Supporting Information

Ligand dynamics control structure, elasticity, and high-pressure behavior of nanoparticle superlattices

Tarak K. Patra,¹ Henry Chan,¹ Elena V. Shevchenko,¹† Subramanian KRS Sankaranarayanan,¹* and Badri Narayanan²,³*

¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439
²Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
³Department of Mechanical Engineering, University of Louisville, Louisville, KY 40292

Force Field

Figure S1. Details of coarse-grained model employed to simulate nanoparticle superlattices. Each PbS nanoparticle is modelled as an indivisible bead called NP. (a) MARTINI mapping scheme is used to obtain coarse-grained model (composed of beads C1-C4) from all-atom configuration of oleic acid. (b) Illustration of the steps used to prepare a CG configuration of NPSL. (c) MARTINI force field parameters used in this study are tabulated.
We employed the well-established MARTINI scheme to coarse-grain the oleic acid ligand molecules; each nanoparticle is modeled as an indivisible bead (Figure S1). The MARTINI force-field parameters are used to model interactions between different ligand molecules, and the nanoparticles (the parameters are summarized in Figure S1c). For unlike interactions, we employed Lorentz-Berthelot mixing rule where the LJ parameters for interactions between beads $i$ and $j$ are given by:

\[ \epsilon_{ij} = \left( \frac{\epsilon_{ii} \epsilon_{jj}}{\epsilon_{ij}} \right)^{1/2}, \]

\[ s_{ij} = \frac{1}{2} \left( s_{ii} + s_{jj} \right), \]

where, $(\epsilon_{ii}, s_{ii})$, and $(\epsilon_{jj}, s_{jj})$ are the LJ parameters for $i$-$i$ and $j$-$j$ interactions respectively.

**Equation of State (EOS)**

We have computed the equation state of the NPSL from our coarse-grained simulation and compare with experiment. At each pressure, the system is equilibrated for 10ns in an isothermal isobaric ensemble at temperature $T = 300$K. The equilibrium volume is computed by averaging over 10000 frames collected over a period of 1 ns. The MARTINI force-field describes the equation of state of NPSLs in good qualitative accordance with experiments (Figure S2). This suggests that the coarse-grained model qualitatively capture the thermophysical properties of the experimental system.

![Figure S2](image.png)

**Figure S2.** Equation of state of a ligand-rich nanoparticle superlattice ($\rho=4.9$/nm$^2$) from coarse-grained molecular dynamics and experiments at 300 K. The unit cell volume ($V$) at a given pressure is normalized by its value at pressure $P = 1$GPa ($V_0$).
Radial Distribution Function (RDF)

Figures S3 shows the NP-NP radial distribution in NPSL (for various ligand coverage densities) at selected pressures during a compression-release cycles. It clearly suggests the NPSL sustain high applied pressure without losing their crystallinity at high ligand coverage densities ($\rho = 1.8 - 5.5$ nm$^2$).

**Figure S3.** Radial distribution functions: a, b, c and d correspond to ligand density $\rho = 1.8$ nm$^2$, 2.4nm$^2$, 3.6nm$^2$ and 5.5nm$^2$, respectively.
Thermogravimetric Analysis

Figure S4. The thermogravimetric analysis (TGA) data obtained for the PbS NPSLs obtained by destabilization of the toluene solution of 7 nm PbS by isopropanol.

Transmission Electron Microscopy (TEM)

Figure S5. The TEM image of a fragment of PbS NPSL after compression.
Small-Angle X-ray Scattering (SAXS) experiments

**Figure S6.** (Left) Optical micrograph and (Right) SAXS data on face-centered cubic NPSLs grown on Si substrate from 9.5 nm PbS NPs compressed up to 55.86 GPa and after pressure release.

**Figure S7.** SAXS of face-centered cubic NPSLs (assembled from 9.5 nm PbS NPs) grown on Si substrate (black), and of individual NPSL at 55.86 GPa (red) and after pressure release (blue).