. This is very important for multiscale calculations in which coarse graining play an important role. We can coarse-grain the particles which have the same energy.

But our definition of monolayers does not give an OS. This is because both f_1 and f_2 defined in section 5.2.1 are members of F but $f_2f_1 \notin F$. Therefore the key property of OS that the equilibrium of one molecule implies the equilibrium of the whole structure does not hold for the defined monolayer. But as we show here there are some cases that for small values of i and j the structure given by (5.9) is close to an OS. We call them *almost objective structures*. In other words, all atoms of almost objective structures see almost the same environment and consequently the unbalanced forces on the atoms are small.

The cases that OS is attained are

- 1. Flat sheet (see Figure 5.2a): $\theta_1 = \theta_2 = 0$,
- 2. Cylinder or nanotube (see Figure 5.2b): $\phi = 0$ and one of the following
 - (a) $\boldsymbol{r}_1 = \boldsymbol{r}_2 = \boldsymbol{r}$: A cylinder with axis $\boldsymbol{n} = \boldsymbol{n}_1 = \boldsymbol{n}_2$ passing through \boldsymbol{r} ,
 - (b) $\theta_1 = 0$: A cylinder with axis $\boldsymbol{n} = \boldsymbol{n}_1 = \boldsymbol{n}_2$ passing through \boldsymbol{r}_2 ,
 - (c) $\theta_2 = 0$: A cylinder with axis $\boldsymbol{n} = \boldsymbol{n}_1 = \boldsymbol{n}_2$ passing through \boldsymbol{r}_1 ,

- 3. Helix: $q_1 = \theta_1 = 0$ or $q_2 = \theta_2 = 0$ (this is trivially an OS because it reduces to only one generator),
- 4. Torus (Not OS, see Figure 5.2c): $q_1 = q_2 = 0$, $r_1 = r_1 n_3$, $r_2 = r_2 n_3$ and $\phi = \pi/2$ ($r = r_2$: radius of the tube and $R = r_2 r_1$: distance from the center of the tube to the center of the torus). Two special cases
 - (a) $r = r_2 = 0$: Circle with radius $R = r_2 r_1$ (OS),
 - (b) $R = r_2 r_1 = 0$: Sphere with radius $r = r_2$ (Not OS).



Figure 5.2: Perfect OS. Non-boundary atoms see the same environment (a) Flat sheet (b) Helix (c) Torus. Blue particles are the unit cells corresponding to i = j = 0 and the green particles are the cells with $i \neq 0$ or $j \neq 0$.

The atoms of the structure given by one of the above cases see exactly the same environment. Therefore the energy and unbalanced forces on all atoms are equal. We denote the atoms of these OS by $\{y_{i,j}\}$. We assume the OS is at equilibrium. In other words the unbalanced forces on all atoms are zero. Disturbing the above quantities may result in an almost OS with atomic position $\{x_{i,j}\}$. Figure 5.1 depicts two almost OS where in the first one θ_1 and θ_2 are the disturbed quantities and in the second one only θ_1 is disturbed. Denote ϑ as the disturbed quantity and $\Delta x_{i,j} = x_{i,j} - y_{i,j}$. The unbalanced forces on the atoms of the almost OS is not anymore zero because $\Delta x_{i,j} \neq 0$. If $\Delta x_{i,j}$ is in the order of the small quantity ϑ we can write the Taylor expansion of the energy E around the equilibrium state $\{y_{i,j}\}$

$$E(\{\boldsymbol{x}_{i,j}\}) = E(\{\boldsymbol{y}_{i,j}\}) + \sum_{(i,j)} \frac{\partial E}{\partial \boldsymbol{x}_{i,j}} \bigg|_{\{\boldsymbol{y}_{i,j}\}} \cdot \Delta \boldsymbol{x}_{i,j}$$
$$+ \frac{1}{2} \sum_{(i,j)} \sum_{(k,l)} \Delta \boldsymbol{x}_{i,j} \cdot \frac{\partial^2 E}{\partial \boldsymbol{x}_{i,j} \partial \boldsymbol{x}_{k,l}} \bigg|_{\{\boldsymbol{y}_{i,j}\}} \Delta \boldsymbol{x}_{k,l} + \cdots$$
(5.10)

The first derivatives vanish because the OS is assumed to be at equilibrium. The second derivative terms are the components of the Hessian matrix, i.e. $H_{(i,j)(k,l)} = \frac{\partial^2 E}{\partial x_{i,j} \partial x_{k,l}} \Big|_{\{y_{i,j}\}}$. Neglecting terms higher than quadratic

$$\Delta E = E(\{\boldsymbol{x}_{i,j}\}) - E(\{\boldsymbol{y}_{i,j}\}) = \frac{1}{2} \sum_{(i,j)} \sum_{(k,l)} \Delta \boldsymbol{x}_{i,j} \cdot \boldsymbol{H}_{(i,j)(k,l)} \Delta \boldsymbol{x}_{k,l}$$
(5.11)

And the force on the atoms are

$$\boldsymbol{f}_{i,j} = -\frac{\partial E}{\partial \boldsymbol{x}_{i,j}} = -\sum_{(k,l)} \boldsymbol{H}_{(i,j)(k,l)} \Delta \boldsymbol{x}_{k,l}$$
(5.12)

Since the components of the Hessian matrix are finite and vanish as the distance between atoms (i, j) and (k, l) increases, and $\Delta \mathbf{x}_{i,j}$ and $\Delta \mathbf{x}_{k,l} \propto \vartheta$ are small we can conclude that $\Delta E \propto \vartheta^2$ and the unbalanced forces $\mathbf{f}_{i,j} \propto \vartheta$. Hence the monolayer structure, given by perturbing the variables of one of the three OS defined above, is almost OS.

We now evaluate the errors associated with almost OS graphene defined by the generators given in the caption of Figure 5.3a. We first consider a flat graphene sheet with $\theta_1 = \theta_2 = 0$ and then start to bend it in both directions by increasing them. The magnitude of vectors \mathbf{r}_1 and \mathbf{r}_2 are restricted to be equal to $3L_{cc}/\theta_1$ and $\sqrt{3}L_{cc}/\theta_2$ to ensure that the structure remains hexagonal and the distances between



Figure 5.3: Two almost objective structures defined by generators $f_1 = (\mathbf{Q}_1 | (\mathbf{I} - \mathbf{Q}_1)\mathbf{r}_1 + \mathbf{q}_1)$ and $f_2 = (\mathbf{Q}_2 | (\mathbf{I} - \mathbf{Q}_2)\mathbf{r}_2 + \mathbf{q}_2)$. (a) Bended membrane with non-zero principle curvatures. Here $\mathbf{n}_1 = \mathbf{e}_2$ and $\mathbf{n}_2 = \sqrt{3}/2\mathbf{e}_1 + 0.5\mathbf{e}_2$ are the axis of the orthogonal tensors and $\theta_1 = 0.062, \theta_2 = 0.036, \mathbf{q}_1 = \mathbf{q}_2 = \mathbf{0}$ and $\mathbf{r}_1 = \mathbf{r}_2 = 7\mathbf{e}_3$ nm. (b) Cylinder bended along the direction normal to the axis. Here $\mathbf{n}_1 = \mathbf{e}_1, \mathbf{n}_2 = \mathbf{e}_2, \theta_1 = 0.004, \theta_2 = 0.4, \mathbf{r}_1 = 10\mathbf{e}_3$ nm, $\mathbf{r}_2 = 0.1\mathbf{e}_3$ nm, $\mathbf{q}_1 = 0$ and $\mathbf{q}_2 = 0.005\mathbf{e}_2$ nm. In section 5.3 a robust explanation on why these structures are indeed almost OS is given.

the nearest neighbor atoms be close to the carbon-carbon bond length L_{cc} (Figure 5.3a corresponds to the final stage of bending). We then calculate the energy and unbalanced forces of the unit cells for each configuration. The energy of unit cell (0,0) is plotted in Figure 5.4a, which as expected from (5.11) is quadratic with respect to curvature. Figure 5.4b shows the ratio of the maximum difference between the energy of all unit cells with $-2 \leq i, j \leq 2$. It clearly indicates that there is almost no difference between the energy of the unit cells.

In order to show that the spurious forces associated with our notion of almost OS are negligible we calculate and compare the magnitude of forces of each unit cell for different curvatures. The magnitude of force of the unit cell (0,0) is plotted in Figure 5.5a, which as expected from eqn. (5.12) has a linear dependence on the curvature.



Figure 5.4: (a) The difference between the energy of almost OS graphene and the corresponding OS. (b) Maximum difference between the energy of unit cells with $-2 \le i, j \le 2$.

As it is clear from Figure 5.5b the maximum difference between the forces of unit cells with $-2 \leq i, j \leq 2$ is negligible implying that the atoms of the constructed almost OS indeed have almost the same environment.



Figure 5.5: (a) The force of the unit cell vs. curvature. (b) Maximum difference between the force of unit cells with $-2 \le i, j \le 2$.

5.3 Examples of almost OS monolayers

In the previous section we defined the monolayer by the application of two generators f_1 and f_2 to a point \boldsymbol{x}_0 as

$$\boldsymbol{x}_{i,j} = f_1^i f_2^j(\boldsymbol{x}_0) = \boldsymbol{x}_0 + \boldsymbol{Q}_1^i [(\boldsymbol{I} - \boldsymbol{Q}_2^j) \hat{\boldsymbol{r}}_2 - \hat{\boldsymbol{r}}_1 + j \boldsymbol{q}_2] + \hat{\boldsymbol{r}}_1 + i \boldsymbol{q}_1$$
(5.13)

and discussed the special cases which are OS. We showed that tweaking some parameters of the generators results in an almost OS in which the atoms see almost the same environment, their energy are almost equal the unbalanced forces are almost zero. In this section we show that a slightly bended sheet and a slightly bended cylinder are indeed almost OS.

First we need to expand (5.13) and write the Euclidean components of the position of the atoms. To do so, we respectively denote the axis of rotation of Q_1 and Q_2 by unit vectors n_1 and n_2 , i.e. $Q_1n_1 = n_1$ and $Q_2n_2 = n_2$, $|n_1| = |n_2| = 1$, $n_1 \cdot n_2 = \cos \phi$ and $\{n_1, n_2, n_3 = n_1 \times n_2 / ||n_1 \times n_2||\}$ defines a basis. We also denote the angle of rotation of Q_1 and Q_2 by θ_1 and θ_2 , respectively. The orthogonal tensors can be written as

$$\boldsymbol{Q}_1 = \boldsymbol{n}_1 \otimes \boldsymbol{n}_1 + \cos \theta_1 (\boldsymbol{I} - \boldsymbol{n}_1 \otimes \boldsymbol{n}_1) + \sin \theta_1 (\bar{\boldsymbol{n}}_1 \otimes \boldsymbol{n}_3 - \boldsymbol{n}_3 \otimes \bar{\boldsymbol{n}}_1)$$
(5.14a)

$$\boldsymbol{Q}_2 = \boldsymbol{n}_2 \otimes \boldsymbol{n}_2 + \cos \theta_2 (\boldsymbol{I} - \boldsymbol{n}_2 \otimes \boldsymbol{n}_2) + \sin \theta_2 (\bar{\boldsymbol{n}}_2 \otimes \boldsymbol{n}_3 - \boldsymbol{n}_3 \otimes \bar{\boldsymbol{n}}_2)$$
(5.14b)

where

$$\bar{\boldsymbol{n}}_1 = \boldsymbol{n}_3 \times \boldsymbol{n}_1 \quad ; \quad \bar{\boldsymbol{n}}_2 = \boldsymbol{n}_3 \times \boldsymbol{n}_2$$
 (5.15)

We denote
$$\mathbf{r}_1 = a_1 \bar{\mathbf{n}}_1 + b_1 \mathbf{n}_3$$
 and $\mathbf{r}_2 = a_2 \bar{\mathbf{n}}_2 + b_2 \mathbf{n}_3$. Then by decomposing
 $\mathbf{n}_2 = \cos \phi \mathbf{n}_1 + \sin \phi \bar{\mathbf{n}}_1$ and $\bar{\mathbf{n}}_2 = \cos \phi \bar{\mathbf{n}}_1 - \sin \phi \mathbf{n}_1$ eqn. (5.13) can be rewritten
 $\mathbf{x}_{i,j} = \mathbf{x}_0 + [iq_1 + jq_2\cos\phi + (b_2\sin j\theta_2 - a_2(1 - \cos j\theta_2))\sin\phi]\mathbf{n}_1$
 $+ [(b_2 - b_1)\sin i\theta_1 - b_2(\sin i\theta_1\cos j\theta_2 + \cos i\theta_1\sin j\theta_2\cos\phi) + jq_2\cos i\theta_1\sin\phi$
 $+ a_1(1 - \cos i\theta_1) + a_2(\sin i\theta_1\sin j\theta_2 - \cos i\theta_1\cos j\theta_2\cos\phi) + a_2\cos i\theta_1\cos\phi]\bar{\mathbf{n}}_1$
 $+ [(b_2 - b_1)\cos i\theta_1 - b_2(\cos i\theta_1\cos j\theta_2 - \sin i\theta_1\sin j\theta_2\cos\phi) - jq_2\sin i\theta_1\sin\phi$
 $+ (a_1 - a_2\cos\phi)\sin i\theta_1 + a_2(\cos i\theta_1\sin j\theta_2 + \sin i\theta_1\cos j\theta_2\cos\phi) + b_1]\bar{\mathbf{n}}_3$
(5.16)

It can be shown that the convected basis vectors (tangents to the surface) corre-

sponding to (5.16) at the origin, i.e. i = j = 0, are

$$\boldsymbol{g}_1 = q_1 \boldsymbol{n}_1 - b_1 \theta_1 \bar{\boldsymbol{n}}_1 + a_1 \theta_1 \boldsymbol{n}_3$$
$$\boldsymbol{g}_2 = q_2 \boldsymbol{n}_2 - b_2 \theta_2 \bar{\boldsymbol{n}}_2 + a_2 \theta_2 \boldsymbol{n}_3$$
(5.17)

In a crystalline structure g_1 and g_2 are the crystal's lattice vectors and their magnitudes are equal to the distances between atoms at equilibrium. Therefore $a_1\theta_1$, $b_1\theta_1$, $a_2\theta_2$, $b_2\theta_2$, q_1 and q_2 should be in the order of the interatomic distances. This implies that if θ_1 (or θ_2) is chosen to be a very small angle then a_1 and b_1 (a_2 and b_2) should be a large number and vice versa.

We now examine two almost OS examples.

5.3.1 Case one: Small θ_1 and θ_2 (Bending membrane with non-zero principle curvatures)

When both θ_1 and θ_2 are small angles equation (5.9) would correspond to a flat sheet slightly bended in two directions. Figure 5.3a illustrates such a case. The atoms of the structure see almost the same environment, because when θ_1 and θ_2 are small angles

$$\boldsymbol{x}_{i,j} = \boldsymbol{x}_0 + i(q_1\boldsymbol{n}_1 - b_1\theta_1\bar{\boldsymbol{n}}_1 + a_1\theta_1\boldsymbol{n}_3) + j(q_2\boldsymbol{n}_2 - b_2\theta_2\bar{\boldsymbol{n}}_2 + a_2\theta_2\boldsymbol{n}_3) + O(a\theta^2, b\theta^2, q\theta)$$
(5.18)

This is an almost OS because the deviation of $\{\boldsymbol{x}_{i,j}\}$ from a perfect OS is in the order of small quantities θ_1 and θ_2 . To show this we define an OS generated by the set of isometries $H = \{h_1^i h_2^j; (i, j) \in \mathbb{Z}^2\}$ where $h_1 = (\boldsymbol{I}|q_1\boldsymbol{n}_1 - b_1\theta_1\bar{\boldsymbol{n}}_1 + a_1\theta_1\boldsymbol{n}_3)$ and $h_2 = (\boldsymbol{I}|q_2\boldsymbol{n}_2 - b_2\theta_2\bar{\boldsymbol{n}}_2 + a_2\theta_2\boldsymbol{n}_3)$. This corresponds to a flat sheet monolayer. Then

$$\boldsymbol{x}_{i,j} = \boldsymbol{y}_{i,j} + O(a\theta^2, b\theta^2, q\theta)$$
(5.19)

5.3.2 Case two: $a_1, q_1, \theta_1 \approx 0$ (or $a_2, q_2, \theta_2 \approx 0$) and $\phi \approx \pi/2$; (Bended cylinder)

As it was stated earlier helices and cylinders are OS. Here we show that a slightly bended cylinder or helix is an almost OS. An example of this case is given in Figure 5.3b. First we construct the OS made by the set of isometries $H = \{h_1^i h_2^j; (i, j) \in \mathbb{Z}^2\}$ where $h_1 = (\boldsymbol{I}| - b_1 \theta_1 \boldsymbol{n}_2)$ and $h_2 = (\boldsymbol{Q}_2|(\boldsymbol{I} - \boldsymbol{Q}_2)\boldsymbol{r}_2 + \boldsymbol{q}_2)$. The position of the atoms of this OS are

$$\boldsymbol{y}_{i,j} = h_1^i h_2^j(\boldsymbol{x}_0) = \boldsymbol{x}_0 + \left[a_2(1 - \cos j\theta_2) - b_2 \sin j\theta_2 \right] \bar{\boldsymbol{n}}_2 + (jq_2 - ib_1\theta_1)\boldsymbol{n}_2 + \left[a_2 \sin j\theta_2 + b_2(1 - \cos j\theta_2) \right] \boldsymbol{n}_3$$
(5.20)

 $\{y_{i,j}\}$ gives us a cylinder of radius $\sqrt{a_2^2 + b_2^2}$ with axis n_2 . This can be rewritten in the form

$$y_{i,j} = x_0 + \left[(jq_2 - ib_1\theta_1)\cos\phi - (a_2(1 - \cos j\theta_2) - b_2\sin j\theta_2)\sin\phi \right] n_1 + \left[(jq_2 - ib_1\theta_1)\sin\phi + (a_2(1 - \cos j\theta_2) - b_2\sin j\theta_2)\cos\phi \right] \bar{n}_1 + \left[a_2\sin j\theta_2 + b_2(1 - \cos j\theta_2) \right] n_3$$
(5.21)

Now we construct the slightly bended cylinder by choosing $\phi = \pi/2 - \psi$ where $\psi \approx 0, a_1 \approx 0, q_1 \approx 0$ and $\theta_1 \approx 0$. Since θ_1 is chosen to be a small angle, a_1 or b_1 should be large values because $a_1\theta_1$ and $b_1\theta_1$ are in the range of interatomic distances. Substituting these values into (5.13) gives

$$\boldsymbol{x}_{i,j} = \boldsymbol{x}_0 + \left[iq_1 + jq_2\cos\phi + (b_2\sin j\theta_2 - a_2(1 - \cos j\theta_2))\sin\phi\right]\boldsymbol{n}_1 \\ + \left[i(b_2 - b_1)\theta_1 - b_2(i\theta_1\cos j\theta_2 + \sin j\theta_2\cos\phi) + jq_2\sin\phi + ij\theta_1\theta_2a_2 + a_2\cos\phi(1 - \cos j\theta_2)\right]\bar{\boldsymbol{n}}_1 \\ + \left[b_2(1 - \cos j\theta_2 + i\theta_1\sin j\theta_2\cos\phi) - ijq_2\theta_1\sin\phi + i\theta_1a_1 + a_2(\sin j\theta_2 - i\theta_1\cos\phi(1 - \cos j\theta_2))\right]\boldsymbol{n}_3$$
(5.22)

Subtracting (5.21) from (5.22) results

$$\boldsymbol{x}_{i,j} = \boldsymbol{y}_{i,j} + O(q_1, a_1, \theta_1, \psi)$$
 (5.23)

Similar to the previous case in which both θ_1 and θ_2 were small angles (see section 5.3.1), $\{y_{i,j}\}$ is an OS and the deviation of $\{x_{i,j}\}$ from $\{y_{i,j}\}$ is in the order

of $(q_1, a_1, \theta_1, \psi)$. Hence, $\{\boldsymbol{x}_{i,j}\}$ is almost an OS because the particles see almost the same environment and the unbalanced forces and energy are in the order of $(q_1, a_1, \theta_1, \psi)$ and $(q_1^2, a_1^2, \theta_1^2, \psi^2)$, respectively.

Similarly we can show that the structure given by the parameters $a_2 \approx 0, q_2 \approx 0, \theta_2 \approx 0$ and $\phi \approx \pi/2$ is also an almost OS.

5.4 Checking if a given membrane is an almost OS

In section 5.1 we developed a multiscale model suitable for molecular simulation of non-crystalline structures such as membranes. We argued that the model is valid when the energy of atoms around the sample atoms are almost equal. We then introduced the notion of almost OS membranes in section 5.2 which satisfies the above-mentioned requirement. In this section, we explain how to check if a sample atom and its neighborhood make an almost OS.

The first step is to fit a membrane with generators described in section 5.2 to the FEM structure at each sample atom. This requires to solve for 12 unknowns at each sample atom since each generator is a function of six parameters, namely $q_m, \theta_m, a_m, b_m, \mathbf{n}_m$ for m = 1, 2. These parameters are explained in section 5.3. We propose two methods for solving for these parameters. In the first method we first find the atomic position around the sample atom from the shape functions and nodal values (see eqn. (5.3)) and then find the best fitting generators by using least-square method [NW06]. This is a simple but not efficient method because the membrane constructed with these generators is highly non-linear with respect to the parameters and lots of successive iterations is required to minimize the square of the offset of the given atoms from the best-fitted membrane.

In the second method we find the parameters by equating the first and second fundamental forms of the generator-based membrane and the corresponding fundamental forms of the FE membrane at each sample atom. The fundamental forms provide us with only 9 equations, not enough to solve for 12 unknowns. On the other hand in all of the examples given in previous sections several parameters were identically zero. For instance in all of them $a_1 = a_2 = 0$. Or a slightly bended sheet with non-zero principle curvatures and arbitrary lattice vectors can be generated if $a_1 = a_2 = 0$ and one of the following: $q_1 = 0$ or $q_2 = 0$ or $\phi = \pi/2$. Therefore we can assume that three of the parameters are given and solve for the rest. This is carefully explained in the following.

5.4.1 First and Second Fundamental Forms of the Monolayer

The monolayer defined in eqns. (5.9) consists of some discrete points, each point corresponds to two integers i and j. But the differential geometry quantities, i.e. the metric tensor and principle curvatures, are defined for continuous surfaces. Therefor we replace integers i and j with real numbers ξ and η , respectively, to define the continuous surface on which all points of eqn. (5.9) lie on it

$$\boldsymbol{x}_{i,j} = \left[(r_2 - r_1) \cos \xi \theta_1 - r_2 (\cos \xi \theta_1 \cos \eta \theta_2 - \sin \xi \theta_1 \sin \eta \theta_2 \cos \phi) - \eta q_2 \sin \xi \theta_1 \sin \phi + r_1 \right] \boldsymbol{n}_3 + \left[(r_2 - r_1) \sin \xi \theta_1 - r_2 (\sin \xi \theta_1 \cos \eta \theta_2 + \cos \xi \theta_1 \sin \eta \theta_2 \cos \phi) + \eta q_2 \cos \xi \theta_1 \sin \phi \right] \bar{\boldsymbol{n}}_1 + \left[\xi q_1 + \eta q_2 \cos \phi + r_2 \sin \eta \theta_2 \sin \phi \right] \boldsymbol{n}_1$$
(5.24)

Then the convected basis vectors (tangent vectors to the surface) are

$$\boldsymbol{g}_{\xi} = \frac{\partial \boldsymbol{x}_{\xi,\eta}}{\partial \xi} = q_{1}\boldsymbol{n}_{1}$$

$$-\theta_{1} [(r_{2} - r_{1})\sin\xi\theta_{1} - r_{2}(\sin\xi\theta_{1}\cos\eta\theta_{2} + \cos\xi\theta_{1}\sin\eta\theta_{2}\cos\phi) + \eta q_{2}\cos\xi\theta_{1}\sin\phi]\boldsymbol{n}_{3}$$

$$+\theta_{1} [(r_{2} - r_{1})\cos\xi\theta_{1} - r_{2}(\cos\xi\theta_{1}\cos\eta\theta_{2} - \sin\xi\theta_{1}\sin\eta\theta_{2}\cos\phi) - \eta q_{2}\sin\xi\theta_{1}\sin\phi]\boldsymbol{\bar{n}}_{1}$$

$$\boldsymbol{g}_{\eta} = \frac{\partial \boldsymbol{x}_{\xi,\eta}}{\partial \eta} = [q_{2}\cos\phi + \theta_{2}r_{2}\cos\eta\theta_{2}\sin\phi]\boldsymbol{n}_{1} \qquad (5.25)$$

$$+ [\theta_{2}r_{2}(\cos\xi\theta_{1}\sin\eta\theta_{2} + \sin\xi\theta_{1}\cos\eta\theta_{2}\cos\phi) - q_{2}\sin\xi\theta_{1}\sin\phi]\boldsymbol{n}_{3}$$

$$+ [\theta_{2}r_{2}(\sin\xi\theta_{1}\sin\eta\theta_{2} - \cos\xi\theta_{1}\cos\eta\theta_{2}\cos\phi) + q_{2}\cos\xi\theta_{1}\sin\phi]\boldsymbol{\bar{n}}_{1}$$

At $\xi=\eta=0$ the basis vectors are

$$\boldsymbol{g}_{\xi} = -\theta_1 r_1 \bar{\boldsymbol{n}}_1 + q_1 \boldsymbol{n}_1 = -\lambda_1 \bar{\boldsymbol{n}}_1 + q_1 \boldsymbol{n}_1$$
$$\boldsymbol{g}_{\eta} = -\theta_2 r_2 \bar{\boldsymbol{n}}_2 + q_2 \boldsymbol{n}_1 = -\lambda_2 \bar{\boldsymbol{n}}_2 + q_2 \boldsymbol{n}_2$$
(5.26)

And the unit normal to the surface is

$$\boldsymbol{N} = \frac{\boldsymbol{g}_{\xi} \times \boldsymbol{g}_{\eta}}{\| \boldsymbol{g}_{\xi} \times \boldsymbol{g}_{\eta} \|} = \boldsymbol{n}_{3}$$
(5.27)

It can be similarly shown that the derivatives of the convected basis vectors at $\xi=\eta=0 \mbox{ are }$

$$g_{\xi,\xi} = \frac{\partial g_{\xi}}{\partial \xi} = \theta_1 \lambda_1 \boldsymbol{n}_3$$

$$g_{\eta,\eta} = \frac{\partial g_{\eta}}{\partial \eta} = \theta_2 \lambda_2 \boldsymbol{n}_3$$

$$g_{\xi,\eta} = \frac{\partial g_{\xi}}{\partial \eta} = \theta_1 (\lambda_2 \cos \phi - q_2 \sin \phi) \boldsymbol{n}_3$$
(5.28)

Hence the curvature tensor is

$$\boldsymbol{K} = \begin{bmatrix} \boldsymbol{g}_{\xi,\xi} \cdot \boldsymbol{N} & \boldsymbol{g}_{\xi,\eta} \cdot \boldsymbol{N} \\ \boldsymbol{g}_{\eta,\xi} \cdot \boldsymbol{N} & \boldsymbol{g}_{\eta,\eta} \cdot \boldsymbol{N} \end{bmatrix} = \begin{bmatrix} \lambda_1 \theta_1 & \Gamma_2 \theta_1 \\ \Gamma_2 \theta_1 & \lambda_2 \theta_2 \end{bmatrix}$$
(5.29)

Where $\Gamma_2 = \lambda_2 \cos \phi - q_2 \sin \phi$. Then the principle curvatures are

$$k_{1} = \frac{1}{2} \left[\lambda_{1}\theta_{1} + \lambda_{2}\theta_{2} + \sqrt{(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2})^{2} + 4\Gamma_{2}^{2}\theta_{1}^{2}} \right]$$

$$k_{2} = \frac{1}{2} \left[\lambda_{1}\theta_{1} + \lambda_{2}\theta_{2} - \sqrt{(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2})^{2} + 4\Gamma_{2}^{2}\theta_{1}^{2}} \right]$$
(5.30)

And the corresponding non-normalized principle directions are

$$\mathbf{V}_{1} = \begin{cases} v_{1} \\ 1 \end{cases}; \quad v_{1} = \frac{1}{2\Gamma_{2}\theta_{1}} \left[(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2}) + \sqrt{(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2})^{2} + 4\Gamma_{2}^{2}\theta_{1}^{2}} \right] \\
\mathbf{V}_{2} = \begin{cases} v_{2} \\ 1 \end{cases}; \quad v_{2} = \frac{1}{2\Gamma_{2}\theta_{1}} \left[(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2}) - \sqrt{(\lambda_{1}\theta_{1} - \lambda_{2}\theta_{2})^{2} + 4\Gamma_{2}^{2}\theta_{1}^{2}} \right] \quad (5.31)$$

Note that $v_1v_2 = -1$. For the special case in which $\phi = \pi/2$ and $q_2 = 0$, i.e. when the underlying structure is a square lattice, $\Gamma_2 = 0$ and the principle curvatures and directions are

$$k_{1} = \lambda_{1}\theta_{1} \quad ; \quad \boldsymbol{V}_{1} = \begin{cases} 1\\ 0 \end{cases}$$

$$k_{2} = \lambda_{2}\theta_{2} \quad ; \quad \boldsymbol{V}_{2} = \begin{cases} 0\\ 1 \end{cases}$$
(5.32)

Finally the mean and Gaussian curvatures becomes

$$H = \frac{k_1 + k_2}{2} = \frac{1}{2} \left(\lambda_1 \theta_1 + \lambda_2 \theta_2 \right)$$
 (5.33a)

$$G = k_1 k_2 = \lambda_1 \lambda_2 \theta_1 \theta_2 - \Gamma_2^2 \theta_1^2$$
(5.33b)

5.4.2 Finding the monolayer's generators from the first and second fundamental forms

In the previous section we assumed that the generators of the almost OS are known and we found the corresponding parameters of a continuous membrane. Now assume that the geometry of the FE membrane is given. The principle curvatures k_1 and k_2 , principle directions v_1 and v_2 and the embedded convected basis vectors $\mathbf{g}_1 = g_1 \mathbf{e}_1$ and $\mathbf{g}_2 = g_2 \mathbf{e}_2$ at each quadrature (equivalently sample atom) can be derived from appendix D. Here we find the generators $f_1 = (\mathbf{Q}_1 | (\mathbf{I} - \mathbf{Q}_1)\mathbf{r}_1 + \mathbf{q}_1)$ and $f_2 =$ $(\mathbf{Q}_2 | (\mathbf{I} - \mathbf{Q}_2)\mathbf{r}_2 + \mathbf{q}_2)$ of the almost OS. The unknowns are $r_1, r_2, q_1, q_2, \theta_1, \theta_2, \mathbf{n}_1$ and \mathbf{n}_2 . We cannot solve for the unknowns because we have 10 unknowns and only 9 equations. Note that the principle directions give us only one equation because they are related by $v_1v_2 = -1$. So we have to pick one of the unknowns and assign a value to it. In this section we solve for the unknowns for two cases. In the first case we assume that q_2 is zero and in the second one we assume $\phi = \pi/2$. (a) First case: $q_2 = 0$

We first start from equations (5.30) and (5.31) and evaluate the sum of the principle curvatures and principle directions

$$\lambda_1 \theta_1 + \lambda_2 \theta_2 = k_1 + k_2$$

$$\lambda_1 \theta_1 - \lambda_2 \theta_2 = (v_1 + v_2) \Gamma_2 \theta_1$$
(5.34)

It can also be easily shown that $\Gamma_2 \theta_1$ is

$$\Gamma_2 \theta_1 = \lambda_2 \theta_1 \cos \phi = \frac{k_1 - k_2}{v_1 - v_2}$$
(5.35)

Therefor $\lambda_1 \theta_1$ and $\lambda_2 \theta_2$ are

$$\lambda_1 \theta_1 = \frac{k_1 v_1 - k_2 v_2}{v_1 - v_2} \tag{5.36a}$$

$$\lambda_2 \theta_2 = \frac{k_2 v_1 - k_1 v_2}{v_1 - v_2} \tag{5.36b}$$

Furthermore, according to eqns. (5.26)

$$\boldsymbol{g}_{\xi} = g_{\xi} \boldsymbol{e}_{\xi} = -\lambda_1 \bar{\boldsymbol{n}}_1 + q_1 \boldsymbol{n}_1 \quad \Rightarrow \quad \lambda_1^2 + q_1^2 = g_{\xi}^2 \tag{5.37a}$$

$$\boldsymbol{g}_{\eta} = g_{\eta} \boldsymbol{e}_{\eta} = -\lambda_2 \bar{\boldsymbol{n}}_2 \quad \Rightarrow \quad \bar{\boldsymbol{n}}_2 = \boldsymbol{e}_{\eta} \quad ; \quad \lambda_2 = -g_{\eta}$$
 (5.37b)

If the angle between e_{ξ} and e_{η} is ψ then by taking the scalar product of them we get

$$\lambda_1 \cos \phi + q_1 \sin \phi = g_\xi \cos \psi \tag{5.38}$$

Combining (5.38) with (5.37a) and eliminating q_1 results

$$\lambda_1^2 - 2g_{\xi}\cos\psi\cos\phi\lambda_1 + g_{\xi}^2(\cos^2\psi - \sin^2\phi) = 0$$
 (5.39)

Also by combining (5.35), (5.36a) and (5.37b) we get the following relation between ϕ and λ_1

$$\cos\phi = -\frac{\lambda_1}{g_\eta} \frac{k_1 - k_2}{k_1 v_1 - k_2 v_2} \tag{5.40}$$

Now we substitute (5.40) into (5.39) and solve for λ_1

$$\lambda_1 = \pm g_{\xi} g_{\eta} \sin \psi \left[g_{\eta}^2 + 2g_{\xi} g_{\eta} \cos \psi \frac{k_1 - k_2}{k_1 v_1 - k_2 v_2} + g_{\xi}^2 \left(\frac{k_1 - k_2}{k_1 v_1 - k_2 v_2} \right)^2 \right]^{-0.5}$$
(5.41)

We can chose one of the solutions derived above because both give the same structure. Solving for the rest of the unknowns results

$$\lambda_{1} = g_{\xi}g_{\eta}\sin\psi\Xi$$

$$q_{1} = g_{\xi}(g_{\eta}\cos\psi + g_{\xi}\Lambda)\Xi$$

$$\cos\phi = -g_{\xi}\sin\psi\Lambda\Xi$$

$$\sin\phi = (g_{\xi}\Lambda\cos\psi + g_{\eta})\Xi$$

$$\theta_{1} = \frac{1}{\lambda_{1}}\frac{k_{1}v_{1} - k_{2}v_{2}}{v_{1} - v_{2}}$$

$$\theta_{2} = \frac{-1}{g_{\eta}}\frac{k_{2}v_{1} - k_{1}v_{2}}{v_{1} - v_{2}}$$
(5.42)

where

$$\Lambda = \frac{k_1 - k_2}{k_1 v_1 - k_2 v_2}$$

$$\Xi = \left(g_{\eta}^2 + 2g_{\xi} g_{\eta} \cos \psi \Lambda + g_{\xi}^2 \Lambda^2\right)^{-0.5}$$
(5.43)

Finally we derive the axis of the orthogonal tensors Q_1 and Q_2 , i.e. n_1 and n_2 . Denote $n_3 = e_{\xi} \times e_{\eta}$ as the normal to the surface. Then

$$\boldsymbol{n}_2 = \bar{\boldsymbol{n}}_2 \times \boldsymbol{n}_3$$
$$\boldsymbol{n}_1 = \boldsymbol{n}_2 \cos \phi - \bar{\boldsymbol{n}}_2 \sin \phi$$
$$\bar{\boldsymbol{n}}_1 = \boldsymbol{n}_2 \sin \phi + \bar{\boldsymbol{n}}_2 \cos \phi \qquad (5.44)$$

where $\bar{\boldsymbol{n}}_2 = \boldsymbol{e}_{\eta}$ was derived earlier.

(b) second case $\phi = \pi/2$

Similarly we can show that if $\phi=\pi/2$

$$\lambda_{1} = g_{\xi}g_{\eta}\sin\psi\Xi , \quad \lambda_{2} = g_{\eta}(g_{\eta} - g_{\xi}\Lambda\cos\psi)\Xi$$

$$q_{1} = g_{\xi}(g_{\eta}\cos\psi - g_{\xi}\Lambda)\Xi , \quad q_{2} = -g_{\xi}g_{\eta}\sin\psi\Lambda\Xi$$

$$\theta_{1} = \lambda_{1}^{-1}(k_{1}v_{1} - k_{2}v_{2})/(v_{1} - v_{2}) , \quad \theta_{2} = \lambda_{2}^{-1}(k_{2}v_{1} - k_{1}v_{2})/(v_{1} - v_{2})$$

$$\boldsymbol{n}_{1} = \Xi[-g_{\xi}\Lambda\boldsymbol{e}_{\xi} + g_{\eta}\boldsymbol{e}_{\eta}] , \quad \boldsymbol{n}_{2} = (\sin\psi)^{-1}\Xi[(g_{\xi}\Lambda\cos\psi - g_{\eta})\boldsymbol{e}_{\xi} + (g_{\eta}\cos\psi - g_{\xi}\Lambda)\boldsymbol{e}_{\eta}]$$

$$(5.45)$$

where

$$\Lambda = \frac{k_1 - k_2}{k_1 v_1 - k_2 v_2}$$

$$\Xi = \left(g_{\eta}^2 - 2g_{\xi}g_{\eta}\cos\psi\Lambda + g_{\xi}^2\Lambda^2\right)^{-0.5}$$
(5.46)

For the special case $\Gamma_2 = 0$ they become

$$\lambda_{1} = g_{\xi} \sin \psi , \quad \lambda_{2} = g_{\eta}$$

$$q_{1} = g_{\xi} \cos \psi , \quad q_{2} = 0$$

$$\theta_{1} = k_{1}/(g_{\xi} \sin \psi) , \quad \theta_{2} = k_{2}/g_{\eta}$$

$$\boldsymbol{n}_{1} = \boldsymbol{e}_{\eta} , \quad \boldsymbol{n}_{2} = (\cos \psi \boldsymbol{e}_{\eta} - \boldsymbol{e}_{\xi})/\sin \psi$$
(5.47)

5.5 Numerical examples

5.5.1 Bending a graphene sheet coarse-grained with uniform mesh

In order to show the power of our model and verify it we perform both full-atomistic and multiscale calculations and compare the results. We simulate a graphene sheet consisting 86822 atoms interacting via Tersoff potential (Figure 5.6). The large spheres in the pictures are the repatoms. The coarse-grained model consists 441 repatoms (each repatom represents about 200 atoms). The initial graphene is slightly bended to bias the upward deformation. We gradually push all four corners along the diagonals and calculate the upward displacement and total energy. These values are plotted in Figure 5.7. As it is obvious from the figures the results of our model closely matches with full atomistic calculation. The speed-up of our model is significant as the multiscale calculation took about 10 hours on a CPU while the full atomistic simulation took more than 1100 hours on the same computer.



Figure 5.6: Coarse-grained membrane being pushed from the corners. (a) Initial and (b) deformed configurations. The colors show the vertical displacement with red being the highest and blue with no displacement.



Figure 5.7: (a) The energy change vs. displacement (b) Displacement of the center point vs. displacement

5.5.2 Localized deformation in graphene

In order to show that our model is capable of capturing localized deformations, we simulate a graphene sheet consisting about 4000 atoms with an indenter pushing the center point. Figure 5.8a depicts the multiscale graphene which is coarse-grained only in the regions away from the center point. Figure 5.8b shows the indenter force with respect to vertical displacement of the center point. The increasing slope of this figure indicates that graphene sheets softens as point loads increases.

5.5.3 Interaction of lipid-bilayer with nano-particles

We use the solvent-free coarse-grained potential proposed in [YHL+10] to model the interactions between lipid molecules. The simple anisotropic pair-wise interaction and solvent-free nature of this potential along with the promising results make it a desirable model for the simulation of biological and biomimetic membranes. Particles modeled with it can be robustly self assemble into membranes with experimentally relevant bending rigidity. The particles' orientations play an important role in the strengths of the interactions. The main difference between the form of this potential and Lennard-Jones is the existence of the orientation of the particles. The lipid - nano-particle interactions are modeled with a LJ-type potential [SC12]. We put two



Figure 5.8: (a) The deformed coarse-grained graphene (b) Force applied by the indenter vs. displacement of the center point.

or five nano-particles away from the lipid-bilayer but within the cut-off radius of their interaction. In both simulations we observed that the nano-particles first try to approach the membrane. Then the localized deformations around the nano-particles lead them to self-assemble into a one-dimensional or two-dimensional ensembles of particles. In Figure 5.9 and Figure 5.10 the deformation evolution of these simulations is plotted. The last pictures in both figures correspond to the equilibrium configuration.


Figure 5.9: The interaction of two nano-particles with the lipid-bilayer. Small particles are non-repatoms.



Figure 5.10: The interaction of five nano-particles with the lipid-bilayer.

Conclusion and Future Works

6

In this thesis the structural symmetries has been incorporated to speed-up three molecular modeling frameworks, namely molecular dynamics, phonon analysis and QC-based multiscale method. The promising results in each section push us to move forward to explore more physics related to nano- and bio- structures.

In chapter 3 we used the OS framework to study the effect of chirality, strain rate, pre-stretching and initial temperature on the mechanical properties and failure modes of pristine single-walled nanotubes. We could also study their effect on multiwalled or already defected nanotubes. We can also use our model to simulate a bundle of nanotubes in networks or composites.

Thermo-elasticity of nanotubes was another important result of chapter 3. In particular we heuristically showed that strain rate does not affect the mechanical properties of nanotubes prior to the failure. We can do more robust study on this issue by relating their OMD results to the statistical mechanics data.

In chapter 4 we developed a symmetry-adapted phonon analysis method by using the OS framework. Our speed-up was significant comparing to conventional phonon models. We can use this property to study more physics (for instance heat conductivity and sound behavior) on large structures.

In chapter 5, we used the notion of OS and developed a novel multiscale technique for multiscale molecular modeling of membranes. Our method extends the quasicontinuum method which is suitable for bulk crystals to non-crystalline but highly symmetric materials. This enables us to model membranes as well as wide range of materials including but not limited to bio-materials, graphene and nanotubes. We can improve the model by adding the internal atomic shifts associated with multilattices [TSBK99].

We can also demonstrate the importance of the model to engineered drug-delivery applications. This includes the modeling of human cells and the interaction of cell membranes with drug capsules. It would be interesting to come up with a strategy towards engineered drug-delivery that is both cell-specific and with controlledrelease-rate. We can then study the interaction between different cell membranes and drug-capsules and the motion of drug molecules through the cells.

Appendix A

Block-Diagonalization of Hessians of Periodic Crystals

In this appendix, we rewrite the standard Discrete Fourier Transform (DFT) in the notation of matrices and apply this to block-diagonalize the Hessian of a periodic crystal. This enables a conceptual understanding of the relation between blockdiagonalization in crystals and OS.

A.1 Discrete Fourier transform and its properties

Consider a space with coordinate y. Define the points y_p :

$$y_p = y_{(p_1, p_2, p_3)} = p_1 a_1 + p_2 a_2 + p_3 a_3$$
 (A.1)

where $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ is a basis for the space.

Consider a family of periodic functions $\hat{\boldsymbol{u}}_{p,l}$ that are defined at \boldsymbol{y}_p , with the family indexed by l. Physically, these correspond to the displacement of the atom l in the unit cell at \boldsymbol{y}_p . From the periodicity, it follows that $\hat{\boldsymbol{u}}_{p+N,l} = \hat{\boldsymbol{u}}_{p,l}$, where $\boldsymbol{N} := (N_1, N_2, N_3)$ defines the periodicity.

Define the reciprocal basis through $a_{\alpha} \cdot b_{\beta} = \delta_{\alpha\beta}$ and the wave vectors as

$$\boldsymbol{k}_{\boldsymbol{q}} = \boldsymbol{k}_{(q_1, q_2, q_3)} = \frac{2\pi q_1}{N_1} \boldsymbol{b}_1 + \frac{2\pi q_2}{N_2} \boldsymbol{b}_2 + \frac{2\pi q_3}{N_3} \boldsymbol{b}_3$$
(A.2)

It follows that $\mathbf{k}_{q} \cdot \mathbf{y}_{p} = \frac{2\pi}{N_{1}} p_{1}q_{1} + \frac{2\pi}{N_{2}} p_{2}q_{2} + \frac{2\pi}{N_{3}} p_{3}q_{3}$, or in one-dimension $\mathbf{k}_{q} \cdot \mathbf{y}_{p} = \frac{2\pi}{N} pq$.

These imply that $\mathbf{k}_q \cdot \mathbf{y}_p = \mathbf{k}_p \cdot \mathbf{y}_q$. It also follows that $\exp[i\mathbf{k}_q \cdot \mathbf{y}_0] = \exp[i\mathbf{k}_q \cdot \mathbf{y}_N] =$ 1 and that $\sum_{j=0}^{N-1} \exp[i\mathbf{k}_p \cdot \mathbf{y}_j] \exp[-i\mathbf{k}_q \cdot \mathbf{y}_j] = N\delta_{pq}$. As we see below, $\exp[i\mathbf{k}_p \cdot \mathbf{y}_q]$ are the components of the basis vectors of the eigenspace of a circulant matrix, and are closely related to the eigenspace for a block-circulant matrix.

The DFT is defined as

$$\tilde{u}_{\boldsymbol{p},l}^{\alpha} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} \exp[i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{q}}] \hat{u}_{\boldsymbol{q},l}^{\alpha} \Leftrightarrow \tilde{\boldsymbol{u}} = \boldsymbol{F}\hat{\boldsymbol{u}}$$

where $N = N_1 N_2 N_3$ and \boldsymbol{F} is the DFT matrix which is independent of l and α . The inverse DFT is

$$\hat{u}_{\boldsymbol{p},l}^{\alpha} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} \exp[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \boldsymbol{y}_{\boldsymbol{p}}] \tilde{u}_{\boldsymbol{q},l}^{\alpha} \Leftrightarrow \hat{\boldsymbol{u}} = \boldsymbol{F}^{-1} \tilde{\boldsymbol{u}}$$
(A.3)

This enables us to now represent the standard DFT in terms of matrix notation. For simplicity, consider a one-dimensional problem, i.e. $\boldsymbol{p} = (p, 0, 0)$ and $\boldsymbol{q} = (q, 0, 0)$, and p and q run over the integers between 0 and N-1. The matrix \boldsymbol{F} can be expressed as

$$\boldsymbol{F} = \begin{bmatrix} [\boldsymbol{F}_{00}] & [\boldsymbol{F}_{01}] & \cdots & [\boldsymbol{F}_{0(N-1)}] \\ [\boldsymbol{F}_{10}] & [\boldsymbol{F}_{11}] & \cdots & [\boldsymbol{F}_{1(N-1)}] \\ \vdots & \vdots & \ddots & \vdots \\ [\boldsymbol{F}_{(N-1)0}] & [\boldsymbol{F}_{(N-1)1}] & \cdots & [\boldsymbol{F}_{(N-1)(N-1)}] \end{bmatrix}$$
(A.4)

and each sub-matrix of \boldsymbol{F} is a $3M \times 3M$ matrix and defined as $[\boldsymbol{F}_{pq}]_{mn} = \frac{1}{\sqrt{N}} \exp[i\boldsymbol{k}_p \cdot \boldsymbol{y}_q] \delta_{mn}$.

The inverse of the Fourier transform matrix \boldsymbol{F}^{-1} is defined as

$$\boldsymbol{F}^{-1} = \begin{bmatrix} [\boldsymbol{F}_{00}^{-1}] & [\boldsymbol{F}_{01}^{-1}] & \cdots & [\boldsymbol{F}_{0(N-1)}^{-1}] \\ [\boldsymbol{F}_{10}^{-1}] & [\boldsymbol{F}_{11}^{-1}] & \cdots & [\boldsymbol{F}_{1(N-1)}^{-1}] \\ \vdots & \vdots & \ddots & \vdots \\ [\boldsymbol{F}_{(N-1)0}^{-1}] & [\boldsymbol{F}_{(N-1)1}^{-1}] & \cdots & [\boldsymbol{F}_{(N-1)(N-1)}^{-1}] \end{bmatrix}$$
(A.5)

where $[\boldsymbol{F}_{pq}^{-1}]_{mn} = \frac{1}{\sqrt{N}} \exp[-i\boldsymbol{k}_q \cdot \boldsymbol{y}_p] \delta_{mn}.$

With these definitions, $F^{-1} = F^{\dagger}$, where † represents the adjoint, and therefore F is unitary.

A.2 Block-diagonalization of a block-circulant matrix using the discrete Fourier transform

Consider a block-circulant matrix, i.e. $A_{pq} = A_{0(q-p)}$, as arises in periodic crystals. The DFT provides the block-diagonal matrix $\tilde{A} = FAF^{-1}$.

$$\tilde{\boldsymbol{A}}_{pq} = \sum_{\boldsymbol{m}} \sum_{\boldsymbol{n}} \boldsymbol{F}_{pm} \boldsymbol{A}_{mn} \boldsymbol{F}_{nq}^{-1}$$

$$= \sum_{\boldsymbol{m}} \sum_{\boldsymbol{n}} \left(\frac{1}{\sqrt{N}} \exp[i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{m}}] \boldsymbol{I} \right) \boldsymbol{A}_{mn} \left(\frac{1}{\sqrt{N}} \exp[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \boldsymbol{y}_{\boldsymbol{n}}] \boldsymbol{I} \right)$$

$$= \frac{1}{N} \sum_{\boldsymbol{m}} \sum_{\boldsymbol{n}} \exp\left[i\boldsymbol{y}_{\boldsymbol{m}} \cdot \left(\boldsymbol{k}_{\boldsymbol{p}} - \boldsymbol{k}_{\boldsymbol{q}}\right)\right] \exp\left[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \left(\boldsymbol{y}_{\boldsymbol{n}} - \boldsymbol{y}_{\boldsymbol{m}}\right)\right] \boldsymbol{A}_{mn}$$

$$= \frac{1}{N} \sum_{\boldsymbol{m}} \sum_{\boldsymbol{n}} \exp\left[i\boldsymbol{y}_{\boldsymbol{m}} \cdot \left(\boldsymbol{k}_{\boldsymbol{p}} - \boldsymbol{k}_{\boldsymbol{q}}\right)\right] \exp\left[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \left(\boldsymbol{y}_{\boldsymbol{n}} - \boldsymbol{y}_{\boldsymbol{m}}\right)\right] \boldsymbol{A}_{0(\mathbf{n}-\mathbf{m})} \quad (A.6)$$

Relabeling r = n - m, we can write $y_r = y_n - y_m$.

$$\tilde{\boldsymbol{A}}_{\boldsymbol{p}\boldsymbol{q}} = \frac{1}{N} \sum_{\boldsymbol{m}} \sum_{\boldsymbol{r}} \exp\left[i\boldsymbol{y}_{\boldsymbol{m}} \cdot \left(\boldsymbol{k}_{\boldsymbol{p}} - \boldsymbol{k}_{\boldsymbol{q}}\right)\right] \exp\left[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \boldsymbol{y}_{\boldsymbol{r}}\right] \boldsymbol{A}_{0\boldsymbol{r}}$$
$$= \sum_{\boldsymbol{r}} \exp\left[-i\boldsymbol{k}_{\boldsymbol{q}} \cdot \boldsymbol{y}_{\boldsymbol{r}}\right] \boldsymbol{A}_{0\boldsymbol{r}} \delta_{\boldsymbol{p}\boldsymbol{q}}$$
(A.7)

using that $\sum_{j=0}^{N-1} \exp[i\mathbf{k}_p \cdot \mathbf{y}_j] \exp[-i\mathbf{k}_q \cdot \mathbf{y}_j] = N\delta_{pq}$. Therefore, $\tilde{\mathbf{A}}$ is block-diagonal. Further, since $\mathbf{F}\mathbf{F}^{\dagger} = \mathbf{I}$, we have

$$Aw = \lambda w \Rightarrow FAF^{\dagger}Fw = \lambda Fw \Rightarrow \tilde{A}\tilde{w} = \lambda \tilde{w}$$
 (A.8)

Consider the specific case of the eigenvalue problem (4.5) in a periodic crystal where \hat{H} is a block-circulant matrix. From (A.7), \tilde{H} is block-diagonal and consequently the eigenvalue problem can be expressed as $(\omega^2)^{[p]}\tilde{u}_p = \tilde{H}_{pp}\tilde{u}_p$, where $\tilde{H}_{pp} = \sum_r \exp\left[-ik_p \cdot y_r\right]\hat{H}_{0r}$.

For each \boldsymbol{p} , corresponding to a specific wave-vector \boldsymbol{k} in (A.1,A.2), we obtain 3M eigenvalues and eigenvectors corresponding to the different phonon branches. Denote each branch by $\nu = 1, \dots, 3M$, so we can write $(\omega^2)^{[\boldsymbol{p},\nu]} \tilde{\boldsymbol{u}}_{\boldsymbol{p}}^{[\nu]} = \tilde{\boldsymbol{H}}_{\mathbf{pp}} \tilde{\boldsymbol{u}}_{\boldsymbol{p}}^{[\nu]}$. In real-space, the atomic displacements corresponding to the normal mode with wave vector $\boldsymbol{k}_{\boldsymbol{p}}$ and ν -th branch is $\hat{\boldsymbol{u}}_{\boldsymbol{q},l}^{[\boldsymbol{p},\nu]} = \frac{1}{\sqrt{N}} \exp[-i\boldsymbol{k}_{\boldsymbol{p}} \cdot \boldsymbol{y}_{\boldsymbol{q}}] \tilde{\boldsymbol{u}}_{\boldsymbol{p},l}^{[\nu]}$.

Appendix B

Cubic B-splines as FEM Shape Functions

B.1 One-dimensional elements

In standard finite element method, shape functions provide a methodology to approximate the continuous model using the information given at a set of points. Several methods, such as Lagrange polynomials, Hermit functions and splines, are available for deriving the shape functions. Lagrange and Hermit functions interpolate the nodal values while splines may or may not interpolate the nodal values depending on how they are defined. Lagrange polynomials only provide us with C^0 continuity irrespective of the bases and make the nodal values to be continuous. On the other hand Hermit functions and splines can be defined such that the derivatives of the nodal points be also continuous. However, for C^k , $k \ge 1$ continuity, Hermit functions requires more efforts to construct and the degree of the resulting polynomials are higher comparing to splines. In other words, the degree of the resulting polynomials are in the order of 2k + 1 for Hermit functions while for splines they are in the order of k + 1. Splines have proven to be efficient in finite element analysis requiring C^k , $k \ge 1$ continuity.

B.1.1 Cubic b-splines for one-dimensional elements

The cubic b-splines of an element between nodes (knots) i and i + 1 with local coordinate $-1 \le \alpha \le 1$ are

$$\begin{cases} S_{i-1}(\alpha) = \frac{1}{48}(1-\alpha)^3 \\ S_i(\alpha) = \frac{1}{48}(23-15\alpha-3\alpha^2+3\alpha^3) \\ S_{i+1}(\alpha) = \frac{1}{48}(23+15\alpha-3\alpha^2-3\alpha^3) \\ S_{i+2}(\alpha) = \frac{1}{48}(1+\alpha)^3 \end{cases}$$
(B.1)

$$u(\alpha, t) = \sum_{j=i-1}^{i+2} S_j(\alpha) \bar{u}_j(t).$$
 (B.2)

The derivatives of the shape functions are

$$\begin{cases} dS_{i-1}/d\alpha = \frac{-1}{16}(1-\alpha)^2 \\ dS_i/d\alpha = \frac{1}{16}(1+\alpha)(3\alpha-5) \\ dS_{i+1}/d\alpha = \frac{1}{16}(1-\alpha)(3\alpha+5) \\ dS_{i+2}/d\alpha = \frac{1}{16}(1+\alpha)^2 \end{cases}$$
(B.3)

$$\begin{cases}
 d^{2}S_{i-1}/d\alpha^{2} = \frac{1}{8}(1-\alpha) \\
 d^{2}S_{i}/d\alpha^{2} = \frac{-1}{8}(1-3\alpha) \\
 d^{2}S_{i+1}/d\alpha^{2} = \frac{-1}{8}(1+3\alpha) \\
 d^{2}S_{i+2}/d\alpha^{2} = \frac{1}{8}(1+\alpha)
\end{cases}$$
(B.4)

Note that the splines defined above constitute the partition of unity, that is, for any α

$$\sum_{j=i-1}^{i+2} S_j(\alpha) = 1$$
 (B.5)

B.1.2 Shape functions of boundary elements

Consider the interval $[x_1, x_N]$ divided into N - 1 elements. The approximation (B.2) can be only used for internal elements, because approximating the first and the last elements requires the displacements of nodes 0 and N + 1, respectively. But

both points are out of the domain and are not defined in the FEM formulation. Disregarding their contributions will contradict the partition of unity identity (B.5). In order to overcome this issue we introduce two fake nodes 0 and N + 1. Then, we calculate their displacements such that the approximation (B.2) be interpolatory at the end nodes 1 and N. For instance, (B.2) approximates the displacement of the first node as

$$u(x_1) = \sum_{j=0}^{3} S_j(\alpha = -1)\bar{u}_j = \frac{1}{6}(\bar{u}_0 + \bar{u}_2) + \frac{2}{3}\bar{u}_1$$
(B.6)

The displacement of the fake node \bar{u}_0 is defined such that (B.2) be interpolatory at node 1, i.e. $u(x_1) = \bar{u}_1$. Hence

$$\bar{u}_0 = 2\bar{u}_1 - \bar{u}_2 \tag{B.7}$$

We can get rid of these fake nodes in our calculations by modifying the shape functions of the boundary elements. This can be done for the first element by substituting (B.7) into (B.2)

$$u(\alpha) = \sum_{j=0}^{3} S_j(\alpha) \bar{u}_j = \left[S_1(\alpha) + 2S_0(\alpha) \right] \bar{u}_1 + \left[S_2(\alpha) - S_0(\alpha) \right] \bar{u}_2 + S_3(\alpha) \bar{u}_3 = \sum_{j=1}^{3} \tilde{S}_j(\alpha) \bar{u}_j$$
(B.8)

where \tilde{N}_j , j = 1, 2, 3 are modified shape functions of the first element and are equal to

$$\begin{cases} \tilde{S}_{1}(\alpha) = S_{1}(\alpha) + 2S_{0}(\alpha) = (25 - 21\alpha + 3\alpha^{2} + \alpha^{3})/48\\ \tilde{S}_{2}(\alpha) = S_{2}(\alpha) - S_{0}(\alpha) = (22 + 18\alpha - 6\alpha^{2} - 2\alpha^{3})/48\\ \tilde{S}_{3}(\alpha) = S_{3}(\alpha) \end{cases}$$
(B.9)

Similarly we can approximate the last element by

$$u(\alpha) = \sum_{j=N-2}^{N} \tilde{S}_j(\alpha) \bar{u}_j \tag{B.10}$$

where the corresponding modified shape functions are

$$\begin{cases} \tilde{S}_{N}(\alpha) = S_{N}(\alpha) + 2S_{N+1}(\alpha) = (25 + 21\alpha + 3\alpha^{2} - \alpha^{3})/48\\ \tilde{S}_{N-1}(\alpha) = S_{N-1}(\alpha) - S_{N+1}(\alpha) = (22 - 18\alpha - 6\alpha^{2} + 2\alpha^{3})/48\\ \tilde{S}_{N-2}(\alpha) = S_{N-2}(\alpha) \end{cases}$$
(B.11)

B.2 Shape functions of two-dimensional elements

Consider a mesh constructing quadrilateral elements with nodes $\{\bar{x}_i\}, i = 1, \dots, NM$ where N and M are the number of nodes in two different directions. The shape functions of the two-dimensional elements are the product of the corresponding onedimensional functions defined in equations (B.1, B.9, B.11), i.e.

$$S_i(\alpha,\beta) = S_i(\alpha)S_i(\beta) \tag{B.12}$$

Then the membrane surface is interpolated as

$$\boldsymbol{x}(\alpha,\beta,t) = \sum_{i} S_{i}(\alpha,\beta)\bar{\boldsymbol{x}}_{i}(t).$$
(B.13)

Appendix C

Evaluation of the derivative of the potential energy for multiscale analysis

In chapter 5 we derived the expression for the coarse-grained energy (eqn. (5.4)). The energy minimization procedure through conjugate-gradient method requires the first derivative with respect to its arguments. In this appendix we simplify the evaluation of the derivative of (5.4) for pair and specific bond-order potentials.

The potential energy is mathematically defined as a function of the positions of all atoms. But many popular potentials including pair and bond-order potentials are written in terms of the distances between the atoms. Nevertheless, it can be shown that all potentials can be written in terms of only the distances between the particles [TM11]. This is the result of the frame-indifference of the energy. In other words

$$E_{s} = E_{s}(\{\boldsymbol{x}_{j}^{h} | j \in \Omega_{s}\}) = \hat{E}_{s}(\{\boldsymbol{x}_{ij}^{h} | i, j \in \Omega_{s}, j > i\})$$
(C.1)

where $x_{ij}^h = |\boldsymbol{x}_i^h - \boldsymbol{x}_j^h|$ is the distance between atoms *i* and *j*.

C.1 Pair potentials

For pair potentials such as Lennard-Jones and Morse, equation (C.1) can be broken to a summation of the energy of every bond

$$\hat{E}_s = \frac{1}{2} \sum_{\substack{j \in \Omega_s \\ j \neq s}} V_{sj}(x_{sj}) \tag{C.2}$$

Then, it can be shown that the minimizing equation (5.4) turns to

$$\frac{\partial W^{h}}{\partial \bar{\boldsymbol{x}}_{r}} = \frac{1}{2} \sum_{s=1}^{N_{S}} n_{s} \left[\sum_{\substack{j \in \Omega_{s} \\ j \neq s}} \frac{\partial V_{sj}}{\partial x_{sj}^{h}} \frac{\boldsymbol{x}_{sj}^{h}}{x_{sj}^{h}} [N_{r}(\xi_{s}, \eta_{s}) - N_{r}(\xi_{j}, \eta_{j})] \right] = 0$$
(C.3)

C.2 Bond-order potentials

For bond-order potentials such as Tersoff and Brenner potentials, the form of the energy at each site is

$$\hat{E}_{s} = \frac{1}{2} \sum_{\substack{j \in \Omega_{s} \\ j \neq s}} V_{sj}(x_{sj}, \{x_{sk}, x_{jk} | k \in \Omega_{s}, k \neq j\})$$
(C.4)

Then, it can be shown that the minimizing equation (5.4) turns to

$$\frac{\partial W^{h}}{\partial \bar{\boldsymbol{x}}_{r}} = \frac{1}{2} \sum_{s=1}^{N_{S}} n_{s} \Biggl\{ \sum_{\substack{j \in \Omega_{s} \\ j \neq s}} \left(\frac{\partial V_{sj}}{\partial x_{sj}^{h}} + \sum_{\substack{k \in \Omega_{s} \\ k \neq s, j}} \frac{\partial V_{sk}}{\partial x_{sj}^{h}} \right) \frac{\boldsymbol{x}_{sj}^{h}}{\boldsymbol{x}_{sj}^{h}} \Biggl[N_{r}(\xi_{s}, \eta_{s}) - N_{r}(\xi_{j}, \eta_{j}) \Biggr] + \sum_{\substack{j \in \Omega_{s} \\ j \neq s}} \sum_{\substack{k \in \Omega_{s} \\ k \neq s, j}} \left(\frac{\partial V_{sj}}{\partial x_{jk}^{h}} + \frac{\partial V_{sk}}{\partial x_{jk}^{h}} \right) \frac{\boldsymbol{x}_{jk}^{h}}{\boldsymbol{x}_{jk}^{h}} N_{r}(\xi_{j}, \eta_{j}) \Biggr\} = 0$$
(C.5)

Appendix D

Deriving differential geometry quantities from FE mesh

FEM framework gives us the membrane deformation in terms of the dimensionless quantities α and β defined in (B.12). We use isoparametric mapping to calculate the convected basis vectors of the membrane which requires the derivation with respect to ξ and η .

$$\boldsymbol{g}_{\xi} = \frac{\partial \boldsymbol{x}}{\partial \xi} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial \xi} \bar{\boldsymbol{x}}_{i} \quad , \quad \boldsymbol{g}_{\eta} = \frac{\partial \boldsymbol{x}}{\partial \eta} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial \eta} \bar{\boldsymbol{x}}_{i}$$
(D.1)

and the derivatives of the convected basis vectors are

$$\boldsymbol{g}_{\xi,\xi} = \sum_{i=1}^{r} \frac{\partial^2 S_i}{\partial \xi^2} \bar{\boldsymbol{x}}_i \quad , \quad \boldsymbol{g}_{\eta,\eta} = \sum_{i=1}^{r} \frac{\partial^2 S_i}{\partial \eta^2} \bar{\boldsymbol{x}}_i \quad , \quad \boldsymbol{g}_{\xi,\eta} = \sum_{i=1}^{r} \frac{\partial^2 S_i}{\partial \xi \partial \eta} \bar{\boldsymbol{x}}_i \tag{D.2}$$

where r is the number of nodes within the one-ring of the element. For a regular quadrilateral mesh r = 16. We must express $\partial S_i / \partial \xi$, $\partial S_i / \partial \eta$, $\partial^2 S_i / \partial \xi^2$, $\partial^2 S_i / \partial \eta^2$ and $\partial^2 S_i / \partial \xi \partial \eta$ in terms of α and β . Because of the inverse form of equation (B.13) by the chain rule of differentiation we write

$$\begin{cases} \frac{\partial S_{i}}{\partial \alpha} \\ \frac{\partial S_{i}}{\partial \beta} \\ \frac{\partial S_{$$

The matrix H is similar to the element Jacobian matrix J. In fact Jacobian matrix is the first 2×2 block of H with determinant

$$|\mathbf{J}| = \frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \beta} - \frac{\partial \eta}{\partial \alpha} \frac{\partial \xi}{\partial \beta}$$
(D.4)

The determinant of \boldsymbol{H} is $|\boldsymbol{H}| = |\boldsymbol{J}|^4$ which is a function of only the components

of the Jacobian. The inverse of \boldsymbol{H} is

$$\boldsymbol{H}^{-1} = \frac{1}{|\boldsymbol{J}|^2} \begin{bmatrix} \frac{\partial \eta}{\partial \beta} |\boldsymbol{J}| & -\frac{\partial \eta}{\partial \alpha} |\boldsymbol{J}| & 0 & 0 & 0 \\ -\frac{\partial \xi}{\partial \beta} |\boldsymbol{J}| & \frac{\partial \xi}{\partial \alpha} |\boldsymbol{J}| & 0 & 0 & 0 \\ \frac{\partial \xi}{\partial \beta} C_1 - \frac{\partial \eta}{\partial \beta} C_2 & \frac{\partial \eta}{\partial \alpha} C_2 - \frac{\partial \xi}{\partial \alpha} C_1 & \left(\frac{\partial \eta}{\partial \beta}\right)^2 & \left(\frac{\partial \eta}{\partial \alpha}\right)^2 & -2\frac{\partial \eta}{\partial \beta} \frac{\partial \eta}{\partial \alpha} \\ \frac{\partial \xi}{\partial \beta} C_3 - \frac{\partial \eta}{\partial \beta} C_4 & \frac{\partial \eta}{\partial \alpha} C_4 - \frac{\partial \xi}{\partial \alpha} C_3 & \left(\frac{\partial \xi}{\partial \beta}\right)^2 & \left(\frac{\partial \xi}{\partial \alpha}\right)^2 & -2\frac{\partial \xi}{\partial \beta} \frac{\partial \xi}{\partial \alpha} \\ \frac{\partial \xi}{\partial \beta} C_5 - \frac{\partial \eta}{\partial \beta} C_6 & \frac{\partial \eta}{\partial \alpha} C_6 - \frac{\partial \xi}{\partial \alpha} C_5 & -\frac{\partial \xi}{\partial \beta} \frac{\partial \eta}{\partial \beta} & -\frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \alpha} & \frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \beta} + \frac{\partial \eta}{\partial \alpha} \frac{\partial \xi}{\partial \beta} \end{bmatrix}$$
(D.5)

where the coefficients C_1, \cdots, C_6 are

$$C_{1} = \frac{1}{|\mathbf{J}|} \left[\left(\frac{\partial \eta}{\partial \beta} \right)^{2} \frac{\partial^{2} \eta}{\partial \alpha^{2}} + \left(\frac{\partial \eta}{\partial \alpha} \right)^{2} \frac{\partial^{2} \eta}{\partial \beta^{2}} - 2 \frac{\partial \eta}{\partial \alpha} \frac{\partial \eta}{\partial \beta} \frac{\partial^{2} \eta}{\partial \alpha \partial \beta} \right]$$

$$C_{2} = \frac{1}{|\mathbf{J}|} \left[\left(\frac{\partial \eta}{\partial \beta} \right)^{2} \frac{\partial^{2} \xi}{\partial \alpha^{2}} + \left(\frac{\partial \eta}{\partial \alpha} \right)^{2} \frac{\partial^{2} \xi}{\partial \beta^{2}} - 2 \frac{\partial \eta}{\partial \alpha} \frac{\partial \eta}{\partial \beta} \frac{\partial^{2} \xi}{\partial \alpha \partial \beta} \right]$$

$$C_{3} = \frac{1}{|\mathbf{J}|} \left[\left(\frac{\partial \xi}{\partial \alpha} \right)^{2} \frac{\partial^{2} \eta}{\partial \beta^{2}} + \left(\frac{\partial \xi}{\partial \beta} \right)^{2} \frac{\partial^{2} \eta}{\partial \alpha^{2}} - 2 \frac{\partial \xi}{\partial \alpha} \frac{\partial \xi}{\partial \beta} \frac{\partial^{2} \eta}{\partial \alpha \partial \beta} \right]$$

$$C_{4} = \frac{1}{|\mathbf{J}|} \left[\left(\frac{\partial \xi}{\partial \alpha} \right)^{2} \frac{\partial^{2} \eta}{\partial \beta^{2}} + \left(\frac{\partial \xi}{\partial \beta} \right)^{2} \frac{\partial^{2} \xi}{\partial \alpha^{2}} - 2 \frac{\partial \xi}{\partial \alpha} \frac{\partial \xi}{\partial \beta} \frac{\partial^{2} \xi}{\partial \alpha \partial \beta} \right]$$

$$C_{5} = \frac{1}{|\mathbf{J}|} \left[- \frac{\partial \xi}{\partial \beta} \frac{\partial \eta}{\partial \beta} \frac{\partial^{2} \eta}{\partial \alpha^{2}} - \frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \beta} \frac{\partial^{2} \eta}{\partial \beta^{2}} + \left(\frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \beta} + \frac{\partial \eta}{\partial \alpha} \frac{\partial \xi}{\partial \beta} \right) \frac{\partial^{2} \eta}{\partial \alpha \partial \beta} \right]$$

$$C_{6} = \frac{1}{|\mathbf{J}|} \left[- \frac{\partial \xi}{\partial \beta} \frac{\partial \eta}{\partial \beta} \frac{\partial^{2} \xi}{\partial \alpha^{2}} - \frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \alpha} \frac{\partial^{2} \xi}{\partial \beta^{2}} + \left(\frac{\partial \xi}{\partial \alpha} \frac{\partial \eta}{\partial \beta} + \frac{\partial \eta}{\partial \alpha} \frac{\partial \xi}{\partial \beta} \right) \frac{\partial^{2} \xi}{\partial \alpha \partial \beta} \right]$$
(D.6)

The coefficients of H and H^{-1} can be computed by using the coordinate trans-

formation (B.13), that is

$$\frac{\partial\xi}{\partial\alpha} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial\alpha} \xi_{i} \quad , \quad \frac{\partial\xi}{\partial\beta} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial\beta} \xi_{i}$$

$$\frac{\partial\eta}{\partial\alpha} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial\alpha} \eta_{i} \quad , \quad \frac{\partial\eta}{\partial\beta} = \sum_{i=1}^{r} \frac{\partial S_{i}}{\partial\beta} \eta_{i}$$

$$\frac{\partial^{2}\xi}{\partial\alpha^{2}} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\alpha^{2}} \xi_{i} \quad , \quad \frac{\partial^{2}\xi}{\partial\beta^{2}} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\beta^{2}} \xi_{i} \quad , \quad \frac{\partial^{2}\xi}{\partial\alpha\partial\beta} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\alpha\partial\beta} \xi_{i}$$

$$\frac{\partial^{2}\eta}{\partial\alpha^{2}} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\alpha^{2}} \eta_{i} \quad , \quad \frac{\partial^{2}\eta}{\partial\beta^{2}} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\beta^{2}} \eta_{i} \quad , \quad \frac{\partial^{2}\eta}{\partial\beta^{2}} = \sum_{i=1}^{r} \frac{\partial^{2}S_{i}}{\partial\alpha\partial\beta} \eta_{i} \qquad (D.7)$$

where the shape functions are evaluated at the quadrature points. With these definitions the convected basis vectors and their derivatives are

$$\begin{cases} \boldsymbol{g}_{\xi} \\ \boldsymbol{g}_{\eta} \\ \boldsymbol{g}_{\xi,\xi} \\ \boldsymbol{g}_{\eta,\eta} \\ \boldsymbol{g}_{\xi,\eta} \end{cases} = \boldsymbol{H}^{-1} \begin{bmatrix} \frac{\partial S_1}{\partial \alpha} & \frac{\partial S_2}{\partial \alpha} & \cdots & \frac{\partial S_r}{\partial \alpha} \\ \frac{\partial S_1}{\partial \beta} & \frac{\partial S_2}{\partial \beta} & \cdots & \frac{\partial S_r}{\partial \beta} \\ \frac{\partial^2 S_1}{\partial \alpha^2} & \frac{\partial^2 S_2}{\partial \beta^2} & \frac{\partial^2 S_2}{\partial \alpha\beta} & \cdots & \frac{\partial^2 S_r}{\partial \beta^2} \\ \frac{\partial^2 S_1}{\partial \alpha \partial \beta} & \frac{\partial^2 S_2}{\partial \beta} & \frac{\partial^2 S_2}{\partial \alpha \beta} & \cdots & \frac{\partial^2 S_r}{\partial \alpha \beta} \end{bmatrix} \begin{cases} \bar{\boldsymbol{x}}_1 \\ \bar{\boldsymbol{x}}_2 \\ \vdots \\ \bar{\boldsymbol{x}}_r \end{cases}$$
(D.8)

Both matrices appearing in (D.8) are functions of isoparametric elements and do not vary as the nodal values change. We can calculate them once for every sample atom at the beginning of the simulation. The time-dependence of the basis vectors and their derivatives are built in the nodal positions $\bar{x}_1, \dots, \bar{x}_r$.

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