Coupling of Organic and Inorganic Vibrational States and Their Thermal Transport in Nanocrystal Arrays

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Supporting Information

ABSTRACT: Through atomistic computational analysis of thermal transport in nanocrystal arrays (NCAs), we find that vibrational states couple elastically across the organic—inorganic interfaces with a resulting flux that depends on the ligand grafting density and the overlap between the core and ligand vibrational spectra. The modeling was performed using molecular dynamics simulations and lattice dynamics calculations on a gold-dodecanethiol NCA built using a robust self-assembly methodology. Our approach is validated by comparing the predicted NCA thermal conductivities against experimental measurements [Ong et al. Nat. Mater. 2013, 12, 410], with agreement found in both magnitude and trends. The self-assembly methodology enables prediction of general NCA behavior and detailed probing of experimentally inaccessible nanoscale phenomena.

INTRODUCTION

A nanocrystal array (NCA) is a close-packed structure of nanocrystals (i.e., inorganic cores 2–20 nm in diameter encapsulated in a layer of organic ligands) that self-assemble from a colloidal solution. The resulting macroscopic three-dimensional superstructure contains well-ordered domains that can span several micrometers.1–3 This organic–inorganic hybrid material has an electronic band structure that is tunable by modifying the nanocrystal composition and size.3 Because of this tunability and inexpensive solution-based fabrication, NCAs have been proposed as cost-effective and versatile alternatives for expensive single-crystal semiconductors in field-effect transistors,4 memory devices,5 light-emitting diodes,6 photodetectors,7,8 solar cells,9–11 and thermoelectric generators.12–14

Self-assembled monolayers (SAMs) on inorganic bulk substrates are a more well-studied organic–inorganic hybrid system than NCAs.5,16 Although the ligand layer on a nanocrystal resembles a SAM on a curved surface, it is distinctly different from a SAM when the nanocrystal is part of an array. An NCA is a three-dimensional material with interdigitated ligands from neighboring cores that themselves form a higher-order periodicity in the material. In contrast, SAMs are two-dimensional molecular monolayers that self-assemble on bulk inorganic substrates in a regular pattern. The added structural complexities in NCAs pose the question of whether the properties of an NCA can be inferred from those of a comparable SAM.

The electrical and optical properties of NCAs have been actively studied for nearly two decades.3–10,12,13,17–21 In any device technological roadmap, however, thermal management issues are also important,12,25 as device efficiency and lifetime degrade at high operating temperature. We recently reported the first-ever experimental measurements of NCA thermal conductivity, studying the effects of the core diameter and the core and ligand compositions.24 In that work, molecular dynamics (MD) simulations were performed using a rudimentary NCA model built by placing simplified nanocrystal motifs into a linear chain. Each motif was composed of a multitatom spherical core and six ligands (equally spaced and oriented along the three Cartesian directions) that weakly interacted with its nearest neighbors. Together with simple inter- and intramolecular potentials (which we will refer to hereafter as potentials), those MD simulations resulted in thermal conductivity predictions that qualitatively captured the measured trends but not their magnitudes. This single NCA thermal transport study stands in contrast to a collection of experimental measurements25–34 performed on SAMs. Specialized synthesis techniques and the challenges of thermal conductivity metrology hinder experimental investigations of NCAs,24 while the need for a large number of atoms (30 000–500 000)35 and the lack of a good methodology to form a full-scale NCA model impede simulation.

In our prior study,24 we found that surface chemistry mediates thermal transport in NCAs by controlling the...
interfacial thermal conductance between the ligands and the core. What remains unknown is how this interfacial thermal conductance, which cannot be directly measured experimentally, will change with various NCA design parameters.

Questions include the following: Will this interfacial thermal conductance be equivalent to that of a SAM with identical species? Will the interfacial thermal conductance change with nanocrystal diameter and, if so, how? How will the mass of the core atoms affect the interfacial thermal conductance? Another important experimental finding is a thermal conductivity plateau at temperatures higher than the core Debye temperature. This result suggests that elastic rather than inelastic vibrational scattering dominates at the interfaces—a hypothesis that requires testing.

In this work, we investigate the above questions, which cannot be readily answered experimentally, using MD simulations and lattice dynamics calculations. Using existing simulation and experimental observations, we formulate a methodical way to build an NCA model for use in MD-based predictions of thermal conductivity and interfacial thermal conductance. The thermal conductivity predictions are assessed by comparing with existing experimental thermal conductivity measurements and interpreted using effective medium approximations (EMAs). Through these studies, we propose a scaling law for predicting the interfacial thermal conductance and a computationally inexpensive framework for estimating NCA thermal conductivity. In addition, we provide strong evidence for the presence of elastic vibrational scattering at the interfaces in an NCA.

**METHODS**

**Self-Assembly and Validation.** We focus on gold–dodecanethiol (Au–C_{12}H_{25}SH) NCA as our case study. This selection is motivated by the availability of experimental thermal conductivity measurements and well-characterized potentials for modeling the NCA species interactions.

The ability of MD simulations to mimic and predict the behavior of real systems hinges on the appropriate choice of potentials and building a physically realistic simulation structure. Details on the potentials used can be found in the Supporting Information, Table S1. The MD simulations were performed using LAMMPS with a time-step of 1 fs. The ligand vibrational density of states was obtained using harmonic lattice dynamics calculations in GULP, and the density of states for the nanoparticles was obtained using the velocity autocorrelation function from MD simulations.

Previous computational work has addressed the interactions between a few nanocrystals and specifically the role of the ligands and the solvent species. To date, only three studies have created full-scale NCAs. Luedtke and Landman used gold cores of 140 atoms (diameter <2 nm) to study how the NCA assembly is influenced by factors including ligand length and temperature. They found that dodecanethiol-grafted gold nanocrystals form a distorted face-centered cubic (FCC) structure at a temperature of 300 K. Kaushik and Clancy studied how the NCA packing structure changed with different solvents. In their model, alkane ligands were preattached using a carbon–lead bond at a grafting density of 3 ligands/nm² onto hollow-core lead selenide nanocrystals that were explicitly surrounded with solvent molecules. The nanocrystals packed into a FCC structure when the ligand length-to-core diameter ratio was below unity. Recently, Zanjani and Lukes assembled a CdSe–hexylthiol NCA to predict its elastic properties. In their approach, ligands are attached one-by-one to the surface cadmium atoms to create the nanocrystals.

To build a full-scale NCA, it is imperative to start by forming a nanocrystal building block. First, a core ranging from 55 to 3925 atoms was carved from a bulk gold FCC lattice (as-cut...
diameters of 0.9, 1.6, 1.8, 3.0, 4.0, and 5.0 nm). For the smallest three diameters, the core is not spherical but rather octahedral or tetrahedral in shape due to the small number of atoms. We did not use the hollow-core approach of Kaushik and Clancy, as all atoms are required to capture the full spectrum of thermal vibrations. To save computational time, we did not consider the effect of the surrounding solvent molecules on the packing structure, as most experimental NCAs have the FCC structure. In analogy to the colloidal synthesis, the gold core was then surrounded by excess dodecanethiol molecules (Figure 1a) and thermalized at a temperature of 300 K using velocity rescaling for 1 ns and subsequently relaxed under a microcanonical ensemble (i.e., constant mass, volume, and total energy) for an additional 5 ns. During this process, the ligands explored the core potential energy surface and encapsulated the whole core in a monolayer (Figure 1b). The sulfur atom of each ligand was trapped slightly above the hollow sites (2-fold, 3-fold, and 4-fold) between the surface gold atoms of the core—an observation consistent with earlier experimental and computational findings. At some positions, the sulfur atoms embedded into the core. Our approach differs from that of Luedtke and Landman, where butanethiol molecules were lengthened to dodecanethiol after the attachment process. Longer dodecanethiol ligands might cause steric hindrances during ligand attachment that would result in a different topological arrangement on the core surface. Unattached ligands were then filtered and the ligand-passivated nanocrystal was duplicated and stacked in the [111] direction to form an open 3 × 2 × 2 FCC unit cell (Figure 1c). Subsequently, the nanocrystals in this unit cell were induced to close pack into a minimal energy configuration under an isothermal— isoobaric ensemble at a temperature and pressure of 300 K and 0 bar using a Nose—Hoover thermostat and barostat for 5–10 ns (Figure 1d). This close-packed structure was then tiled to obtain the desired NCA thickness (9–90 nm) for thermal conductivity predictions (Figure 1e).

The NCA thermal conductivity, $k_{\text{NCA}}$, is predicted using the direct method in nonequilibrium MD simulations. In this approach, a constant heat flux is imposed across the NCA model by adding and removing an equivalent amount of heat from the two ends. To predict thermal conductivity, the resulting steady-state temperature gradient, $dT/dx$, between regions $L_1$ and $L_2$ is then used in the Fourier law, $\dot{Q} = -k_{\text{NCA}}A(dT/dx)$, where $A$ is the area perpendicular to the heat flow. Thermal conductivity predictions were made at an average system temperature of 300 K with a target temperature difference of $30 \pm 10$ K. Further details can be found in the Supporting Information.

As shown in Figure 2, the full-scale NCA model captures both the magnitude and trend of the experimental thermal conductivity measurements with respect to the film thickness. Both simulation and experiment show a thickness-invariant thermal conductivity. This invariance indicates diffusive thermal transport in the NCAs with scattering from the boundaries playing a negligible role.

Although there is only a single experimental datum in the core diameter series (which agrees with the simulation results, see Figure 4b), the overall simulation trend matches that obtained experimentally for other nanocrystal types. These agreements give confidence to the chosen potentials and their extension to future predictions.

## RESULTS AND DISCUSSION

### Diameter-Dependent Ligand Footprint

The average area occupied by a ligand grafted on a surface, $\sigma$, is termed the ligand footprint and is the reciprocal of the grafting density. The footprint of an optimally grafted alkanethiol SAM on a flat gold surface, $\sigma_{\text{SAM}}$, is $21.6 \pm 0.2 \, \text{Å}^2/\text{ligand}$. Experimental and simulation results, however, suggest that alkanethiols are more closely packed on curved nanocrystal cores, giving a lower footprint at smaller core diameters. Our prior study found that the thermal conductivity of an NCA depends on the diameter, $d$, of its constituent nanocrystals. A natural question is whether the ligand grafting density (i.e., the number of ligands per unit surface area, $1/\sigma$) influences NCA thermal conductivity.

In a prior simulation study, Jimenez et al. found the optimal footprint by changing the surface area required for a predetermined number of ligands to get a net-zero surface pressure across the nanocrystal surface. Our alternative approach of forming an optimally grafted nanocrystal allows the ligands to naturally explore the potential energy surface on a core. Our diameter-dependent footprints, $\sigma_d$, are plotted in Figure 3, normalized by the footprint value for a SAM. The data agree with the geometry-based analytical model of Jimenez et al.

![Figure 2](image-url) Predicted thermal conductivities and corresponding experimental measurements of varying the NCA thickness.

![Figure 3](image-url) Diameter-dependent footprint of dodecanethiol ligands on a gold core. The MD-predicted footprints agree well with predictions from equation 1 (dotted line). The $R^2$ value of the fit is 0.86. See Supporting Information for a discussion of error bars.
Figure 4. EMA investigation for diameter series. (a) Interfacial thermal conductance from the FCC NCA cuboid scales according to eq 2, where \( h_{\text{SAM/gold}} \) is the predicted SAM thermal conductance and \( c = 0.76 \text{ nm} \) is obtained from the footprint scaling law (Figure 3). The red shaded region depicts the uncertainty in the \( h_{\text{SAM/gold}} \) value (see Supporting Information). The value of \( h_{\text{SAM/gold}} \) is plotted as a blue dotted line with its associated uncertainty (blue shaded area). Inset: interfacial thermal conductance shows no temperature dependence between 200 and 400 K, indicating a dominance of elastic scattering between the core and ligands. (b) MD diameter series is well-described by EMA-\( h \) using the interfacial thermal conductance values calculated from eq 3. The red shaded region marks the uncertainty range associated with the EMA-\( h \) model due to the uncertainties in the inputs to eq 2 (see Supporting Information). The EMA-\( h \) trend calculated using \( h_{\text{SAM/gold}} \) underestimates the simulated diameter series by at most 10%. Note that the top axis is nonlinear. The inset identifies the different inputs to the EMA-\( h \) formulation, eq 2.

\[
\frac{\sigma_d}{\sigma_{\text{SAM}}} = \frac{1}{1 + \frac{d}{\alpha}} \tag{1}
\]

giving a fitted \( c \) value of 0.76 nm, which is comparable with the 0.8 nm obtained in the original study. The bigger footprint for the larger cores implies a smaller grafting density due to increased steric hindrance from smaller surface curvature. At the largest nanocrystal diameter of 5 nm, the footprint is 71% of that for the SAM.

**Core Diameter Series.** In simple EMA formulations, the effective thermal conductivity of a composite material is a function of the volume fractions (\( \nu_p, \nu_m \)) and bulk thermal conductivities (\( k_p, k_m \)) of the solid particle and matrix phases.\(^{60}\) By including a finite interfacial thermal conductance, \( h \) (which is a per unit area quantity), between the particle and matrix phases, the resulting formulations have been found to better match experimental measurements for some composites.\(^{36,61}\) The Hasselman–Johnson EMA-\( h \) model for spherical inclusions is

\[
k_{\text{EMA-}h} = k_m \left[ \frac{k_p(1 + 2\alpha) + 2k_m}{k_p(1 + 2\alpha) + 2k_m - u_p[k_p(1 - \alpha) - k_m]} \right] \tag{2}
\]

where \( \alpha \equiv (k_m/h)/(d/2) \). Here, \( \alpha \) can be viewed as a ratio between the matrix Kapitza length and the particle diameter. When the diameter is smaller than or similar in magnitude to the Kapitza length, the interfacial thermal conductance becomes important in determining the composite thermal conductivity. On the other hand, when the diameter is much bigger than the Kapitza length, \( \alpha \) tends to zero, and eq 2 simplifies to an EMA formulation that has no dependence on the interfacial thermal conductance.\(^{36}\)

In our previous study,\(^{24}\) the experimentally measured thermal conductivities of PbS NCAs with diameters greater than 3.5 nm agree with the predictions of eq 2 when the interfacial thermal conductance between the core and ligands is used as a fitting parameter. We now use this EMA-\( h \) model to interpret our simulation predictions. Our MD-based approach allows us to specify all unknown inputs to the EMA-\( h \) formulation in a self-consistent manner, thus requiring no approximations or fitting parameters. To evaluate eq 2, we require the bulk solid thermal conductivities and volume fractions of the particle (i.e., gold core) and the matrix (i.e., dodecanethiol ligands) phases and the interfacial thermal conductance between the particle and the matrix (see schematic diagram in inset in Figure 4b). The volume fraction is determined from the NCA geometry. The bulk solid thermal conductivity of the core is obtained by applying the direct method to a block of FCC gold atoms at an average temperature of 300 K with heat flow in the [111] direction. The resulting thermal conductivity is 1.8 ± 0.3 W/(m K) (details in Supporting Information). This small thermal conductivity of gold compared to its textbook value is due to the absence of electrons in MD simulations. The assumption of neglecting electrons in our model is supported by the negligible electronic contribution to thermal transport in NCAs with dielectric ligands longer than 0.5 nm (the dodecanethiol molecule is 1.5 nm long).\(^{5,24}\) The thermal conductivity of the ligand solid is obtained using the direct method on a solid block of amorphous dodecanethiol ligands at an average temperature of 300 K, to extract a value of 0.15 ± 0.01 W/(m K) (details in Supporting Information).

The last component of the EMA-\( h \) model is the interfacial thermal conductance. This value is obtained by imposing a heat flow on 10% of the gold atoms located in the heart of a central core that is surrounded by 34 other cores to form a FCC NCA.
cuboid with periodic boundary conditions. This arrangement allows heat to flow radially outward from the central core to the surrounding cores, which act as heat sinks. Ligands attached to the central core can be assumed to be isothermal internally and with one another due to the short chain length, strong carbon–carbon bonds, and geometric symmetry of the radial heat flow. The interfacial thermal conductance is obtained by dividing the imposed heat flow by the core surface area and the average temperature difference between the unheated atoms in the central core and the attached ligands. The temperature difference in these simulations is 15 ± 5 K.

The predicted interfacial thermal conductance varies with the core diameter, as seen in Figure 4a. The grafting density, plotted in Figure 3, also changes with diameter. We thus postulate that the thermal energy crossing the inorganic–organic interfaces depends on the number of ligands grafted per unit area on the core. By assuming that the interfacial thermal conductance scales proportionally to the grafting density, a scaling model was derived from eq 1:

\[
\frac{h}{h_{\text{SAM/gold}}} = 1 + \frac{2c}{d}
\]  (3)

Using \(c = 0.76 \text{ nm} \) (as obtained from Figure 3) and \(h_{\text{SAM/gold}} = 220 \pm 20 \text{ MW/(m}^2\text{ K)} \) (the predicted interfacial thermal conductance of a dodecanethiol SAM on a flat Au surface, see Supporting Information), we plot eq 3 in Figure 4a. The good agreement between the raw MD data and eq 3 indicates that the diameter dependence of interfacial thermal conductance (which is a per unit area quantity) can be attributed to the changing ligand grafting density that results from steric hindrance. A smaller core has a larger grafting density, allowing for increased thermal transport per unit area. The agreement between eq 3 and the simulation data also indicates that the interfacial thermal conductance per ligand is independent of core diameter. The per ligand interfacial thermal conductance calculated from the different diameter cores fluctuates between 42 and 62 pW/K, while the SAM/gold interface has a value of 48 ± 4 pW/K. This scaling model provides a computationally inexpensive method for obtaining the diameter dependence of interfacial thermal conductance for other NCA systems. Once the grafting density is known, only one further simulation is required to predict \(h_{\text{SAM/gold}}\) which can then be used in eq 3. Deviations may exist at smaller diameters, where the shape of the nanocrystal core becomes irregular.

As MD is a classical technique where all vibrational states are fully activated, any temperature-related increase in the interfacial thermal conductance will be a result of inelastic scattering at the interface. Inelastic scattering increases the number of pathways for heat to move across interfaces, increasing the interfacial thermal conductance and hence the overall NCA thermal conductivity. As seen from the inset in Figure 4a, the predicted interfacial thermal conductance for a 4.0 nm diameter core is constant between average system temperatures of 200–400 K. This result confirms that, in agreement with our previous assertion, elastic vibrational scattering at the core–ligand interfaces is responsible for the plateau in the experimentally measured NCA thermal conductivity.

The EMA-\(h\) and EMA (setting \(\alpha = 0\) in eq 2) predictions are plotted together with the MD thermal conductivities for the NCA diameter series in Figure 4b. The diameter-dependent interfacial thermal conductance values for EMA-\(h\) are obtained from eq 3. The MD data agree poorly with the EMA predictions but match well with EMA-\(h\) predictions, indicating the importance of including the interfacial thermal conductance in describing the thermal transport in an NCA. The EMA-\(h\) model predicts a thermal conductivity trend with two distinct regimes: (i) diameter independence at small core diameters (\(d < 2 \text{ nm for this system}\)) and (ii) monotonic increase at larger core diameters. Previous experimental measurements were only able to observe the second regime. In comparison, our MD results span a larger diameter range, capturing and verifying the full EMA-\(h\) prediction. We attribute the invariant thermal conductivity at small core diameters, which is close to the bulk ligand value, to the high volume fraction of the matrix phase, which forms a percolating network. The predictions of eq 2 using the single \(h_{\text{SAM/gold}}\) are also plotted in Figure 4b. This set of results is at most 10% lower than the predictions using the diameter-dependent \(h\). This close agreement further substantiates that \(h_{\text{SAM/gold}}\) is a computationally cost-effective approximation for the interfacial thermal conductance needed to predict NCA thermal conductivity in the EMA-\(h\) formulation.

**Core Mass Series.** Experiments found that increasing the core Debye temperature, which is inversely proportional to the square root of atomic mass, increased the NCA thermal conductivity. This result was attributed to an increase in interfacial thermal conductance due to a higher number of overlapping vibrational states between the cores and ligands. This proposition holds true only in the event of elastic vibrational scattering at the core–ligand interfaces—a condition that we validated in the previous section. To further probe the underlying transport physics, we now isolate the core mass effect by using core atoms of different atomic mass while using the same potentials for all interactions.

To create cores of different Debye temperature, we set the core atomic mass to 0.01, 0.05, 0.3, 1, 2, 4, 8, and 16 times that of gold for a core diameter of 4.0 nm. The NCA interfacial thermal conductance and thermal conductivity are plotted in Figures 5a and 5b. The interfacial thermal conductance first increases, peaks, and then decreases as the mass multiple decreases from 16 to 0.01 (Figure 5a). To gain insight into this nonmonotonic trend, we calculated the vibrational density of states of bulk gold and examined its overlap with the vibrational density of states of a dodecanethiol ligand (see Figure 5c). The number of ligand vibrational modes overlapping with the gold density of states increases as the gold mass multiple decreases from 16 to 0.01. The corresponding number of overlapping gold vibrational modes, on the other hand, remains constant (±9% about the average value) before dropping rapidly when the gold mass multiple becomes smaller than 0.3. This rapid decrease happens because the overlap occurs mostly in the low-frequency region of the gold density of states, where the number of states follows a Debye-like frequency scaling. On the basis of the thermal conductance trend, we postulate that the maximum conductance exists when the density of states on both sides are high. One should also consider the transmission coefficient and group velocity of each mode in order to fully account for the observed interfacial thermal conductance trend.

The NCA thermal conductivity shows a similar nonmonotonic trend, as plotted in Figure 5b. The similarities between Figures 5a and 5b, together with the diameter series result, point convincingly to the importance of the interfacial thermal conductance in NCA thermal transport. We can set the
upper and lower limits on the NCA thermal conductivity using eq 2. The upper line in Figure 5b is calculated using an infinite interfacial thermal conductance and a very high core thermal conductivity (1000 W/(m K)). The lower line uses a zero core thermal conductivity. These two lines bound the MD predictions in Figure 5b. The EMA-h results in Figure 5b are calculated with eq 2 using the predicted interfacial thermal conductance and core thermal conductivity at each mass multiple and are in close agreement with the MD results.

**CONCLUSIONS**

Our computationally self-assembled gold NCA model gives thermal conductivity values and trends that agree well with experimental measurements. Using this NCA model, the interfacial thermal conductance between the core and ligands was investigated—a quantity not directly measurable in experiments. We arrive at a scaling law between the interfacial thermal conductance and core diameter (eq 3) that clarifies the importance of curvature-dependent ligand grafting density and enables a computationally inexpensive framework for estimating the NCA thermal conductivity diameter series. Observations of invariant interfacial thermal conductance at different system temperatures provides evidence that only elastic vibrational scattering occurs at the core—ligand interfaces. By changing the atomic mass of the core atoms while keeping the bonding environment constant, we find a nonmonotonic relationship between the core atomic mass and the interfacial thermal conductance. This relationship, which propagates to the NCA thermal conductivity, can be qualitatively explained by considering the overlap between the ligand and gold density of states. While we focused on thermal transport properties, our methodology for quickly building an NCA superstructure has general utility for studying other properties of an NCA.

**ASSOCIATED CONTENT**

* Supporting Information
  Details of the potentials used; MD simulation of NCA thermal conductivity; thickness- and diameter-dependent MD predictions; MD simulation of thermal conductivities of bulk gold and dodecanethiol solid; MD simulation of interfacial thermal conductance of self-assembled monolayer on gold; uncertainty analysis for the presented results. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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