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Phonon-engineered solids constructed from nanocrystals

Here, we present the concept of colloidal nanocrystal-based solids as solution-processed, phonon-engineered materials. In particular, we discuss superlattice phonons, the vibrational modes associated with the motion of the nanocrystals away from their equilibrium positions in the nanocrystal solid (or superlattice). We calculate the characteristic energies and density of states of these superlattice phonons by modeling the nanocrystal solids as three-dimensional mass-spring networks. In this model, the nanocrystals correspond to the masses and their surface terminating organic or inorganic moieties (i.e., ligands) act as springs. We parameterize this model by determining nanocrystals masses based on crystal size and material density and by using density functional theory to determine the spring constant associated with ligand-mediated bonding between the nanocrystals. We show that by varying the type of nanocrystals, their ligands, and the topology of the nanocrystal superlattice, it is possible to systematically tune the density of states of the superlattice phonons in the energy range of 0.01 meV–10 meV. We then highlight how the construction of binary nanocrystals superlattices can be used, for example, to introduce phononic bandgaps at specific energies. Finally, we show that even with disorder stemming from finite nanocrystal size distributions and variations in the bonding between the nanocrystals and the ligands, distinct superlattice phonons modes will still be present.

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INTRODUCTION

Since phonon engineering allows the manipulation of the elastic, acoustic, and thermal properties of materials, phonon engineered solids are considered paramount for enabling control of the dissipation, insulation, and transmission of heat in next generation electronics as well as for the creation of higher performance thermoelectric devices. Further, they are envisioned for optoacoustic applications, phononic waveguides, signal sensing, and in quantum computing. Phonon engineered solids can be made in various ways, including through the creation of superstructures by layering, alloying, and etching materials or by leveraging low dimensionality materials. In this context, phonon engineering with nanostructures such as phononic crystals, nanorods, and nanocomposites has been explored extensively. Here, we investigate the potential of phonon engineered solids processed from solution using colloidal synthesis as building blocks.

Colloidal nanocrystals are small crystallites made of semiconducting or metallic materials that have 1–10 nm diameters and surfaces which are passivated with organic or inorganic moieties ("ligands"). Through precise control of their synthesis, the composition and size of nanocrystals, and therefore their electronic and optical properties, can be systematically engineered. They can be deposited from solution into solid thin films of wafer-scale dimensions and periodic arrangement of the nanocrystals into highly ordered superlattices can be achieved on a micron scale. The superlattice structure and the lattice constant (interparticle distances) can be determined through small angle x-ray scattering measurements (SAXS) and controlled through the nanocrystal size, size dispersity, choice of ligand, ligand coverage, and the drying dynamics.

A number of studies have focused on the phononic properties of the individual nanocrystals coming from the motion of atoms in the nanocrystal, how they can be systematically tuned, and how these phonon modes couple to their environment. However, relatively little work has been carried out on the long-range vibrations that occur in nanocrystals solids and superlattices consisting of individual nanocrystals. Recently, however, initial work in this direction showed acoustic standing wave excitations. Studies on the thermal transport in such nanocrystal thin films have shown that ligand and...
nanocrystal size can be used to tune the thermal conductivity and highlight the need to understand the complete phononic properties of these systems.\textsuperscript{35,36,37}

Here, we present a mathematical framework for describing the phonons stemming from the vibration of the nanocrystals about their equilibrium positions in the nanocrystal solid, which we refer to as superlattice phonons. We determine realistic parameters for the masses and force constants in nanocrystal superlattices and investigate the phonon density of states, considering the impact of disorder from finite nanocrystal size distributions and variations in ligand coverage and binding. We then show examples of how arrangements of two types of nanocrystals into different superlattice topologies can be used to generate solids with phononic bandgaps.

THREE-DIMENSIONAL MASS-SPRING MODELS

We model the long-range phonon modes in a nanocrystal solid using a three-dimensional mass-spring model with harmonic forces.\textsuperscript{35,36} Here, as shown schematically in Fig. 1(a), the individual nanocrystals correspond to masses, \( m \), and the moieties on the surface of the nanocrystals (i.e., ligands) act as springs with force constant \( k \).

The classical equations of motions for a mass \( m_i \) with displacement \( \vec{u}_i \) from its equilibrium position can be written as the sum of the contributions from all neighbors, \( n \), to which it is interconnected with springs \( k_{ij} \),

\[
m_i \ddot{u}_i = \sum_{l=1}^{n} \sum_{j=1}^{n} k_{ij} (\vec{u}_j - \vec{u}_i).
\]

By expressing the displacement as \( \ddot{u}_i(t) = \ddot{\vec{u}}_i e^{\omega^2 t} \), the system of equations can be rewritten in matrix notation with the mass and spring matrices \( M \) and \( K \) and the displacement matrix \( U \) forming an eigen-system with the eigenvalues \( -\omega^2 \), where \( \omega \) are the normal modes of the system.

The term \( M^{-1}K \) is referred to as the dynamical matrix and can be diagonalized to obtain the vibrational modes of the system and their energies. Analytical solutions exist, among others, for the face-centered cubic (fcc), body-centered cubic (bcc), and simple cubic (sc) systems.\textsuperscript{37–40} They are shown in Fig. 1(b) with the frequency axis normalized by the highest frequency mode (\( \omega_{\text{max}} \)) to emphasize how different nanocrystal packing geometries will result in differing phonon density of states profiles. The peaks in these vibrational spectra correspond to van Hove singularities.\textsuperscript{40} Eigenvalue solutions will scale linearly with \( \sqrt{k/m} \) as shown in Fig. 1(c). Thus, lower frequency (energy) superlattice phonons are expected for systems with weaker effective spring constants and larger mass nanocrystals.

We are interested in introducing realistic nanocrystal parameters, including nonuniform size distributions, nonuniform packaging, and ligand interactions, as well as more complex arrangements of different types of nanocrystals. Such a system lacks a defined unit cell, and Eq. (2) needs to be solved numerically (details in the supplementary material).\textsuperscript{41–43}

Here, the calculations are performed for a system size of 18 \( \times \) 18 \( \times \) 18 unit cells (32\textsuperscript{3} mass positions in total for the bcc structure) with periodic boundary conditions. For the force calculations, only nearest neighbor interactions are included. Due to the finite sized system in a numerical calculation, the resulting density of states profile is discretized, but reflects the true shape of the phonon density of states correctly as shown for the case of \( k/m = 2 \) in Fig. 1(c).

To introduce different degrees of disorder, values for each mass and each spring connection are randomly picked from normal distributions with centers \( \bar{m} \) and \( \bar{k} \), respectively. By increasing the standard deviations of the distributions, \( \sigma \), the disorder of the system is increased. To avoid unphysical negative mass or force constants, the distributions are truncated at zero. Figure 2 shows the impact

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (a) Schematic representation of a nanocrystal solid indicating how the nanocrystals can be considered as masses and the organic or inorganic moieties as springs. (b) Vibrational density of states for perfect, face centered cubic (fcc), body centered cubic (bcc), and simple cubic (sc) mass spring systems. The x-axis is normalized by the highest frequency of the respective lattice systems, \( \omega_{\text{max}} \). (c) The density of states profile for random distributions of different types of nanocrystals. They are shown in Fig. 1(b) with the frequency axis normalized by the highest frequency mode (\( \omega_{\text{max}} \)) to emphasize how different nanocrystal packing geometries will result in differing phonon density of states profiles.
of increased mass disorder [Fig. 2(a)] or spring disorder [Fig. 2(b)] for a bcc lattice, where \( m \) and \( k \) are set to a value of 1 and the disorder is quantified as the ratio of standard deviation to mean value. The case of no disorder is shown in gray shading. As the disorder is further increased, the density of state distribution shifts to a broad peak at lower energy. This is a phenomenon referred to as the boson peak, which is commonly observed in disordered and amorphous structures with only near-range order such as glasses.

We note that disorder in the nanocrystal mass has a larger impact than disorder in the spring constant. This is due to the fact that changing the mass of a single site affects the coupling to all eight nearest neighbors, while changing a spring constant only affects the two masses connected by the spring. In reality, nanocrystal solids will have both mass and spring disorder, and these types of disorder will also cause positional disorder in the superlattice. Greater than 20% size disorder, for example, will hinder superlattice formation and lead to random close packing of particles in a solid.

**PARAMETERIZATION OF THE 3D MASS-SPRING MODEL FOR NANOCRYSTALS**

Determining the vibrational density of states expected from nanocrystal solids requires realistic values as input parameters to the mass-spring model. Different nanocrystal synthesis routes enable different nanocrystal sizes and size distributions, which can be quantified, for example, from transmission electron microscopic (TEM) images (e.g., Weidman et al.\(^{25}\)). The mass of a single nanocrystal can be approximated from the nanocrystal radius and the materials density, by assuming the nanocrystal shape to be spherical. It has been shown that the mass of the surface ligands affects low-frequency acoustic vibrations,\(^{28}\) so the mass loading due to the mass of the ligand needs to be considered when calculating the nanocrystal mass. This additional contribution to the mass depends on the molecular weight and grafting density of the ligand\(^{51}\) and will be of higher relevance for smaller nanocrystals due to a larger surface to volume ratio. An example calculation for the case of PbS nanocrystals can be found in the supplementary material. In general, for nanocrystals with radii ranging from 1 to 10 nm, a typical nanocrystal mass will be in the range of \( 10^{-22} \) to \( 10^{-19} \) kg.\(^{47}\)

To approximate the spring constant of a ligand between the nanocrystals, \( k \), we turn to density functional theory (DFT).\(^{52}\) We calculate the total energy, \( E \), of the system (details in the supplementary material) as a function of the ligand distortion, \( \Delta x \), away from the equilibrium length \( L \) and fit the resulting \( E \) vs \( \Delta x \) dependence with a relation: \( E = k/2(\Delta x)^2 \). With this approach, we perform calculations for two types of ligands: (1) organic dithiol ligands, which have been used extensively in creating electronically active nanocrystal solids,\(^{53,54}\) and (2) inorganic, halide ions, which decrease the inter-nanocrystal spacing enabling even higher mobilities.\(^{27,55–58}\)

First, these calculations are performed for a series of dithiol ligands. Following literature reports,\(^{25,59}\) we assume that dithiol ligands bridge between two nanocrystals by tethering the sulfur atom at each end of the ligand to neighboring nanocrystal surfaces. For each DFT calculation, the ligands then are stretched and compressed along the axis between the functional sulfur groups. The energy vs deformation curves for the case of HDT (stars) is shown in Fig. 3(a).
The quadratic dependence of the energy for small ligand compressions and extensions indicates the applicability of the harmonic approximation. To obtain an effective spring constant value describing how two nanocrystals are linked, the spring constant value for a single ligand needs to be multiplied by the total number of ligands, $N$, bridging between neighboring NCs. $N$ can either be approximated via the ligand grafting density and the NC surface area, or it can be calculated more accurately by considering the surface reconstruction and number of ligand binding sites.\(^7\)

Next, we calculate the spring constant for inorganic halide ions, which can bind to the nanocrystal surface and stabilize the nanocrystals in a lattice electrostatically.\(^{22,61}\) For our calculations, two PbS nanocrystals decorated with $\Gamma^-$, $\text{Cl}^-$, or $\text{Br}^-$ on the Pb-rich $\{111\}$ surfaces are arranged with parallel $\{111\}$ facets. By changing the spacing between the two facets and performing an energy minimization at each step, an energy vs deformation curve can be obtained [e.g., for $\Gamma^-$ ligands in Fig. 3(a) (squares)] from which a spring constant can be extracted. In contrast to the calculation for the thiol ligands, where a single ligand is stretched and compressed, the energy calculations here include all the atoms of the nanocrystal core as well as the ligand atoms. The extracted spring constant value hence already includes the contributions of all inorganic moieties on the $\{111\}$ surface. To find the average spring constant contribution per ligand site, the calculations are repeated systematically for different nanocrystal sizes such that a per ligand spring constant can be determined (see the supplementary material).

The resulting spring constants for various organic and inorganic ligands are presented in Fig. 3(b). For linear hydrocarbon chains, the force constant increases with decreasing ligand length [here, the short 1,2-ethanedithiol (EDT) has a force constant of 82 Nm\(^{-1}\) per ligand site, while 1,2-dodecanedithiol (DDT) has a force constant of 34 Nm\(^{-1}\) per ligand site]. Ligands containing cyclic structures, such as 1,4-benzenedithiol, exhibit a larger force constant (120 Nm\(^{-1}\)) compared to similar length linear ligands (e.g., BDT with 45 Nm\(^{-1}\)), as the benzene ring stiffens the ligand backbone. Compared to the spring constants of the thiols in the range of 34–120 Nm\(^{-1}\), the value of $\approx0.5$ Nm\(^{-1}\) for the halide ions is significantly lower.

Thus, while inorganic ligands tend to improve the electronic coupling between nanocrystals,\(^{62,63}\) they result in weaker long-range vibrational coupling compared to nanocrystals crosslinked with organic ligands.

These calculated values for spring constants in Fig. 3(b) should be taken as upper limits. In our calculation of the spring constant of thiol ligands, we assume that the ligands bridge two nanocrystals. However, if both functional groups tether to the same nanocrystal surface,\(^{32}\) the inter-nanocrystal spring constant will also contain a component coming from weaker van der Waals ligand-ligand interactions and the effective spring constant will be reduced. An effective spring constant for these systems could also be calculated through the same approaches described earlier. We also assume full ligand coverage without steric hindrance and perfect ordering. Misaligned ligands or lower ligand density on the surface also decrease the value of the effective spring constant. Finally, our approach assumes that the nanocrystal surface is not deformed as the ligand stretches and compresses.\(^2\) However, softer atomic surface bonds could also behave as springs, and, because the nanocrystal surface modes can be in a similar energy regime\(^7\) as the superlattice phonons, interactions are likely.

**TUNING THE CHARACTERISTIC ENERGY OF THE SUPERLATTICE PHONONS**

Figure 4(a) plots the characteristic energy of the superlattice phonons $\hbar\omega_{\text{max}}$ as function of the nanocrystal mass ($x$-axis) and ligand spring constant ($y$-axis). The location of several different nanocrystal and ligand systems, which have been experimentally achieved, is indicated, including PbS nanocrystals 1–5 nm in radius with 1,4-benzenedithiol ligands (black triangles) or with 1,2-dodecanedithiol (DDT) ligands (black circles), PbS nanocrystals 0.9–2.2 nm in radius with $\Gamma^-$ ligands (black squares), and Au nanocrystals 10–15 nm in radius with DDT ligands (golden circles). For this parameter space of masses and spring constants, we find that values of $\hbar\omega_{\text{max}}$ for a perfectly ordered system can range from a few 100 $\mu$eV for large, dense nanocrystals linked with low spring constant ligands up to a few millielectronvolt for small nanocrystals linked with rigid ligands.

As sketched out in Fig. 4(b), these superlattice phonons lie predominately below the characteristic phonon energies of the
material itself (i.e., the phonon modes stemming from vibration of the atoms). This highlights a clear element of novelty in phonon engineering afforded by building up solids from nanocrystals. Although the density of these superlattice phonons will be small compared with the vibrational density of states coming from atoms [i.e., there will only be $3N_{NC} \cdot 6$ inter-nanocrystal vibrational modes, where $N_{NC}$ is the number of nanocrystals of compared to $N_{NC}(3N_A - 6)$ vibration modes of atoms, where $N_A$ is the number of atoms in the system], superlattice phonons are low energy, long range vibrations not present in amorphous or crystalline solids. Nanocrystal superlattices thus offer new possibilities for designing the acoustic and thermal transport of materials, particularly at ultralow temperatures, where only superlattice phonons will be thermalized. For example, one can envisage an electronically insulating nanocrystal superlattice with reasonably large thermal conductivity at temperature below 10 K, a regime where high thermal conductivity would typically require high electronic conductivity. Alternatively, one could imagine incorporating nanocrystal superlattices (or superparticles) into resonators to create nanomechanical oscillators for phononic computing operating in the terahertz regime.

Although the characteristic energy of the superlattice phonons is typically an order of magnitude smaller than that of atomic lattice vibrations (i.e., $\sim 0.01$–1 meV vs 1–100 meV), the group velocities of superlattice modes ($v_g \approx \omega/k = \omega a_{SL}/\pi$) will be comparable to the group velocity of atomic vibrations since the lattice constant of the superlattice ($a_{SL} \sim 4$ nm) is an order of magnitude larger than for atomic vibrations ($a \sim 0.4$ nm). With careful design of these nanocrystal structures, one can thus develop thin films that have specifically tuned thermal or acoustic transmission or reflection below 100 K.

**PHONON ENGINEERING WITH BINARY NANOCRYSTAL SUPERLATTICES**

Nanocrystal superlattices containing more than one type of nanocrystal have been achieved and offer unique possibilities for independent tuning of electrical, optical, and thermal properties. For example, for thermoelectric applications, semiconductor and metallic nanocrystals such as PbS and Au can be combined to achieve films of higher electrical conductivity and lower thermal conductivity. Alternatively, one could create a superlattice with two different semiconductor nanocrystals of different materials but sized to have the same bandgap. Because the electronic band structures between the two materials would be offset, oxidation or reduction of one species of nanocrystal would result. The oxidized (or reduced) nanocrystals would thus serve as “dopant” nanocrystals, thereby tuning the free charge carriers to create an electronically doped film without impacting the optical absorption or emission. For example, this could be achieved by mixing two different nanocrystals with the same bandgap energy but made of different materials, such as 1.9 nm radii PbS and 5.1 radii CdSe nanocrystals, which both have bandgaps of 2 eV.

The vibrational spectra of such a binary nanocrystal superlattice is not simply the superposition of the vibrational spectra of the constituents and depends on the arrangement of different nanocrystals in the superlattice. Figure 5(a) shows the distribution expected for a perfectly arranged bcc lattice of 5.1 nm radii CdSe linked with EDT, while Fig. 5(b) shows the distributions for a perfectly arranged bcc lattice of 1.9 radii PbS linked with EDT. First, we consider the case where the heavy and light nanocrystals arranged as multilayers [Fig. 5(c)], which could be easily available for spin-coating, dip coating, or printing of nanocrystals. Additionally, we calculate the case of a center-substituted lattice (i.e., nanocrystals arranged in a CsCl structure) [Fig. 5(d)], which has previously been achieved for Fe$_3$O$_4$/PbSe, Au/Au, and Au/CdSe systems. For both systems, the superlattice contains narrowly distributed high frequency modes opening up a phononic bandgap, which is particularly pronounced in the center-substituted case. Adding even an unrealistically high amount of mass disorder of 20%, broadens the distribution of the higher frequency modes and reduces the energy range of the phononic bandgap [Figs. 5(e) and 5(f)], but does not eliminate it entirely. These two examples highlight how binary nanocrystal superlattices can be used as 2D or 3D phononic crystals, additionally offering tunable electronic and photonic properties depending on application requirements.

**CONCLUSION**

In summary, we show that long range vibrations are expected in nanocrystal solids in the energy range of 0.01 meV–10 meV. The characteristic energy of these vibrations can be changed by varying the size of the nanocrystal, the ligand species surrounding the nanocrystals, and the packing of the nanocrystal in the solid. Finally, as highlighted in our discussion of phonon engineering, the ability to introduce compositional and structural variations in solids using simple solution-based fabrication techniques offers opportunities for creating functional solids with independently tunable electronic, optical, and thermal properties. Simulations indicate that disorder...
values typical in nanocrystal superlattices will result in a smearing out of the distinct features in the vibrational density of states, but that key features will be retained. The approach to material parameterization and mathematical framework presented here can be used to assist with the selection of nanocrystal and ligand systems and the theory-based design of the superlattice to enable solution processed phononic materials and devices.

SUPPLEMENTARY MATERIAL

See supplementary material for details on the approximations used in the model, the numerical methods, example calculations, and additional material on calculating the spring constants of halide ligands.

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