Supplementary Information for "Simulating facet-dependent aggregation and assembly of distributions of polyhedral nanoparticles"

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I. Nanoparticle Model Setup

The construction of the three different types of nanoparticles was performed in the SNAP Generator by initially generating a mesh of equidistance protoparticles. In our model, a nanoparticle is composed of a surface mesh of protoparticles where a protoparticle is a point on a facet which represents a coarse-grained approximation of the atoms normally found there. The great rhombicuboctahedron (GRO) for the 22Å, 27Å and 32Å sizes contained 340, 510 and 726 protoparticles. Similarly, the small rhombicuboctahedron (SRO) contained 344, 520 and 732 protoparticles and the modified truncated octahedron (mTO) contained 346, 514, 734 protoparticles for the three sizes. This corresponds to a uniform mesh density across all nanoparticle facets of 0.2 protoparticles/Å The equidistant spacing was obtained by a Monte Carlo based movement procedure of the protoparticles across the facets. The mass of a nanoparticle was distributed equally amongst the protoparticle mesh which represents an approximation to the moment of inertia, with an overall density equal to carbon diamond. This corresponded to a mass of 11867 amu, 21944 amu and 36537 amu for the 22Å, 27Å and 32Å sizes.

Once the nanoparticle models were constructed, they were inserted into a simulation cell of 661.91Å to ensure a nanoparticle density of 2.0×10^{19} particles/cm^3. Random rotations and switching moves were then used to mix the polydispersed models along with equilibration in the liquid state at a high pseudo-temperature prior to the simulation quenches.

Two types of force field were used within the MD simulations with details found elsewhere[2]. The first is a harmonic potential between neighbouring protoparticles on the same nanoparticle used to preserve nanoparticle shape. This field had a maximum range of 5Å and a spring constant of 320N/m (reduced unit spring constant of 20) which is on the order of spring constants of molecular bonds. The interactions between different nanoparticles occurred via the use of a Morse potential between the protoparticles on separate nanoparticles. Three different types of protoparticles were defined corresponding to the three different facet types in the models, namely 100, 111) and 110. This results in a total of six unique protoparticle interactions and parameters sets for this potential. The parameters themselves were obtained from Tight Binding (DFTB) calculation of the separation and orientation-dependent potential energy binding curves between pairs of unpassivated atomistic nanodiamond models[3,4]. These curves (shown in figure 1) were input into the SNAP Generator where they were converted to protoparticle-protoparticle interaction parameters via a Monte Carlo fitting procedure described elsewhere[1,2]. Briefly, the binding curves (in units of eV/Å) are converted into facet binding curves (in units of eV) by multiplication of the appropriate facet area of the model nanoparticle used and then the interaction is spread out over the protoparticles of that facet (in units of eV/protoparticle).

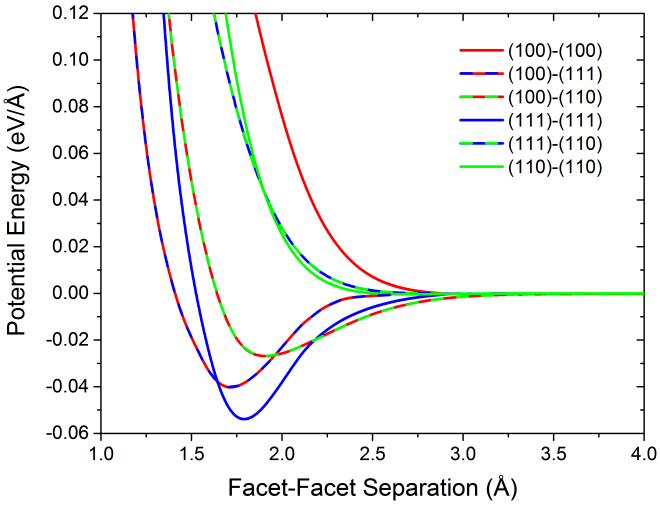

Fig. 1 The six facet type pair combinations (also protoparticle type combinations) used in this study.

It should be noted that the protoparticle-protoparticle Morse parameters are dependent upon the protoparticle mesh density. In this work, with a density of 0.2 protoparticles/Å^2 used, Table 1 lists the interaction parameters that were obtained from the Monte Carlo fitting procedure to the above binding curves in the SNAP Generator.

Additionally, the Morse potential was smoothly truncated to zero between 4Å and 6Å to ensure proper energy conservation.

II. Simulation Details

Using the initial nanoparticle configuration and the Morse interaction parameters generated in the SNAP Generator, simulations using a constant number of nanoparticle, volume and temperature (NVT) were performed in the SNAP Simulator. The velocity Verlet integration algorithm was used with a 3fs timestep and

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Table 1 Protoparticle-protoparticle Morse parameters used in this work.

	100-100	100-111	100-110	111-111	111-110	110-110
D (eV)	0.002897	0.140320	0.075839	0.220832	0.004879	0.003980
A ($Å^{-1}$)	1.70666	2.63760	2.42320	3.03714	1.69103	2.37810
R_e (Å)	3.76665	1.98905	2.25164	1.98353	3.46390	3.11329

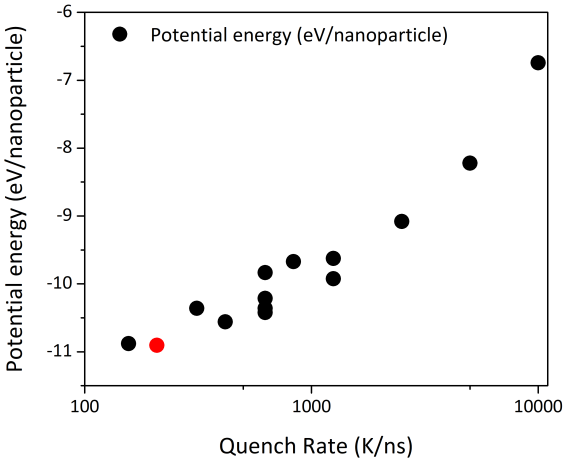

Fig. 2 Test simulations at different quench rates investigating the potential energy of the final configuration. The red datapoint of 208K/ns was used.

simple velocity rescaling. Due to the coarse-grained nature of the models and lack of internal bonding, a pseudo-temperature T was defined as,

$$T = \frac{2E}{3k_B P} \tag{1}$$

where E is the total kinetic energy, k_B is Boltzmann's constant and P is the total number of protoparticles. The configurations were initially equilibrated for 1 million steps at 7500K before a linear quench to 0K over 12 million steps (208K/ns quench rate). The choice of this quench rate was based on several smaller simulations (using more general polydisperse systems with also a mix of the three shapes) at different quench rates looking at the potential energy behaviour and computational tractability.

References

1 G. Opletal, M. Golebiewski and A. S. Barnard, *Simulated Nanoparticle Assembly with Protoparticles (SNAP), v1. CSIRO Software Collection*, 2020, https://doi.org/10.25919/5e5c662a0597e

2 G. Opletal, M. Golebiewski and A. S. Barnard, *J. Phys. Mater.*, 2020, **3**, 026001.

3 A. S. Barnard, *J. Mater. Chem.*, 2008, **18**, 4038.

4 L. Lai and A. S. Barnard, *J. Phys. Chem. Lett.*, 2012, **3**, 896.