# Thermal Conductivity of Gold-Phenylethanethiol (Au<sub>144</sub>PET<sub>60</sub>) Nanoarrays: A Molecular Dynamics Study

Suzanne M. Neidhart and J. Daniel Gezelter\*

251 Nieuwland Science Hall, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

E-mail: gezelter@nd.edu

#### Abstract

Solvated nanoarrays of Au<sub>144</sub> nanoparticles capped with 60 phenylethanethiol (PET) moieties were studied using reverse non-equilibrium molecular dynamics (RNEMD) simulations. The thermal conductivities of the nanoarrays were computed for two chemically dissimilar solvents. These were compared to an effective medium theory (EMT) model based solely on bulk and interfacial properties and the volume fraction taken up by the particles. The interfacial thermal conductance for isolated particles was also estimated via RNEMD, using individual solvated particles in non-periodic geometries. A strong system-size dependence was found in bulk conductivity calculations, particularly in the polar solvent, dichloromethane, but was found to be unimportant in a second non-polar solvent (toluene). However, the bulk conductivity of solvated nanoarrays also requires projection to infinite system size. The  $Au_{144}PET_{60}$  particles were found to display a molten core at the temperatures used in this study. Our primary finding is that the volume fraction of the metal particles is the primary variable controlling the thermal conductivity of the nanoarrays, and that simulated conductivities are predicted well by the EMT model.

# Introduction

Thiolated gold nanoclusters have been studied in great detail, both experimentally and theoretically.<sup>1–4</sup> Their electronic,<sup>5,6</sup> optical,<sup>7</sup> and catalytic properties<sup>8,9</sup> suggest that they may be useful building blocks for nanotechnology applications.<sup>10–13</sup> These properties depend on the size of the particles, as well as the chemical identities of the protecting ligand groups. Nanocrystal arrays, which are close-packed structures of nanoparticles in a colloidal solution, have been proposed as alternatives to more expensive single-cystal semiconductor materials in transistors,<sup>14</sup> memory devices,<sup>15</sup> solar cells,<sup>16–18</sup> and thermoelectrics.<sup>19–22</sup>

One of the first theoretical studies of nanocrystal arrays was performed by Luedtke and Landman.<sup>23</sup> They examined small clusters with alkanethiol ligands placed on a graphite surface and in superlattices. A more recent experimental study by Liu *et al.* explored the effect of surface chemistry on the thermal conductivity of a nanocrystal array.<sup>24</sup> The study by Liu *et al.* varied the nanocrystal core size, the binding group of the ligand, and the ligand length. The primary finding was that, with a decrease in ligand length or an increase in the core size, the thermal conductivity of the array increased. The volume fraction of the insulating material (the ligand) was reduced in both of those cases.

Similar results (with respect to the core diameter) have been seen in theoretical studies of nanocrystal arrays by Ong *et al.*<sup>25</sup> and Zanjani *et al.*<sup>26</sup> In particular, Ong *et al.* found that in nanocrystal arrays, vibrational states are able to elastically couple across the interfaces, yielding a thermal conductivity that is dependent on the density of the ligand layer.<sup>25</sup> The coupling was further studied by varying the core atomic mass and finding the relationship between core vibrational states and the interfacial thermal conductivity.

The study by Zanjani *et al.* on gold nanocrystals with hexylthiol capping ligands varied both core size and ligand density.<sup>26</sup> The phonon dispersion of the superlattice structures was obtained and the thermal conductivity of the nanocrystal arrays displayed the same trends oberved by Liu *et al.*, specifically an increase in thermal conductivity of the array with decreased volume percentage of the ligand layer.<sup>24</sup>

Recent work by Pohjolainen *et al.* provides structures and force field parameters based upon crystal structures for thiolated gold nanoclusters found in a matching crystallography study of the clusters in arrays.<sup>27</sup> These structures contain individual particles as well as nanoarrays, with the largest of the structures containing 144 Au atoms. All of the characterized nanoclusters have a ligand with a "staple"-motif that was shown to be thermally stable in this force field. The two ligands used in the study by Pohjolainen *et al.* were para-mercaptobenzoic acid and phenylethanethiol (PET), which is the focus of this work. Some of the parameters in use here were adapted from work by Banerjee *et al.* that explored Au<sub>25</sub> and Au<sub>38</sub> nanoclusters.

The staple motif in these nanoclusters presents an interesting test for theories of thermal transport. The staple motif (for the largest particle) has three gold atoms, where two of the gold atoms in the staple are in direct contact with the core of the particle. The remaining gold atom resides in the ligand layer, bonded to two sulfur atoms from adjacent PET ligands. In our previous work, we saw direct correlation between the degree of undercoordination of gold atoms at the surface and interfacial thermal conductance.<sup>28</sup> The gold atoms in the staple motif present an interesting test of this idea, as they are significantly undercoordinated compared with other gold atoms in the particles. For this reason, we have simulated single particles and arrays of  $Au_{144}PET_{60}$  clusters in two solvents (one polar, and one nonpolar which is structurally similar to the PET ligand groups).

Conductive thermal transport in complex molecular systems has two main avenues to relay energy across the system: ballistic transport and diffusive transport. Ballistic transport is seen in materials where the mean free path of a phonon is longer than the length of the medium along the axis of propagation.<sup>29</sup> Experimentally, this transport has been correlated with rapid heat transport through the material.<sup>30</sup> Yang and Chen have shown temperature profiles of nanocomposite materials that differ from other composite materials and assign discontinuities in the temperature profile to ballistic transport at the nanoscale.<sup>31</sup> Diffusive transport, on the other hand, follows Fourier's law, and results in a linear thermal gradient in response to a constant kinetic energy flux, indicating that the material reaches a local steady state. This behavior is crucial when calculating thermal properties using various forms of non-equilibrium molecular dynamics.<sup>28,32–34</sup> However, when calculating the thermal conductivity of a solvated nanoarray, it is less clear which regime the material will follow.

Recent work by Li *et al.* examined single-layer graphene sheets in the ballistic regime and proposed a method using the extremes of the temperature profiles in order to calculate the thermal properties.<sup>35</sup> This study examined the thermal gradient over time and observed that the extrema of temperature profiles did not change while the slope of the thermal gradient eventually converged to match this temperature difference. Pandey and Leitner have also been exploring molecular junctions in a regime where Fourier's law is not valid.<sup>29</sup> In their work, the Landauer method (where inelastic scattering is disregraded) is used to model thermal conduction through molecular junctions. The Landauer method is typically used to measure the electrical conduction of a system, but has since been applied to phonon transport through molecules where the "leads" are connected

to hot and cold regions.

#### Theory

Hasselman and Johnson first proposed a formula for the effective thermal conductivity of a composite material using bulk properties of the two components separately.<sup>36</sup> Their expression for the effective thermal conductivity of the composite,

$$\lambda_e = \lambda_s \left( \frac{\lambda_p (1+2\alpha) + 2\lambda_s + 2\nu_p \left[\lambda_p (1-\alpha) - \lambda_s\right]}{\lambda_p (1+2\alpha) + 2\lambda_s - \nu_p \left[\lambda_p (1-\alpha) - \lambda_s\right]} \right)$$
(1)

uses the particle and solvent thermal conductivities ( $\lambda_p$  and  $\lambda_s$ ), and  $v_p$ , the volume fraction of the nanoparticles.  $\alpha$  is an interfacial term relating the thermal boundary resistance,  $R_{\text{TBR}}$ , to the radius of the particles,  $r_p$ ,

$$\alpha = \frac{R_{\text{TBR}}}{r_p} = \frac{\lambda_s}{G \cdot r_p} \tag{2}$$

Here, G is the interfacial thermal conductance from the particle and into the solvent. Modifications to the Hasselman and Johnson effective medium theory (EMT) have been made by Minnich *et al.* to include an interface density for the spherical particles and a more formal volume fraction of the nanoparticles.<sup>37</sup>

Each portion of Eq. (1) can be calculated separately in order to predict a composite thermal conductivity. The thermal conductivities of the solvent,  $\lambda_s$ , and particle  $\lambda_p$ , can be found through simulations of the bulk materials. The volume fraction of the particles can be estimated via the density of the composite, or from crystallographic information about the arrays. The most difficult piece to obtain is usually  $\alpha$ , where the interfacial thermal conductance (or equivalently, the thermal boundary resistance) of the particles is the primary quantity of interest. In this study, the interfacial thermal conductance values from the nanoclusters into the two solvents were found using the same method used by Stocker *et al.* for thiolate-protected nanospheres.<sup>34</sup>

We note that molecular modelling of heat conduction in nanoarrays considers only one mechanism for thermal transport: conduction. Additionally, this work is a purely classical model of nanoarrays and does not consider electronic effects (due to polarization of the gold surface) or radiative transfer between the particles. While convection can be seen in large classical simulations, it is not likely to be a significant contribution to thermal transport in a densely-packed array.

# **Computational Details**

Nanoarrays of  $Au_{144}PET_{60}$  solvated with either toluene or dichloromethane were simulated using reverse non-equilibrium molecular dynamics (RNEMD). Individual components of these systems: e.g. single particles in each solvent, pure solvent, and bulk (liquid) gold were also prepared and simulated using RNEMD. The following sections describe the potentials used to model the particles and solvents as well as details on how the systems were prepared.

#### **Force Fields**

In the bare particle and the bulk gold simulations, the gold–gold interactions are modeled using the Quantum Sutton-Chen (QSC) potential.<sup>38</sup> In the Au<sub>144</sub>PET<sub>60</sub> particles (seen in Fig. 1), however, there are three distinct gold atom types: Au<sub>B</sub>, Au<sub>S</sub>, and Au<sub>L</sub>, denoting body, surface, and ligand locations, respectively. These atom types are depicted in Fig. 2. The gold atoms interior to the particle (the icosahedral core) are defined as Au<sub>B</sub> atoms. The other two gold atom types belong to the ligand staple motif and are directly bonded to sulfur atoms. Au<sub>S</sub> atoms are in direct contact with the surface of the particle and are treated with QSC in interactions with Au<sub>B</sub> but with a Lennard-Jones potential for interactions with Au<sub>L</sub>, which are further from the surface of the particle and are covalently bonded to two sulfur atoms. Au<sub>L</sub> atoms are treated as purely Lennard-Jones atoms with parameters taken from Pohjolainen *et. al.*.<sup>27</sup> Additional parameters for the staple motif are from Refs. 27 and 39 with parameters for a united-atom treatment of the PET groups taken from TraPPE-UA.<sup>40,41</sup> All parameters used in this study can be found in Tables S1 – S4 in the Supporting Information (SI). Additional parameters used to model dichloromethane, toluene, and the organic ligands are also included in the SI.



Figure 1: One  $Au_{144}PET_{60}$  cluster with the icosahedral core atoms shown as spheres. The "staple" ligands (including the Au atoms that are part of the ligands) are displayed as skeletal structures to show the details of the internal structure of the particles.



Figure 2: The Au and S atoms in the staple motif are shown as spheres, while the PET R groups are displayed as skeletal structures. The  $Au_S$  atoms sit directly on the icosahedral core of the nanocluster, while the  $Au_L$  atom is separated from the gold surface and is covalently bonded to the sulfur atoms in each of two PET ligands.

#### **Simulation Protocol**

Details of system preparation and equilibration of the bulk, isolated particle, and nanoarray systems can be found in the SI.

After equilibration of the bulk systems (liquid gold, toluene, and dichloromethane), the relevant thermal flux was applied for at least 3 ns. To achieve a comparable temperature difference across the three box sizes (for all bulk simulations), the applied thermal flux was adjusted (see Table S5). Depending on the size of the simulation box, longer times (up to 10 ns) are necessary to allow a steady-state thermal gradient to develop, so all systems were allowed to run for the the duration required to achieve this steady state.

The isolated particles (Fig. 3) were simulated using RNEMD for 1 ns after equilibration to apply a thermal flux between the outer shell of solvent and the inner gold core. This allowed thermal gradients (and a temperature discontinuity across the Au–solvent interface) to develop. As with previously simulated thiolated nanoparticles, RNEMD with a moderate flux (for 1 ns) developed a boundary temperature discontinuity that allowed for straightforward calculation of interfacial thermal conductance.<sup>34</sup>



Figure 3: A single  $Au_{144}PET_{60}$  nanoparticle in a solvent cloud of dichloromethane, simulated using Langevin Hull dynamics. Gold atoms are represented with spheres, the PET ligands with a skeletal bond structure, and the solvent is translucent. At a simulated temperature of 250 K, the icosahedral cores of the nanoparticles melt and display liquid-like structure and dynamics.

Nanoarrays were constructed using eight different randomly sampled particle geometries from equilibrated systems, packed in a  $2 \times 2 \times 2$  array, with a distance between particle centers of mass of 30 Å. After initial equilibration, the structures were replicated in the *z*-direction to create multiples of the unit cell, up to a  $2 \times 2 \times 8$  particle array as seen in Fig. 4. For more details on the protocol for construction and equilibration of the arrays, see the SI, specifically table S7. Solvated arrays were simulated with an applied thermal flux for at least 60 ns or until a steady state was reached. To achieve similar temperature differentials across the box, the applied thermal flux was adjusted for the different array sizes.

The average temperature of the systems remained at 250K for the pure solvent, isolated nanoparticle, and nanoarray systems (1500K for the liquid gold simulations). In the pure solvent, isolated nanoparticle, and nanoarray systems this temperature maintained the solvent cloud close to the bulk density near the interface of the particle. Additionally, during RNEMD simulations, thermal coupling to the external temperature bath for the single nanoparticle systems was removed to avoid interference with the imposed flux.

All simulations were carried out using the open source molecular dynamics package, OpenMD.<sup>42</sup> Thermal conductivity and interfacial thermal conductance values were calculated using methods described in works by Kuang *et. al.* for periodic systems,<sup>43</sup> and Stocker *et. al.* for non-periodic systems.<sup>44</sup>

#### **Calculating thermal conductivity**

For small perturbations from equilibrium, the thermal conductivity,  $\lambda$ , is related to the applied thermal flux,

$$J_z = \lambda \left(\frac{\partial T}{\partial z}\right) \tag{3}$$

where  $J_z$  is the applied thermal flux and  $\partial T/\partial z$  is the temperature gradient that develops in the simulation in response to that flux. The thermal gradient created from the applied flux in a box of solvent is shown in Fig. S3. The red and blue bands denote the hot and cold RNEMD exchange



Figure 4: The solvated nanoarray systems used to compute the infinite-length thermal conductivity,  $\lambda_{\infty}$ . Gold atoms are represented with spheres, the organic parts of the PET "staple" ligands are represented with skeletal structures, and the solvent (dichloromethane for these configurations) is translucent. The nanoparticles are free to diffuse through the solvent, so particles that appear smaller have crossed simulation cell boundaries and appear on both sides of the figure. Note that these particles maintain their gold cores and ligand shells.

regions, respectively.

If the thermal transport is diffusive in nature, the relevant thermal gradients can be measured in the regions of the simulation cell that are *not* being modified by the RNEMD velocity moves. We refer to this method of computing the gradient as the "Fourier" method and this provides an upper bound on the calculated thermal conductivities. However, if the transport is governed by ballistic transport, the relevant gradients should include the two RNEMD regions that are being used to modify velocities. This "ballistic" method will result in larger thermal gradients, and will provide a lower bound on  $\lambda$ .

In some materials, the simulated thermal conductivity can depend on the length of the simulation box, so the "infinite box" thermal conductivity,  $\lambda_{\infty}$ , is extrapolated using the expression of Chantrenne and Barrat,

$$\frac{1}{\lambda_{\infty}} = \frac{1}{\lambda_L} + \frac{C}{L} , \qquad (4)$$

where *C* is a constant and *L* is the length of the simulation box in the *z*-direction.<sup>33,45</sup> This extrapolation is carried out by fitting a line through the conductivity values,  $\lambda_L$ , from two (or more) separate box lengths.

### **Results and Discussion**

For a simple array of  $Au_{144}PET_{60}$  particles, a prediction using Eq. (1) can be made using separate simulations of each of the components of the system. The bulk gold conductivity is compared to a previous study looking at gold particles in an array. Ultimately, as observed in previous work by Zanjani *et al.*<sup>26</sup> and Ong *et al.*,<sup>25</sup> the volume fraction of the array occupied by the particles is the essential portion of the predictive equation. While the interfacial details are of lesser importance to the prediction of the thermal conductivity of the arrays, the two solvents can alter heat transport out of the nanoclusters. This confirms previous findings regarding solvent penetration being instrumental in conducting heat through a ligand layer. In the following sections, each of the individual components of Eq. (1), as well as the overall prediction will be presented. Additionally, thermal

conductivity of the arrays will be discussed in comparison to the predicted values.

#### **Bulk Solvent and Gold Conductivities**

For bulk dichloromethane and toluene, the results of small-box simulations were projected to find the infinite system size thermal conductivity,  $\lambda_{\infty}$ , using Eq. (4). This projection is shown graphically in Fig. 5. The infinite system projection is necessary for dichloromethane, but does not appear to be required for toluene and liquid gold. For dichloromethane we find  $\lambda_{\infty} = 0.11(9) \text{ W/m} \cdot \text{K}$ and for toluene,  $\lambda_{\infty} = 0.1132(1) \text{ W/m} \cdot \text{K}$  where the uncertainty in the last digit is indicated in parentheses. These compare reasonably well with experimental thermal conductivities measured at 250 K ( $\lambda_{\text{DCM}} = 0.157$ ,  $\lambda_{\text{Toluene}} = 0.145$ , both in  $\text{W/m} \cdot \text{K}$ ).<sup>46</sup> If the array comprises mostly solvent, Eq. (1) predicts these same conductivities for the arrays, and these values can be taken as lower-bounds for the array conductivities. It is important to note that the applied flux was kept small enough so that the density of the solvent across the simulation boxes was uniform.



Figure 5: Bulk simulations of dichloromethane (green circles), toluene (black squares), and liquid gold (yellow diamonds) show that infinte-box projections are important in dichloromethane.

Bulk gold simulations are essential for estimating  $\lambda_p$  in Eq. (1). Previous work by Ong *et al.*<sup>25</sup>

used a bulk gold thermal conductivity value of  $1.8 \pm 0.3$  W/m·K obtained from simulations of bulk 'fcc' gold at 300 K. Because the cores of our particles are liquid-like, we compare to the conductivity of a bulk gold simulation done at 1500 K, past the melting point of the gold in this model. QSC reproduces the size-dependent melting phenomenon, and previous simulations of particles with a slightly larger radius have also been shown to display liquid-like structures.<sup>34</sup> Experimentally, particles with  $N_{Au} < 219$  have been observed with an approximate melting temperature of 500 K,<sup>47</sup> while the particles simulated here are significantly smaller. High temperature (1500 K) simulations of 100, 200, and 300 Å boxes of bulk Au were carried out. For liquid gold, we calculate  $\lambda_{\infty} = 0.39(2)$  W/m·K. This lower conductivity makes physical sense; when the gold melts, the phonons traveling through the gold lattice are disrupted, reducing the heat-carrying capacity of the material. It is important to note that the gold simulations here and those from Ong *et al.* only consider the phononic contributions to thermal transport. Electronic contributions would change the thermal properties of a metal considerably.

#### **Interfacial Thermal Conductance** (G)

Calculations of *G* traditionally use planar surfaces, densely packed with a ligand layer, which is exposed to solvent. The staple ligands used in this study stabilize nanoparticles with a high surface curvature, so it is most appropriate to measure interfacial thermal conductivity with a method that works in non-planar geometries. We have adopted the non-periodic RNEMD method to carry out these simulations with solvent clouds of both toluene and dichloromethane.<sup>44</sup> We measured the temperature jump across the solvent-ligand-particle interface and computed *G*, assuming a constant heat rate at the surface of the particle. The interfacial thermal conductance for the particles was found in both solvents.

In toluene, solvent outside of the interfacial region of the system is approximately twice the density of bulk toluene, but this is largely an excluded volume effect from the planar rings of the PET ligands. We note that this was not an issue with the dichloromethane systems, where solvent interpenetration results in interfacial solvent densities that are essentially bulk-like. Across the

staple motif, the interfacial thermal conductance to the toluene yields  $G = 11.3(7) \text{ MW/m}^2 \cdot \text{K}$ . With dichloromethane as the solvent, we find  $G = 74(4) \text{ MW/m}^2 \cdot \text{K}$ 

#### **Prediction of Array Thermal Conductivity**

Along with the individual component thermal conductivities,  $v_p$ , the partial volume of the Au<sub>144</sub>PET<sub>60</sub> particles is required to predict array conductivity. Partial volumes are approximated using the effective radius of the particles, which is taken as the average of the radius of the outermost gold atoms ( $v_p = 0.082$ ) and the radius of the total assembly including the staple motif ( $v_p = 0.477$ ). This approximations gives a partial volume of  $v_p = 0.225$  for the simulated nanoarrays. A value of  $v_p$  that includes the entire ligand layer would allow solvent to penetrate into the particle, and would significantly overestimate the volume fraction of the particles.

Using bulk and interfacial thermal properties calculated in this study ( $\lambda_s$ ,  $\lambda_p$ , and *G*), Eq.1 was used to predict the effective thermal conductivity of the array. With the bulk gold thermal conductivity reported by Ong *et al.* and the value calculated here at 1500 K, the array thermal conductivity estimates are provided in Table 1. In agreement with previous studies,<sup>24–26</sup> the volume fraction of the particles is the principal determining factor of the array thermal conductivity. With small  $v_p$ ,  $\lambda_s$  dominates  $\lambda_e$ , thus there is a similar predicted conductivity for the array in the two solvents (as  $\lambda_s$  is nearly the same for toluene and dichloromethane using  $\lambda_{\infty}$  projections) while  $\lambda_p$  remains the same.

Table 1: The effective array thermal conductivity,  $\lambda_e$  (in W/m·K), of the Au<sub>144</sub>PET<sub>60</sub> array predicted using bulk gold thermal conductivities at 1500 K (liquid) and 300 K (solid). Solvent thermal conductivities,  $\lambda_s$ , and interfacial conductance values, *G* were computed using RNEMD simulations.

| Solvent         | $v_p = 0$           | ).082              | $v_p = 0$           | 0.225              | $v_p = 0$           | ).477              |
|-----------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|
| Solvent         | $\lambda_p^{1500K}$ | $\lambda_p^{300K}$ | $\lambda_p^{1500K}$ | $\lambda_p^{300K}$ | $\lambda_p^{1500K}$ | $\lambda_p^{300K}$ |
| Dichloromethane | 0.118               | 0.121              | 0.124               | 0.131              | 0.134               | 0.146              |
| Toluene         | 0.117               | 0.120              | 0.124               | 0.131              | 0.133               | 0.145              |

#### **Simulations of Arrays**

RNEMD simulations of the nanoarrays involve extensive (60-170 ns) simulations to develop measurable thermal gradients in the simulation cells. Here we have used both a Fourier or upper-bound method to calculate thermal gradients outside of the RNEMD regions as well as the "ballistic" or lower-bound method using the full simulation cells. The calculated thermal conductivities for all of the simulation cells are given in Table 2. Note that simulation setup includes five statisticallyindependent replicas of each  $2 \times 2 \times 2$  through  $2 \times 2 \times 8$  solvated configuration of the Au<sub>144</sub>PET<sub>60</sub> nanoarrays. After equilibration, each of these systems was simulated for at least 60 ns (up to 170 ns in the larger systems) to obtain the thermal gradients used in this work.

For comparison, predictions of the array thermal conductivities using the effective medium theory (EMT) given by Eq. 1 are shown, as well as infinite-length projections of the thermal conductivities from the simulations themselves.

Table 2: Calculated thermal conductivities,  $\lambda$  (W m<sup>-1</sup> K<sup>-1</sup>), of simulated nanoarrays. Uncertainties in the last digits are indicated in parentheses. Column headers correspond to the system composition (in units of Au<sub>144</sub>PET<sub>60</sub> particles). The Fourier method is an upperbound estimate on  $\lambda$  using thermal gradients in the non-RNEMD regions, while the ballistic method is a lower-bound using thermal gradients from the entire simulation cell. The effective medium theory (EMT) estimates from Eq. (1) using a particle volume of 22.5% are given for comparison. NB: for dichloromethane, the infinite box projection was taken from the  $2 \times 2 \times 4$  and  $2 \times 2 \times 6$  systems.

| Solvent         | Method    | $2 \times 2 \times 2$ | $2 \times 2 \times 4$ | $2 \times 2 \times 6$ | $2 \times 2 \times 8$ | $\lambda_{\infty}$ | EMT   |
|-----------------|-----------|-----------------------|-----------------------|-----------------------|-----------------------|--------------------|-------|
| Diabloromathana | Fourier   | 0.036(2)              | 0.126(2)              | 0.13(3)               | 0.8(8)                | 0.14*              | 0.124 |
| Dicinoromethane | Ballistic | 0.0239(9)             | 0.084(7)              | 0.09(1)               | 0.07(1)               | 0.12*              | 0.124 |
| Toluono         | Fourier   | 0.066(7)              | 0.08(1)               | 0.10(2)               | 0.11(4)               | 0.30               | 0.124 |
| Toluene         | Ballistic | 0.032(2)              | 0.060(3)              | 0.083(7)              | 0.09(2)               | 0.14               | 0.124 |

As seen in Tab 2 the infinite length projections following Eq. (4) of the nanoarrays are in reasonable agreement with the effective medium predictions. In all solvated arrays a length dependence of the thermal conductivity is observed, where as in the bulk solvent systems only dichloromethane displayed this length-dependence.

# Conclusions

There are two significant findings of this work. First, the effective medium theory (EMT) does an excellent job at predicting array thermal conductivity as long as the volume fraction of the nanoparticles is captured correctly. According to this model, the differences in solvent thermal conductivities are washed away when the particles make up a significant fraction of the array. The main contributing factor in the Eq. (1) is  $v_p$ , the volume fraction due to the particles. The nanoparticle density in the array is therefore predicted to be the most important aspect contributing to the thermal conductance of these materials.

The second major finding of this work is that simulations of nanoarrays have a significant system size dependence when calculating thermal conductivity. Although one of the solvents (dichloromethane) also exhibits this behavior, the presence of the particles appears to create conditions where long wavelength phonons must be represented to capture thermal transport properties. However, this does not appear to be captured in the vibrational densities of states.

While there is still much more that needs to be explained in the nanoarrays of the  $Au_{144}PET_{60}$  particles, interesting results have been found using the effective medium predictions. Notably, the two solvents do not exhibit the same size-dependence in thermal transport properties. This suggests interesting differences for density dependent or polarity-dependent thermal conductivity in liquids. Similarly, the large difference in *G* between the solvent-to-particle interfaces suggests new avenues of inquiry about what is most important designing ligand–solvent interfaces for heat transport.

### Acknowledgement

Support for this project was provided by the National Science Foundation under grant CHE-1663773. Computational time was provided by the Center for Research Computing (CRC) at the University of Notre Dame.

# **Supporting Information Available**

Details of system composition, force field parameters, size-dependent melting data, and vibrational densities of states for all of the systems described in this work

# References

- (1) Häkkinen, H. The Gold—Sulfur interface at the nanoscale. Nat. Chem. 2012, 4, 443.
- (2) Sardar, R.; Funston, A. M.; Mulvaney, P.; Murray, R. W. Gold nanoparticles: Past, present, and future. *Langmuir* 2009, 25, 13840 – 13851.
- (3) Jin, R. Quantum sized, thiolate-protected gold nanoclusters. *Nanoscale* **2010**, *2*, 343–362.
- (4) Tsukuda, T. Toward an atomic-level understanding of size-specific properties of protected and stabilized gold clusters. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 151–168.
- (5) Lopez-Acevedo, O.; Clayborne, P. A.; Häkkinen, H. Electronic structure of gold, aluminum, and gallium superatom complexes. *Phys. Rev. B* **2011**, *84*, 1–6.
- (6) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci.* **2008**, *105*, 9157–9162.
- (7) Cui, M.; Zhao, Y.; Song, Q. Synthesis, optical properties and applications of ultra-small luminescent gold nanoclusters. *Trends Anal. Chem.* **2014**, *57*, 73–82.
- (8) Chen, X.; Häkkinen, H. Protected but accessible: Oxygen activation by a calixarenestabilized undecagold cluster. *J. Am. Chem. Soc.* **2013**, *135*, 12944–12947.
- (9) Lopez-Acevedo, O.; Kacprzak, K. A.; Akola, J.; Häkkinen, H. Quantum size effects in ambient CO oxidation catalysed by ligand-protected gold clusters. *Nat. Chem.* **2010**, *2*, 329–334.

- (10) Dong, A.; Chen, J.; Ye, X.; Kikkawa, J. M.; Murray, C. B. Enhanced thermal stability and magnetic properties in NaCl-Type FePt-MnO binary nanocrystal superlattices. *J. Am. Chem. Soc.* 2011, *133*, 13296–13299.
- (11) Podsiadlo, P.; Krylova, G.; Lee, B.; Critchley, K.; Gosztola, D. J.; Talapin, D. V.; Ashby, P. D.; Shevchenko, E. V. The role of order, nanocrystal size, and capping ligands in the collective mechanical response of three-dimensional nanocrystal solids. *J. Am. Chem. Soc.* 2010, *132*, 8953–8960.
- (12) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. Structural diversity in binary nanoparticle superlattices. *Nature* 2006, 439, 55–59.
- (13) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of colloidal nanocrystals for electronic and optoelectronic applications. *Chem. Rev.* 2010, *110*, 389–458.
- (14) Talapin, D. V.; Murray, C. B. PbSe nanocrystal solids for n- and p-channel thin film fieldeffect transistors. *Science* **2005**, *310*, 86–9.
- (15) Sun, S.; Murray, C. B. Synthesis of monodisperse cobalt nanocrystals and their assembly into magnetic superlattices. J. Appl. Phys. 1999, 85, 4325–4330.
- (16) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D. et al. Colloidal-quantum-dot photovoltaics using atomic-ligand passivation. *Nat. Mater.* 2011, *10*, 765–771.
- (17) Gur, I.; Fromer, N. a.; Geier, M. L.; Alivisatos, A. P. Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science* 2005, *310*, 462–466.
- (18) Ehrler, B.; Walker, B. J.; Böhm, M. L.; Wilson, M. W.; Vaynzof, Y.; Friend, R. H.; Greenham, N. C. In situ measurement of exciton energy in hybrid singlet-fission solar cells. *Nature Commun.* 2012, *3*.

- (19) Ong, W.-L.; Rupich, S. M.; Talapin, D. V.; McGaughey, A. J. H.; Malen, J. A. Surface chemistry mediates thermal transport in three-dimensional nanocrystal arrays. *Nat. Mater.* 2013, *12*, 410–415.
- (20) Kovalenko, M. V.; Spokoyny, B.; Lee, J. S.; Scheele, M.; Weber, A.; Perera, S.; Landry, D.; Talapin, D. V. Semiconductor nanocrystals functionalized with antimony telluride zintl ions for nanostructured thermoelectrics. *J. Am. Chem. Soc.* **2010**, *132*, 6686–6695.
- (21) Wang, R. Y.; Feser, J. P.; Lee, J. S.; Talapin, D. V.; Segalman, R.; Majumdar, A. Enhanced thermopower in PbSe nanocrystal quantum dot superlattices. *Nano Lett.* **2008**, *8*, 2283–2288.
- (22) Ko, D. K.; Murray, C. B. Probing the Fermi energy level and the density of states distribution in PbTe nanocrystal (Quantum Dot) solids by temperature-dependent thermopower measurements. ACS Nano 2011, 5, 4810–4817.
- (23) Luedtke, W. D.; Landman, U. Structure, dynamics, and thermodynamics of passivated gold nanocrystallites and their assemblies. *J. Phys, Chem.* **1996**, *100*, 13323–13329.
- (24) Liu, M.; Ma, Y.; Wang, R. Y. Modifying thermal transport in colloidal nanocrystal solids with surface chemistry. *ACS Nano* **2015**, *9*, 12079–12087.
- (25) Ong, W.-L.; Majumdar, S.; Malen, J. A.; McGaughey, A. J. H. Coupling of organic and inorganic vibrational states and their thermal transport in nanocrystal arrays. *J. Phys. Chem. C* 2014, *118*, 7288–7295.
- (26) Zanjani, M. B.; Lukes, J. R. Phonon dispersion and thermal conductivity of nanocrystal superlattices using three-dimensional atomistic models. *J. Appl. Phys.* **2014**, *115*.
- (27) Pohjolainen, E.; Chen, X.; Malola, S.; Groenhof, G.; Häkkinen, H. A unified AMBERcompatible molecular mechanics force field for thiolate-protected gold nanoclusters. *J. Chem. Theory Comput.* **2016**, *12*, 1342–1350.

- (28) Neidhart, S. M.; Gezelter, J. D. Thermal transport is influenced by nanoparticle morphology: A molecular dynamics study. *J. Phys. Chem. C* 2018, *122*, 1430–1436.
- (29) Pandey, H. D.; Leitner, D. M. Influence of thermalization on thermal conduction through molecular junctions: Computational study of PEG oligomers. J. Chem. Phys. 2017, 147, 084701.
- (30) Rubtsova, N. I.; Qasim, L. N.; Kurnosov, A. A.; Burin, A. L.; Rubtsov, I. V. Ballistic energy transport in oligomers. *Accounts of Chemical Research* 2015, 48, 2547–2555.
- (31) Yang, R.; Chen, G. Thermal conductivity modeling of periodic two-dimensional nanocomposites. *Phys. Rev. B* 2004, *69*, 195316.
- (32) Kim, B. H.; Beskok, A.; Cagin, T. Molecular dynamics simulations of thermal resistance at the liquid-solid interface. *J. Chem. Phys.* **2008**, *129*, 174701.
- (33) Hannah, D. C.; Gezelter, J. D.; Schaller, R. D.; Schatz, G. C. Reverse non-equilibrium molecular dynamics demonstrate that surface passivation controls thermal transport at semiconductor-solvent interfaces. ACS Nano 2015, 9, 6278–6287.
- (34) Stocker, K. M.; Neidhart, S. M.; Gezelter, J. D. Interfacial thermal conductance of thiolateprotected gold nanospheres. *J. Appl. Phys.* **2016**, *119*, 025106.
- (35) Li, Z.; Xiong, S.; Sievers, C.; Hu, Y.; Fan, Z.; Wei, N.; Bao, H.; Chen, S.; Donadio, D.; Ala-Nissila, T. Influence of thermostatting on nonequilibrium molecular dynamics simulations of heat conduction in solids. *J. Chem. Phys.* **2019**, *151*, 234105.
- (36) Hasselman, D.; Johnson, L. F. Effective thermal conductivity of composites with interfacial thermal barrier resistance. *J. Compos. Mater* **1987**, *21*, 508–515.
- (37) Minnich, A.; Chen, G. Modified effective medium formulation for the thermal conductivity of nanocomposites. *Appl. Phys. Lett.* **2007**, *91*, 1–4.

- (38) Qi, Y.; Çağin, T.; Kimura, Y.; Goddard III, W. A. Molecular-dynamics simulations of glass formation and crystallization in binary liquid metals: Cu-Ag and Cu-Ni. *Phys. Rev. B* 1999, 59, 3527–3533.
- (39) Banerjee, S.; Montgomery, J. A.; Gascón, J. A. A QM/MM approach for the study of monolayer-protected gold clusters. J. Mater Sci. 2012, 47, 7686–7692.
- (40) Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. J. Phys. Chem. B 1998, 102, 2569–2577.
- (41) Wick, C. D.; Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. 4.
  United-atom description of linear and branched alkenes and alkylbenzenes. *J. Phys. Chem. B* 2000, *104*, 8008–8016.
- (42) Gezelter, J. D.; Louden, P.; Bhattarai, H.; Neidhart, S.; Latham, A.; Lamichhane, M.; Parsons, T.; Michalka, J.; Kuang, S.; Marr, J. et al. OpenMD, an Open Source Engine for Molecular Dynamics. Available at: http://openmd.org (Version 2.6, accessed November 20, 2019).
- (43) Kuang, S.; Gezelter, J. D. Simulating interfacial thermal conductance at metal-solvent interfaces: The role of chemical capping agents. *J. Phys. Chem. C* **2011**, *115*, 22475–22483.
- (44) Stocker, K. M.; Gezelter, J. D. A method for creating thermal and angular momentum fluxes in nonperiodic simulations. *J. Chem. Theory Comput.* **2014**, *10*, 1878–1886.
- (45) Chantrenne, P.; Barrat, J.-L. Finite size effects in determination of thermal conductivities: Comparing molecular dynamics results with simple models. *J. Heat Transfer* 2004, *126*, 577–585.
- (46) Vargaftik, N. B.; Filippov, L. P.; Tarzomanov, A. A.; Totskii, E. E. *Handbook of thermal conductivity of liquids and gases*; CRC Press, 1994.

(47) Ercolessi, F.; Andreoni, W.; Tosatti, E. Melting of small gold particles: Mechanism and size effects. *Phys. Rev. Lett.* **1991**, *66*, 911–914.

# **Graphical TOC Entry**



# Supporting Information: Thermal Conductivity of Gold-Phenylethanethiol (Au<sub>144</sub>PET<sub>60</sub>) Nanoarrays: A Molecular Dynamics Study

Suzanne M. Neidhart and J. Daniel Gezelter\*

251 Nieuwland Science Hall, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

E-mail: gezelter@nd.edu

#### Abstract

This supporting document provides details of system composition, force field parameters, size-dependent melting data, and vibrational densities of states for all of the systems described in the accompanying paper.

# **System Details**

This section contains the parameters for atom types (see Fig. S1) and non-bonded interactions (table S1), harmonic bonds (table S2), harmonic bends (table S3), and torsional potentials (table S4) used to simulate the  $Au_{144}PET_{60}$  systems.

#### **Force Fields**

To model the solvents, dichloromethane and toluene, and the organic ligands, we use parameters from united atom (UA) models. Dichloromethane is modeled using UA Lennard-Jones sites with partial charges taken from Meyer *et. al.*<sup>S8</sup> while the bond and bend parameters use harmonic force constants were adopted from OPLS-AA.<sup>S11</sup> Toluene is modeled as a rigid body using parameters from TraPPE-UA.<sup>S7</sup> In the ligand staple motif, the carbon and sulfur atoms were treated with TraPPE-UA.<sup>S6,S7,S9</sup> Bond, bend, and torsion parameters for the staple were adopted from Pohjolainen *et al.*<sup>S2</sup>

Non-bonded interactions between the staple motif and icosahedral core of the particles are modeled using parameters derived from adsorption studies of thiolates on Au surfaces. The S—-Au non-bonded parameters are adopted from work from Luedtke and Landman.<sup>S4</sup> Other interactions between Au and non-metal atoms in the staple ligand are adapted from an adsorption study by Vlugt *et. al.*,<sup>S5</sup> of alkyl thiols on gold surfaces. The pairwise Lennard-Jones potential for the interactions between Au and CH<sub>x</sub> and S based upon the Hautman and Klein potential for Au(111) surfaces.<sup>S12</sup> The non-bonded interactions between Au and toluene solvent sites use parameters from the same work. Au and dichloromethane interactions use the previously mentioned work of

| Site             | atoms         | mass<br>(amu) | $\sigma_{ii}$<br>(Å) | $\varepsilon_{ii}$ (kcal/mol) | $\sigma_{\mathrm{Au}-i}$ (Å) | $\varepsilon_{\mathrm{Au}-i}$ (kcal/mol) | charge<br>(e) | source   |
|------------------|---------------|---------------|----------------------|-------------------------------|------------------------------|--|---------------|--|
| AuB              | 54            | 196.97        |                      | parameters                    | from QS                      | SC                                       | 0             | Ref. S1  |
| Aus              | 09            | 196.97        |                      | parameters                    | trom QS                      | SC                                       | 0             | Ref. S1  |
| $Au_L$           | 30            | 196.97        | 2.629                | 5.2899                        | 2.629                        | 5.2899                                   | 0             | Refs. S2 and S3                                |
| S                | 09            | 32.0655       | 4.45                 | 0.2504                        | 2.40                         | 8.465                                    | 0             | Refs. S4 ( $\sigma$ ) and S5 ( $\varepsilon$ ) |
| $CH_2$           | 120           | 14.03         | 3.95                 | 0.09141                       | 3.54                         | 0.1749                                   | 0             | Refs. S6, S5 and S4                            |
| CHar             | 300           | 13.02         | 3.695                | 0.1004                        | 3.4625                       | 0.1680                                   | 0             | Refs. S7 and S5                                |
| CHar             | 60            | 12.02         | 3.88                 | 0.04173                       | 3.555                        | 0.1604                                   | 0             | Refs. S7 and S5                                |
| CH <sub>3</sub>  | Ntoluene      | 15.04         | 3.75                 | 0.1947                        | 3.54                         | 0.2146                                   | 0             | Refs. S6, S5 and S4                            |
| DCH <sub>2</sub> | $N_{\rm DCM}$ | 14.03         | 3.95                 | 0.09141                       | 3.54                         | 0.1749                                   | 0.5           | Refs. S8                                       |
| C                | $2N_{DCM}$    | 35.45         | 3.4                  | 0.3                           | 3.265                        | 0.266387                                 | -0.25         | Refs. S8                                       |



Figure S1: Structures of the capping agent and solvents utilized in these simulations. The chemically-distinct sites (a-e) are expanded in terms of constituent united atom (UA) atom types. Cross-interactions with the Au atoms are given in Table S1. Note that in the dichloromethane, the DCH<sub>2</sub> atom type is identical with  $CH_2$ , but carries an additional +0.5 e charge.

Table S2: Harmonic bond parameters for the flexible (non-rigid) bonds in the simulated systems. Atom types at the top of the table are in the staple ligands bound to the nanoparticles. The bottom section contains atom types found in dichloromethane. Toluene is simulated as a rigid body, so no bonded interactions are used. Note that RCHar atoms inherit bonding properties from CHar atoms types.

| i               | j                | <i>r</i> <sub>0</sub><br>(Å) | $k_{bond}$ (kcal/mole/Å <sup>2</sup> ) | source           |
|-----------------|------------------|------------------------------|--|------------------|
| Au <sub>S</sub> | S                | 2.41                         | 149.9283                               | Ref. S2          |
| $Au_L$          | S                | 2.33                         | 149.9283                               | Ref. S2          |
| S               | $CH_2$           | 1.820                        | 444                                    | Refs. S9 and S10 |
| $CH_2$          | $CH_2$           | 1.540                        | 536                                    | Refs. S6 and S10 |
| CHar            | $CH_2$           | 1.540                        | 536                                    | Refs. S7 and S10 |
| CHar            | CHar             | 1.40                         | 938                                    | Refs. S7 and S10 |
| Cl              | DCH <sub>2</sub> | 1.789                        | 489.2                                  | Ref. S11         |

Table S3: Harmonic bend angle parameters for the flexible (non-rigid) bends in the simulated systems. The central atom in the bend is atom j. Atom types at the top of the table are in the staple ligands bound to the nanoparticles. The second section are atom types found in dichloromethane.

| i      | j                | k      | <b>θ</b> 0<br>(°) | <i>k</i> <sub>bend</sub><br>(kcal/mol/rad <sup>2</sup> ) | source           |
|--------|------------------|--------|-------------------|--|------------------|
| Aus    | S                | $Au_L$ | 91.3              | 460.24   | Ref. S3          |
| S      | $Au_L$           | S      | 172.24            | 240.24   | Ref. S3          |
| Aus    | S                | $CH_2$ | 111.6             | 146.37   | Ref. S3          |
| $Au_L$ | S                | $CH_2$ | 106.8             | 146.37   | Ref. S3          |
| S      | $CH_2$           | $CH_2$ | 114.0             | 124.20   | Ref. S9          |
| $CH_2$ | $CH_2$           | CHar   | 114.0             | 124.20   | Ref. S9          |
| $CH_2$ | CHar             | CHar   | 120.0             | 140.0  | Refs. S7 and S10 |
| CHar   | CHar             | CHar   | 120.0             | 126.0  | Refs. S7 and S10 |
| Cl     | DCH <sub>2</sub> | Cl     | 111.8             | 155.39   | Ref. S8          |

| In         | $\parallel$        | ely                | all         |                       |
|------------|--------------------|--------------------|-------------|-----------------------|
| als.       | $\mathbf{n}(\phi)$ | ativ               | atch        |                       |
| enti       | orsio              | l rel              | t m         | S.                    |
| pot        | 5, <i>u</i> t      | in a               | that        | ellite                |
| ıgle       | ion                | inta               | rds         | sate                  |
| n ar       | tors               | ma                 | d ca        | are                   |
| rsio       | nic                | d to               | wild        | l br                  |
| s to       | rm0                | uire               | are         | k, aı                 |
| nse        | Ha                 | req                | /pes        | s j,                  |
| nds        | $\phi$ )].         | are                | m ty        | tom                   |
| liga       | s(30               | )/2                | ato         | nd a                  |
| ET         | + 50               | \$0))              | I. X        | n, ai                 |
| he P       | 3[1.               | $-\phi$            | /mo         | aton                  |
| of tl      | +                  | s(2)               | kcal        | ral                   |
| ion        | $2\phi$            | - COS              | in          | cent                  |
| port       | cos(               | ý – 1<br>-         | gies        | the (                 |
| ng l       | -<br>-             | Î                  | enel        | ı is 1                |
| ne ri      | $-c_{2}[$          | $r(\phi)$          | ide         | rsio                  |
| ly th      | + [(4              | prope              | <b>Drov</b> | r toi                 |
| On]        | os(q               | $u_{\rm im}$       | ers J       | obe                   |
| nds.       | +<br>+             | ons                | met         | npr                   |
| igar       | $c_{1}[1$          | torsi              | ara         | he i                  |
| ET]        | $+ 0_{2}$          | per                | All F       | in1                   |
| le PJ      |                    | prol               | ds. 2       | <b>n</b> ( <i>i</i> ) |
| or th      | $\mathbf{n}(\phi)$ | e im               | gan         | ator                  |
| rs fo      | torsio             | style              | TI          | irst                  |
| letei      | IS, U              | ber-               | e PE        | he fi                 |
| ran        | sion               | Aml                | n the       | 3.: t                 |
| n pa       | tor                | nd.                | re ii       | I.N.                  |
| rsio       | ityle              | /2 <b>, a</b>      | actu        | pes.                  |
| Tol        | PE-S               | $b_0)^2/$          | stri        | m ty                  |
| <b>S</b> : | raPl               | ) – ¢              | ring        | atoi                  |
| able       | le T               | $rs(\phi)$         | gid         | her                   |
| Ĩ          | th                 | $k_{\mathrm{til}}$ | Ē           | 0                     |

| i      | j               | k      | 1     | Type           | $c_0$ | $c_1$              | $c_2$        | <i>c</i> 3            | source  |
|--------|-----------------|--------|-------|----------------|-------|--------------------|--------------|-----------------------|---------|
| S      | CH <sub>2</sub> | $CH_2$ | RCHar | TraPPE         | 0.0   | 0.7055             | -0.13551     | 1.5725                | Ref. S9 |
| $CH_2$ | $CH_2$          | RCHar  | CHar  | TraPPE         | 0.0   | 0.0                | 0.260318     | 0.0                   | Ref. S7 |
|        |                 |        |       |                | ¢     | ( <sub>0</sub> ) 0 | ktors (kcal/ | 'mol/° <sup>2</sup> ) |         |
| X      | RCHar           | CHar   | X     | Harmonic       |       | 80.0               | 0.0081       | 112                   | Ref. S7 |
| X      | CHar            | CHar   | X     | Harmonic       |       | 0.0                | 0.0081       | 112                   | Ref. S7 |
|        |                 |        |       |                | 6     | (°)0               | v (kcal/     | mol)                  |         |
| RCHar  | CHar            | CHar   | CH2   | Amber Improper |       | 0.0                | 1.1          |                       | Ref. S2 |

Vlugt for the central carbon and the Au-Cl interactions were computed using Lorentz-Berthelot mixing rules.

The initial structures of the nanoclusters were taken from crystal structures.<sup>S2</sup> However, nine independent geometries of the ligand (PET) layer were found and were used as statistically-independent structures in the interfacial thermal conductance simulations (and as the building blocks in the array simulations). Details of the composition of the array simulations and the solvated nanoparticles are found in Tables S7 and S6.

#### Size-dependent melting

In previous work, <sup>S13</sup> we have seen that thiolated nanoparticles with  $r \approx 10$ Å simulated with QSC exist as liquid droplets at 250K, and adopt shapes that vary significantly from the fcc-based structures used as initial conditions. Experimentally, particles with N < 219 have been seen with an approximate melting temperature of 500 K.<sup>S14</sup> Additionally, Buffat and Borel's observed relationship for the melting temperature vs. diameter for bare particles suggests that the Au<sub>144</sub>PET<sub>60</sub> clusters (with a diameter of  $\approx 18$  Å) should melt at approximately 600 K,<sup>S15</sup> although the PET staple-motif ligands disrupting the surface layer of gold and may drive the effective melting point down in temperature. We do observe that the particles simulated here are liquid-like in internal structure and allow significant Au-atom mobility in the core.

#### **System Preparation and Equilibration**

The gold nanoparticle simulations are started from perfect icosahedral core structures provided in Ref. S2. The crystal structures were thermalized to 250 K, and were then solvated using Pack- $mol^{S16}$  with either dichloromethane or toluene solvent clouds that had also been equilibrated at 250 K. The spherical solvent clouds were created to be at least  $3 \times$  the radius of the particle, with solvent maintaining bulk density near the interface (see Table S5 for packing details). Nine statistically independent configurations of the nanoparticles were created. However, two of these particles diffused to the surface of their toluene solvent clouds. These were excluded from calculations of

| la-           |     |
|---------------|-----|
| nu            |     |
| Sil           |     |
| m 5           |     |
| fro           |     |
| 0L            |     |
| err           |     |
| urd           |     |
| nda           |     |
| stai          |     |
| th            |     |
| Î. M.         |     |
| nes           |     |
| val           |     |
| Z             |     |
| age           |     |
| ver           |     |
| d a           |     |
| an            |     |
| ns,           |     |
| oisu          |     |
| ner           |     |
| dir           |     |
| XOC           |     |
| ls, t         |     |
| ion           |     |
| ılat          |     |
| imi           |     |
| ds            |     |
| qui           |     |
| e li          |     |
| Inc           |     |
| he J          |     |
| of tl         |     |
| <b>) n</b> (  |     |
| sitic         |     |
| bog           |     |
| Om            |     |
| 0             |     |
| SS            |     |
| ble           | ns. |
| $\mathbf{Ta}$ | tio |

| System               | molecules | box<br>1 (Å)              | dimensio | ns<br>T (Å ) T | applied flux<br>trai mol-1 Å-2 fe-1 | run time | М/тК                           |
|----------------------|-----------|---------------------------|----------|----------------|-------------------------------------|----------|--------------------------------|
|                      |           | $(\mathbf{v}) \mathbf{x}$ |          |                | <b>NUAL IIIUL A 13</b>              | (cII)    |                                |
|                      | 2816      | 60.16                     | 60.16    | 82.73          | $1	imes 10^{-7}$                    | 10       | $0.0263 \pm 7.0 	imes 10^{-4}$ |
| Dichloromethane      | 5632      | 60.16                     | 60.16    | 169.1          | $5	imes 10^{-8}$                    | 10       | $0.0390\pm2.0	imes10^{-3}$     |
|                      | 8448      | 60.16                     | 60.16    | 253.35         | $5	imes 10^{-8}$                    | 10       | $0.0595\pm4.6	imes10^{-3}$     |
|                      | 1764      | 62.3                      | 62.3     | 80.1           | $1 	imes 10^{-7}$                   | 10       | $0.1036 \pm 4.0 	imes 10^{-3}$ |
| Toluene              | 3528      | 62.3                      | 62.3     | 160.2          | $5	imes 10^{-8}$                    | 10       | $0.1147 \pm 1.0 	imes 10^{-2}$ |
|                      | 5292      | 62.3                      | 62.3     | 240.5          | $5	imes 10^{-8}$                    | 10       | $0.1062\pm 6.3	imes 10^{-3}$   |
|                      | 5040      | 32.03                     | 30.82    | 106.4          | $6.5	imes 10^{-6}$                  | 3        | $0.3407 \pm 1.0 	imes 10^{-2}$ |
| Gold (1500 K Liquid) | 10080     | 32.03                     | 30.82    | 212.8          | $6.5	imes 10^{-6}$                  | б        | $0.3800 \pm 1.9 	imes 10^{-2}$ |
|                      | 15120     | 32.03                     | 30.82    | 319.26         | $6.5	imes 10^{-6}$                  | 3        | $0.3645\pm2.0	imes10^{-2}$     |

Table S6: Composition of solvated nanoparticle systems used in interfacial thermal conductivity simulations. Note that the toluene- and DCM-solvated systems are separate (only one solvent is in use at a time).

|  | Dichloromethane | Toluene |
|--|-----------------|---------|
| molecules  | 4807            | 12075   |
| solvent cloud radius (Å)                                   | 52              | 85      |
| average solvent $\rho$ ( $r < 20$ Å) (g/cm <sup>3</sup> )  | 0.77            | 1.02    |
| average solvent $\rho$ ( $r > 20$ Å) (g/cm <sup>3</sup> )  | 1.33            | 1.74    |
| $\rho_{solv}$ in the bulk simulations (g/cm <sup>3</sup> ) | 1.33            | 0.87    |

Table S7: Composition of nanoarray systems (including the number of molecules of each component). Note that the toluene- and DCM-solvated systems are separate (only one solvent is in use at a time).

| System                | Au <sub>144</sub> PET <sub>60</sub> | N <sub>DCM</sub> | N <sub>toluene</sub> | $\begin{pmatrix} L_x \\ (Å) \end{pmatrix}$ | Ly<br>(Å) | L <sub>z</sub><br>(Å) | applied flux (kcal mol <sup>-1</sup> Å <sup>-2</sup> fs <sup>-1</sup> ) |
|-----------------------|-------------------------------------|------------------|----------------------|--|-----------|-----------------------|---|
| $2 \times 2 \times 2$ | 8                                   | 1100             | 450                  | 61   | 61        | 61                    | $1.0 \times 10^{-7}$  |
| $2 \times 2 \times 4$ | 16                                  | 2200             | 900                  | 61   | 61        | 122                   | $5.0 	imes 10^{-8}$   |
| $2 \times 2 \times 6$ | 24                                  | 3300             | 1350                 | 61   | 61        | 183                   | $3.33	imes10^{-8}$  |
| $2 \times 2 \times 8$ | 32                                  | 4400             | 1800                 | 61   | 61        | 244                   | $2.5 	imes 10^{-8}$   |

the interfacial thermal conductance.

Individual solvated particles were then brought to 250 K using the Langevin Hull ensemble.<sup>S17</sup> Once equilibrated with thermal coupling to the bath for at least 1 ns, the system evolved without coupling to the bath for another 1 ns. The particles were then simulated for 1 ns using RNEMD to apply a thermal flux and develop the resulting thermal gradients.

Pure solvent simulations were prepared starting with the experimental bulk density at 250 K.<sup>S18</sup> Five statistically independent simulations for each of three different simulation box lengths were created. These simulations were equilibrated in the isothermal-isobaric (NPT) ensemble for 1 ns followed by further relaxation with a target temperature of 250 K using the canonical (NVT) ensemble for at least 1 ns. Finally, the pure solvent systems were equilibrated for at least 1 ns in the microcanonical (NVE) ensemble before undergoing 10 ns RNEMD simulations.

The pure gold systems followed the same protocol as the dichloromethane and toluene systems, although the temperature for the pure gold system was set to 1500K, above the melting point of

bulk gold.

The nanoarrays were constructed using eight different particle geometries, packed in a  $2 \times 2 \times 2$  array, with a 30 Åseparation between particle centers of mass. The gold – gold distance from production simulations (Fig. S2) show that Au–Au contact is largely contained within the bounds of a single particle, while the particles maintain an average center-to-center distance of 30 Å. More details on nanoarray composition can be found in Table S7. The arrays were thermalized to 250 K, and were solvated with either toluene or dichloromethane with separate random seeds to create five different configurations of the solvent.<sup>S16</sup>



Figure S2: The gold-gold radial distribution function,  $g_{Au-Au}(r)$ , computed after 60 ns of simulation time. For r < 10 Å, the gold–gold pair density is mostly contained within single nanoparticles (only the  $2 \times 2 \times 4$  dichloromethane simulation shows significant interparticle contact). The population at  $r \approx 10$  Å corresponds to the edges of different particles, separated by ligands. The broad peak at 30 Åindicates the particle center-to-center distance observable in the simulations.

Solvated arrays were equilibrated at 250 K in the canonical ensemble, and were further equilibrated for at least 1 ns in the microcanonical ensemble. These simple structures were replicated in the *z*-direction to create multiples of the unit cell, up to a  $2 \times 2 \times 8$  particle array, which were separately equilibrated to 250 K in the canonical ensemble and for at least 1 ns in the microcanonical ensemble.

After systems reached equilibrium, they were simulated using RNEMD until stable, approximately linear, thermal gradients developed in the bulk regions. Fig. S3 is the thermal gradient that developed in a dichloromethane simulation in response to a moderate thermal flux. The thermal conductivity,  $\lambda$ , is directly related to the thermal gradient, which are determined by fitting through the fluid regions outside the RNEMD-exchange regions. The bulk solvent simulations maintained bulk density values throughout the RNEMD simulations, as seen in Fig. S4 for the smallest system size. This is due to the small thermal flux applied on the system and as the system size increases the applied flux decreases to maintain the same temperature change over the length of the simulation box.

# **Vibrational Densities of States**

The vibrational density of states (VDOS) projected normal to the *z* direction for periodic systems and projected normal to the interface for single nanoparticle systems were calculated for components of each system. In the bulk simulations, the VDOS is largely independent of system size, but displays the differences in occupied vibrational states between the two solvents. The components in the single nanoparticle simulations; gold, ligand, interfacial solvent (within 5 Å of the ligand), and all solvent; display a more detailed picture of the possible paths for heat transfer at that interface.

The bulk VDOS of the liquid gold, toluene and dichloromethane are shown in Fig. S5. The primary observation of these materials is that toluene is able to populate a significantly larger fraction of the low-frequency (heat-carrying) modes in the bulk. The three simulation cell lengths



Figure S3: The thermal gradient that develops in a bulk (liquid) simulation with a moderate thermal flux applied using RNEMD. The red region is the "hot" RNEMD exchange region and the two blue regions are "cold" RNEMD exchange regions. The temperature gradient that develops in response to the applied flux is related to the thermal conductivity of the material,  $\lambda$ .



Figure S4: The densities of the bulk solvents for the smallest system size averaged over the five RNEMD simulations. The temperature gradient that develops in response to the applied flux creates a secondary density gradient, but this is a small perturbation. Note that these systems have the largest imposed flux for the bulk simulations and the larger simulation cells display an even less-pronounced density gradient.



Figure S5: Bulk simulations of gold, toluene, and dichloromethane (with three different *z*-axis lengths) display normalized low frequency vibrational density of states that are largely independent of the length of the simulation box.

are shown and the differences between the VDOS of the different simulation cells is negligible.



Figure S6: Vibrational density of states of each component in solvated single nanoparticle systems. Gold (yellow) between the two systems remains the same. Similarly, the staple motif subunit (green) is the same in the two solvents below  $250 \text{ cm}^{-1}$ . The all solvent (black) component has the same spectra as the bulk systems, while the interfacial solvent (cyan) component has been altered below  $50 \text{ cm}^{-1}$  in both systems.

Individual components of the single nanoparticle system VDOS are given in Fig. S6. The gold (Au) VDOS displays minor low-frequency (50 - 100 cm<sup>-1</sup>) differences between the two solvents, but they are otherwise identical. The subunit similarly has a region that is unaffected by a difference is solvent. The changes in VDOS are slight and can be seen by the intensity differences of the peaks at  $280 \text{ cm}^{-1}$  and  $475 \text{ cm}^{-1}$ . As mentioned in the previous section, the toluene and dichloromethane solvents display very different low frequency populations, and this persists when those solvents are in contact with the nanoparticle assemblies. Interfacial solvent

blue-shifts the low-frequency solvent population due to the proximity to the staple motif subunit. All high frequency VDOS peaks appear to be identical in the bulk simulations and in the solvent components of the single nanoparticle systems.

# References

- (S1) Kimura, Y.; Qi, Y.; Çağin, T.; Goddard III, W. A. The Quantum Sutton-Chen Many Body Potential for Properties of FCC metals. 1998; Downloaded from: http://wag.caltech.edu/home-pages/tahir/psfiles/51.ps.
- (S2) Pohjolainen, E.; Chen, X.; Malola, S.; Groenhof, G.; Häkkinen, H. A unified AMBERcompatible molecular mechanics force field for thiolate-protected gold nanoclusters. *J. Chem. Theory Comput.* 2016, *12*, 1342–1350.
- (S3) Banerjee, S.; Montgomery, J. A.; Gascón, J. A. A QM/MM approach for the study of monolayer-protected gold clusters. J. Mater Sci. 2012, 47, 7686–7692.
- (S4) Luedtke, W. D.; Landman, U. Structure and thermodynamics of self-assembled monolayers on gold nanocrystallites. J. Phys. Chem. B 1998, 102, 6566–6572.
- (S5) Schapotschnikow, P.; Pool, R.; Vlugt, T. J. Selective adsorption of alkyl thiols on gold in different geometries. *Comput. Phys. Commun.* 2007, 177, 154 – 157.
- (S6) Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. J. Phys. Chem. B 1998, 102, 2569–2577.
- (S7) Wick, C. D.; Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. 4.
  United-atom description of linear and branched alkenes and alkylbenzenes. *J. Phys. Chem. B* 2000, *104*, 8008–8016.
- (S8) Meyer, A.; Allinger, N. Conformational analysis—CX: Applications of the molecular mechanics method to organic halides. *Tetrahedron* 1978, *31*, 1971 – 1978.

- (S9) Lubna, N.; Kamath, G.; Potoff, J. J.; Rai, N.; Siepmann, J. I. Transferable potentials for phase equilibria. 8. United-atom description for thiols, sulfides, disulfides, and thiophene. *J. Phys. Chem. B* 2005, *109*, 24100–24107.
- (S10) Jorgensen, W. L.; Maxwell, D. S.; ; Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. J. Am. Chem. Soc. 1996, 118, 11225–11236.
- (S11) Jorgensen, W. L. In *The Encyclopedia of Computational Chemistry*; v. R. Schleyer, *et al.*, P., Ed.; John Wiley & Sons: New York, 1998; Vol. 3; pp 1986–1989.
- (S12) Hautman, J.; Klein, M. L. Simulation of a monolayer of alkyl thiol chains. J. Chem. Phys. 1989, 91, 4994–5001.
- (S13) Stocker, K. M.; Neidhart, S. M.; Gezelter, J. D. Interfacial thermal conductance of thiolateprotected gold nanospheres. J. Appl. Phys. 2016, 119, 025106.
- (S14) Ercolessi, F.; Andreoni, W.; Tosatti, E. Melting of small gold particles: Mechanism and size effects. *Phys. Rev. Lett.* **1991**, *66*, 911–914.
- (S15) Buffat, P.; Borel, J. P. Size effect on the melting temperature of gold particles. *Phys. Rev. A* 1976, *13*, 2287–2298.
- (S16) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.* 2009, *30*, 2157–2164.
- (S17) Vardeman, C. F.; Stocker, K. M.; Gezelter, J. D. The Langevin Hull: Constant pressure and temperature dynamics for nonperiodic systems. *J. Chem. Theory Comput.* **2011**, *7*, 834–842.
- (S18) Haynes, W. CRC Handbook of Chemistry and Physics, 97<sup>th</sup> Edition; CRC Press / Taylor & Francis: Boca Raton, FL, 2012; Chapter 14, Geophysics, Astronomy, and Acoustics; Speed of Sound in Various Media.