Nanocrystalline Nanowires: 2. Phonons

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ABSTRACT

Nanocrystalline nanowires (NCNW) are fragments of bulk crystals that are infinite in only one direction. A construction is given for calculating eigenstates belonging to the symmetry labels (k,m) (wavevector and rotational quantum number). Vibrational harmonic eigenstates are worked out explicitly for a simple model, illustrating the general results: the LA mode has $m = 0$, while with sufficient rotational symmetry, the TA branch is doubly degenerate, has $m = \pm 1$, and has quadratic dispersion with k for k less than the reciprocal diameter of the NCNW. The twiston branch (a fourth Goldstone boson) is an acoustic $m = 0$ branch, additional to the LA and two TA branches.

For most nanoparticles, except carbon nanotubes (CNTs),[1,2] we have limited information about atomic structure or vibrational spectra. Nanowires (also known as nanorods)[3] repeat periodically after a distance c in the growth (z) direction. Many materials with known 3-D crystal structures may be grown as nanowires, whose structure is based on a fragment of the bulk crystal, or a metastable relative.[4] This helps with guessing where atoms might be, as discussed in the previous paper.[5] I call these systems nanocrystalline nanowires (NCNW). This paper is about phonons in NCNWs. The phonon is a propagating vibrational wave. Propagation is permitted by translational symmetry. Because the translations are an Abelian group, the vibrational eigenstates can be chosen as eigenstates of translation, with eigenvalue $\exp(ikc)$ under translation by $c\hat{z}$. Such states, with frequency $\omega(k)$, are used to make propagating wavepackets, with group velocity $v(k) = d\omega(k)/dk$.

Usually a NCNW will have some rotational symmetry around the z-axis. In 3-D crystals, rotations do not commute with translations, so it is impossible to use rotational symmetry to simplify the eigenvalue problem, except at special k-points, which are invariant under rotation. However, because NCNWs have translational symmetry only in one direction, all rotations, simple or screw, around this axis commute among themselves and with the translations. Translations and rotations can therefore be simultaneously diagonalized. This means that the eigenvalue of rotation by angle φ, namely $\exp(im\varphi)$, with m the rotational quantum number, an integer, can be used as an additional label for eigenstates.

Corresponding ideas for CNTs have been explained and exploited for both electronic single-particle eigenstates[6] and phonons.[2,7] However, the 2-D surface net,[8] which explains CNTs, is not a very valuable tool for NCNWs. Similarly, the full apparatus of line and rod groups[9] is not much needed here. The concepts we need are the unit wedge and the symmetry-adapted basis vectors that span the space under consideration: the space of displacements of atoms. The space of single-particle electronic wavefunctions can be treated by exact analogy.

Let us take as an example, $z = c$-axis hexagonal close-packed (hcp) NCNWs, illustrated in Figure 1. The NCNW is assumed to grow symmetrically around an axis, which can be chosen either as a 3-fold simple axis passing through an atom or a 6-fold screw axis passing through a symmetrical empty site.[10] The minimum size NCNW of the 6-fold kind is the main example used here. It has three atoms in the plane $z = 0$ and three more rotated by 60° in the plane $z = c/2$. In ideal packing of touching spheres, the hcp parameter a is the sphere diameter, and $c = \sqrt{(8/3)}a$. Every atom of this nanowire can be generated by choosing one with coordinates $x = (a/\sqrt{3})\,\hat{x}$, $y = z = 0$, and applying translations by Lc, $\hat{T}(L) = \hat{T}^L$, and screw rotations by $2\pi\lambda/6$, $\hat{R}^\lambda = (C_6|c/2)^\lambda$, with screw translation $\lambda c/2$. The integers obey $\lambda \in (0,1,2,3,4,5)$, and $L \in (-N/2 + 1, ..., N/2)$. After generating N double layers, it is convenient to imagine everything repeated periodically in the usual Born−von Karman fashion. Thus there are 6N atoms in the NCNW, and one atom in the "unit wedge", which generates the structure. Two equivalent versions of the unit wedge are shown in Figure 1. Larger NCNWs with 6-fold rotational symmetry are generated by having more atoms in the unit wedge.

Each atom now has a label $i = (L,\lambda,n)$, where i is a composite index; the last index n denotes a particular atom of the unit wedge and is not needed in our primitive example with only one atom. It is inconvenient that atoms of index

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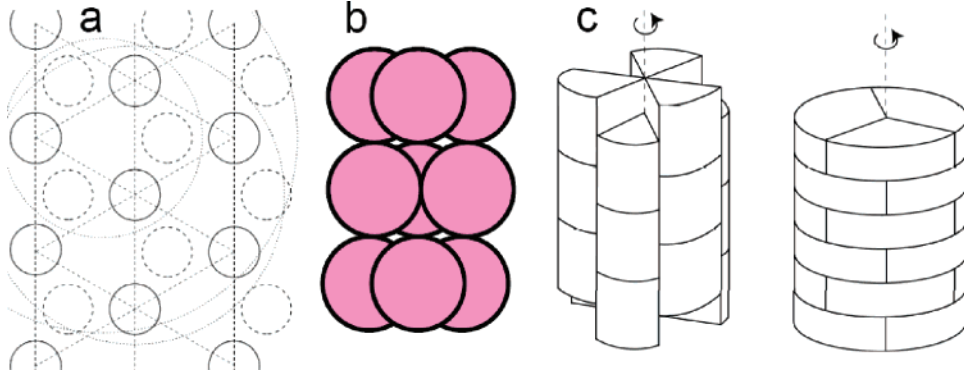
Figure 1. (a) A z-projection of an hcp crystal, showing atoms in the $z = 0$ plane as closed circles, and in the $z = c/2$ plane as dashed circles. The dotted circles illustrate various ways of cutting a NCNW out of the crystal. The smallest dotted circle gives the NCNW shown in (b). It has a 6-fold screw axis ($C_6|c/2$) with translation by $(c/2)\,\hat{z}$ for each $2\pi/6$ rotation. The structure is drawn with $c/a = 2$ rather than with the ideal value 1.633. In (a), the intermediate dotted circle shows a NCNW grown on a 3-fold axis, while the largest dotted circle shows a larger 6-fold NCNW. (c) Equivalent definitions of a unit wedge for a 6-fold hcp NCNW. The small 6-fold NCNW has only one atom in the unit wedge, while the next larger one has four.

L, with $\lambda = 2,3$, lie in a layer higher by c than atoms with the same index L and $\lambda = 0,1$. Similarly, atoms with the same L and $\lambda = 4,5$ are higher by $2c$. To simplify the notation, a layer index l is used, which is the same as L when $m = 0,1$ but equal to $L - 1$ for $m = 2,3$ and $L - 2$ for $m = 4,5$. Now atoms labeled by $(l\lambda n)$ all lie in the same double layer.

We are interested in normal mode solutions of Newton equations for the displacement components $u_{i\alpha} = \langle i\alpha|u\rangle$ of the ith atom in the α direction. The vector $|u\rangle$ has dimension 3 times $6N$ for the three components of the $6N$ displacements. Instead of atom basis vectors $|i\alpha\rangle$, it is desirable to use a basis of eigenstates of $\hat{T}$ and $\hat{R}$. Start with any vector $|pn\rangle$ that is zero except on the nth atom of the "first" wedge $i = (l = 0, m = 0, n)$, and define

$$|kmnp\rangle = \frac{1}{\sqrt{\rho N}}\sum_{l}\sum_{\lambda} e^{-ikz(l\lambda n) - im\phi(l\lambda n)}\hat{T}^{L}\hat{R}^{\lambda}|pn\rangle \quad (1)$$

where the number of rotations ρ is 6 in our example, and where $z(l,\lambda,n)$ and $\varphi(l,\lambda,n)$ are the height and azimuth of atom (l,λ,n). The eigenvalue property is

$$\hat{T}^{M}\hat{R}^{\mu}|knmp\rangle = e^{i\phi_{M\mu}(km)}|kmnp\rangle \quad (2)$$

$$\phi_{M\mu}(km) = [kc]M + [2\pi m/\rho + kc]\mu \quad (3)$$

Equation 1 differs from the usual Bloch–Floquet basis used for translations only. For crystals, the starting basis vector $|pn\rangle$ is simply translated to new positions, but for NCNWs, the basis vector has to be rotated as well. For vector atomic displacements, this is naturally accomplished by expressing each atom's displacement vector in local cylindrical coordinates, $\hat{r},\hat{t},\hat{z}$, pointing locally in the radial, tangential, and axial ($\hat{z}$) direction of each atom, respectively. Under rotations around the $\hat{z}$ axis, these components on one atom rotate simply into corresponding components on other atoms. The designator p in $|kmnp\rangle$ thus stands for one of the three cylindrical directions $\hat{r},\hat{t},\hat{z}$.
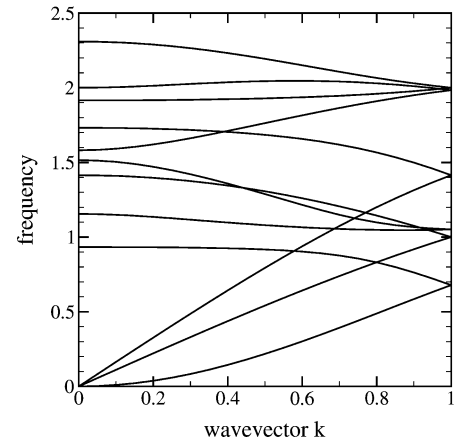

Figure 2. All 18 normal modes vs wavevector for the one-atom unit wedge. The wavevector is relative to π/c, and the frequency to $\sqrt{(K/M)}$

Time reversal symmetry in bulk crystals gives the mode degeneracy between **k** and −**k**. In NCNWs, the corresponding degeneracy is $\omega(k,m) = \omega(-k,-m)$. There is an additional *modular* symmetry in NCNWs with screw rotations. The quantum numbers k and m are defined only *modulo* $2\pi/c$ and ρ ($\rho = 6$ in our example.) But wavevector and angular quantum numbers modulate each other in an interesting way. According to eq 3,

$$\phi_{M\mu}(k + 2\pi/c, m) = \phi_{M\mu}(k, m + \rho/2) + 2\pi M \quad (4)$$

This will show up in the spectrum as $\omega(k + 2\pi/c, m) = \omega(k, m + \rho/2)$. Even though k is only meaningful *modulo* $2\pi/c$, that is, in the range $-\pi/c < k < \pi/c$; nevertheless, if we compute outside this range, the branch that had quantum number m inside the range smoothly evolves into $m + \rho/2$ outside that range. This will appear in Figure 2 as a double degeneracy at the point $k = \pi/c$ and is used in Figure 3 to simplify the plotting of ω vs k. The interpretation of this equation is that adding $2\pi/c$ to the k-vector causes a phase shift of π between sites separated by $c/2$, while adding $\rho/2$ to the m quantum number accomplishes exactly the same phase shift.

The basis vector construction, eq 1, does not work for atoms that lie on the $\hat{z}$ axis. The solution is to omit the sum over rotations λ. Then it is necessary to pick "by hand" the starting vector $|pn\rangle$ to transform according the rotational representation m. For displacement vectors, the unit vector $\hat{z}$ transforms as $m = 0$, while $\hat{x} \pm i\hat{y}$ transform according to $m = \pm 1$. Our example has no on-axis atoms. In simple cases where there are atoms on the axis, the rotations would have no screw component like $c/2$.

The 3 times $6N$ coupled equations of motion, in harmonic approximation, become

$$\hat{M}\frac{d^2}{dt^2}|u\rangle = -\hat{K}|u\rangle \tag{5}$$

where $\hat{M}$ is the mass matrix and $\hat{K}$ is the force constant matrix, the second derivative of the total potential. Take as the simplest model nearest-neighbor spring forces

$$V_{\text{tot}} = \frac{K}{2}\sum_{\langle ij\rangle}(|\vec{r}_i - \vec{r}_j| - a)^2 \approx$$

$$\frac{K}{2}\sum_{\langle ij\rangle}[(\vec{R}_i - \vec{R}_j)\cdot(\vec{u}_i - \vec{u}_j)/a]^2 \tag{6}$$

The second form of eq 6 is the harmonic expansion of the first, where the atom coordinate $\vec{r}_i$ is written as the symmetric position $\vec{R}_i$ plus the deviation $\vec{u}_i$ and the sum goes over each nearest neighbor pair, with $|\vec{R}_i - \vec{R}_j|$ equal to a, with ideal close-packing assumed. The components of the bond stretches in cylindrical coordinates are

$$\frac{1}{a}(\vec{R}_i - \vec{R}_0)\cdot(\vec{u}_i - \vec{u}_0) = \frac{\sqrt{3}}{2}(u_{i,r} + u_{0,r}) \pm \frac{1}{2}(u_{i,t} - u_{0,t})$$
$$\text{(in-plane) (7a)}$$

$$\frac{1}{a}(\vec{R}_i - \vec{R}_0)\cdot(\vec{u}_i - \vec{u}_0) = \frac{1}{2\sqrt{3}}(u_{i,r} + u_{0,r}) \pm \frac{1}{2}(u_{i,t} - u_{0,t}) \pm$$
$$\sqrt{\frac{2}{3}}(u_{i,z} - u_{0,z}) \text{ (out-of-plane) (7b)}$$

for the two in-plane neighbors and the four out-of-plane neighbors of each atom. The plus sign is used with u_t when the neighbor angular position is ahead, and with u_z when the neighbor has vertical coordinate above. Otherwise the minus sign is used.

By using eqs 1 and 7, the force constant matrix eq 5 can be constructed. The $m = 0$ part is

$$\hat{K}(k,0) = \begin{vmatrix} \frac{10}{3} + \frac{1}{3}\cos z & 0 & i\frac{2\sqrt{2}}{3}\sin z \\ 0 & 1 - \cos z & 0 \\ -i\frac{2\sqrt{2}}{3}\sin z & 0 & \frac{8}{3}(1 - \cos z) \end{vmatrix} \tag{8}$$

where $z = kc/2$ and $-\pi/2 < z < \pi/2$. For z outside this range, but $|z| < \pi$, this is the $m = 3$ matrix. The numbering scheme
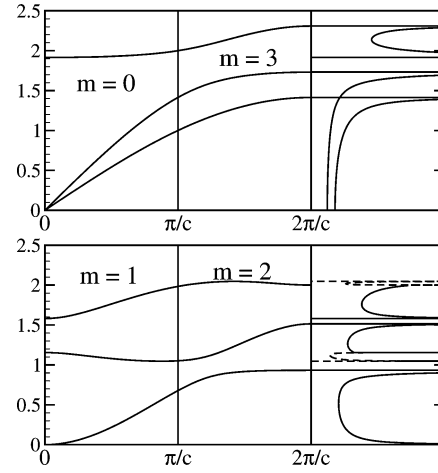

Figure 3. States segregated by rotational quantum number m and unfolded around $k = \pi/c$. The density of states is plotted on the right for each band. The dashed curves are regions where the density of states is plotted after reduction by 10 in order to fit on the graph.

for rows and columns is $(1,2,3) = (r,t,z)$. The spring constant K has been set to 1. The $m = 1$ (and $m = 2$ when k is increased) matrix is

$$\hat{K}(k,1) = \begin{vmatrix} \frac{13}{12} + \frac{1}{6}\cos z & i\left(\frac{3}{4} + \frac{1}{2}\cos z\right) & i\frac{\sqrt{2}}{3}\sin z \\ -i\left(\frac{3}{4} + \frac{1}{2}\cos z\right) & \frac{7}{4} - \frac{1}{2}\cos z & \sqrt{2}\sin z \\ -i\frac{\sqrt{2}}{3}\sin z & \sqrt{2}\sin z & \frac{8}{3} - \frac{4}{3}\cos z \end{vmatrix} \tag{9}$$

The eigenvalues of these matrices are plotted in Figures 2 and 3.

At wavevector $k = 0$, there are four null eigenstates, two in the $m = 0$ channel and one each in the degenerate $m = \pm 1$ channels. When continued to $k \neq 0$, these are the Goldstone bosons associated with the homogeneity of space under translations and rotation around the z-axis. Specifically, uniform z-translations have no restoring force. This gives the null eigenvector of eq 8, $|k = 0, m = 0, z\rangle$, the $k = 0$ longitudinal acoustic (LA) mode. In the $m = 0$ channel, tangential (t) modes decouple from radial (r) and z modes, generating an eigenvalue $1 - \cos z$ of $\hat{K}$ or a vibrational eigenfrequency $\omega_{\text{TW}} = \sqrt{(2K/M)}|\sin(kc/4)|$ which has $m = 0$ for $0 < k < \pi/c$ and $m = 3$ for $\pi/c < k < 2\pi/c$. This acoustic mode, known as the "twiston",[11,12] is the Goldstone boson associated with the nanowire breaking continuous rotational symmetry around the z-axis. Being a pure t mode, it is easy to understand. The $k = 0$ version is a rigid rotation of the whole NCNW around the $\hat{z}$ axis, while $k \neq 0$ versions are torsional oscillations. Such a branch, with $m = 0$, is generic in nanowires, but has been little discussed except in the case of CNTs. The reason for the decoupling of t modes from r and z is that $m = 0$ basis vectors are invariant under reflections in mirror planes containing the $\hat{z}$ axis, $m = 3$ vectors are invariant except for a sign change, but the $m = \pm 1$ and ± 2 vectors have more complicated transformations. Therefore $m = 0,3$ basis vectors and eigenstates are either even (r and z) or odd (t) under such mirrors.
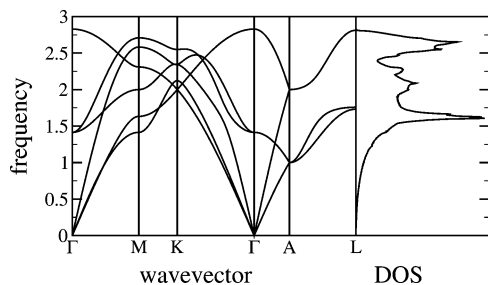
Figure 4. Dispersion curves for the hcp lattice with nearest-neighbor springs. The direction from Γ to A has $\mathbf{k} = (0,0,k_z)$, and the direction from A to L has $\mathbf{k} = (0,k_y,\pi/c)$ where $\hat{y} = (0,1,0)$ points toward a second neighbor in the x,y plane.

In the $m = \pm 1$ channel at $k = 0$, there is an state of pure z polarization with frequency $\sqrt{(4K/3M)}$, with adjacent planes "rocking" in phase, which evolves into one with $k = 2\pi/c$, $m = \pm 2$, and frequency $2\sqrt{(K/M)}$, with adjacent planes rocking out of phase. The r and t modes are mixed. At $k = 0$, the eigenstates are $(|r\rangle \pm i|t\rangle)/\sqrt{2}$. The plus sign is the null state, and the minus sign has frequency $\sqrt{(5K/2M)}$. The null state corresponds to pure in-plane translations $\hat{x}$ and $\hat{y}$ (i.e., transverse acoustic, TA) when appropriate real combinations of $m = \pm 1$ are used, while the other states correspond to the in-plane E_g state of triangular molecules.

A curious feature is that the TA modes have quadratic rather than linear dispersion in k. This is generic to TA modes of NCNWs as long as their wavelengths are long compared with the diameter. The bending energy in continuum approximation is $\int dz (\partial^2 u/\partial z^2)^2$, that is, given by the square of the curvature rather than the square of the strain $\partial u/\partial z$, because constant strain gives uniform bending for which there is no restoring force. The corresponding wave equation relates acceleration to $\partial^4 u/\partial z^4$, giving $\omega \propto k^2$, as is known in the theory of elasticity.[13] It is interesting to ask how this arises from atom displacements. If one uses as a variational trial eigenvector for small k, the exact $k = 0$ state ($|r\rangle + i|t\rangle)/\sqrt{2}$), one gets an acoustic eigenfrequency $\omega = \sqrt{(K/3M)}(kc/2)$. However, the off-diagonal linear-in-k terms of the matrix couple to the $|z\rangle$ state with mixing coefficient $-ikc/4$. When this revised state is used to compute the eigenfrequency, the linear term in the dispersion exactly cancels. This ability of z-components to cancel (within lowest "$\vec{k}\cdot\vec{p}$" perturbation theory) the restoring forces from transverse components of bending is not special to small chains or near-neighbor models, but is general.

The TA branches can be called "bendons" by analogy with the appropriately named "twiston" branch. The analysis here using eigenstates of rotations for the basis makes it clear how the $m = 0$ twiston mode is totally distinct from the $m = \pm 1$ bendon or TA modes. Having $m = 0$ endows the twiston with a special property. Interactions of quasiparticles (for example, electron–phonon or anharmonic phonon–phonon) are governed by symmetry-induced selection rules. In 3-D crystals, the rule $\Delta \vec{k} = 0$ (modulo a reciprocal lattice vector) is a consequence of the destructive interference of

the Bloch–Floquet phases of the translational eigenstates. In the same way, for an NCNW, destructive interference of rotational–translational phases will give selection rules $\Delta k = 0$ (modulo $2\pi/c$) and $\Delta m = 0$ (modulo the rotational index ρ). Therefore, the twiston with $m = 0$ is always available to scatter within an angular momentum channel. The canonical example is backscattering of an electron state from (k,m) to $(-k,m)$. Of course, there are other modes with $m = 0$. In particular, the r and z modes, being even under vertical mirrors, can cause back scattering of $m = 0$ states, whereas the twiston cannot. The $m = \pm 1$ and $m = \pm 2$ states have mixed symmetry under vertical mirrors, and therefore lack mirror selection rules.

Figure 4 shows the phonons of a bulk hcp crystal, computed for the same model of a nearest-neighbor harmonic spring. The points of similarity are (1) a surprisingly similar frequency scale, considering that the number of first neighbors is twice as large compared to the minimal nanowire, and (2) double degeneracy for all states with $k_z = \pi/c$. This latter feature has a technical explanation[14] in the theory of nonsymmorphic space groups. This paper offers a simple algebraic proof using the rotation–translation eigenstates of a nanowire with screw rotations.

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