Supplementary Information: Dynamics of DNA-Programmable Nanoparticle Crystallization: Gelation, Nucleation and Topological Defects.

C. Knorowski and A. Travesset

May 21, 2012

The coarse-grained model has been presented in Ref. [1] and is summarized in Fig. 1. The ssDNA are modeled as n_s beads (the coarse grained number of spacers) and n_l number of linker beads (the coarse grained number of linkers) both of size σ connected by harmonic springs Eq. 1, with $k = 330$ and $r_0 = 0.84$. The units are in terms of σ,

$$V(r) = \frac{1}{2}k(r - r_0)^2 \tag{1}$$

Linker beads have additional structure, modeling the ability to hybridize (form hydrogen bonds) complementary base-sequences. This is modeled by adding an additional smaller bead (CT) of size 0.6σ on top of each linker bead via harmonic spring. A harmonic angle (CT-CT-CT) aligns CT beads

$$V(r) = \frac{1}{2}k(\theta - \theta_0)^2 \ , \tag{2}$$

where $k = 120$ and $\theta_0 = \pi$. Two additional beads (FL) of size 0.6σ flank each CT bead, with CT and FT connected by harmonic spring. A harmonic angle (FT-CT-FT) aligns the CT with their FT beads. The comparison between simulation and experimental beads can be done through $\sigma = 2nm$, $n_s = 8 = 50bp$ and $n_l = 3 = 20bp$.

The interaction between spacers, linkers and FL beads is repulsive.

$$U(r) = 4\epsilon \left(\frac{\sigma}{r}\right)^{12} . \tag{3}$$

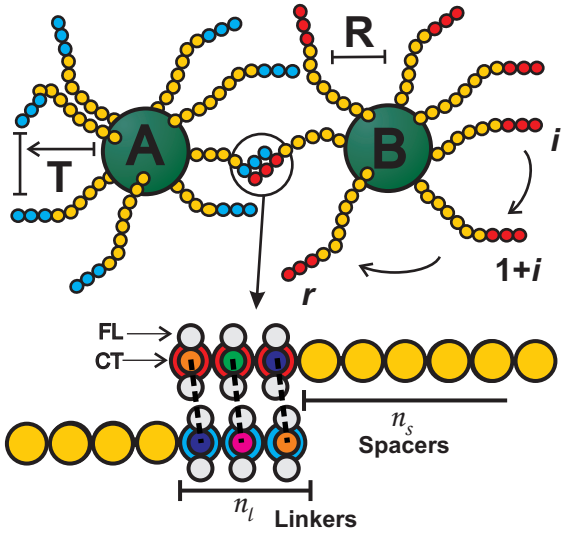

Figure 1: Coarse grained Model of ssDNA-GNP. n_s and n_l are the coarse-grained number of spacer and linker beads respectively. r is the number of ssDNA attached to each NP. R is the radius of a NP and T is the average end to end distance of the ssDNA. The structure of the ssDNA linker is modeled with central beads(CT), the complementary basis, and flanking beads(FL).

The interaction between CT beads is repulsive, unless bases are complementary (A-T, C-G), in which case the interaction is of the Lennard-Jones (LJ) type

$$U(r)_{FL} = 4\epsilon_{bp}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] , \quad (4)$$

where ϵ_{bp} is the characteristic attraction free-energy between complementary bases. All interactions are cut-off at a distance 3σ. Throughout this work, the parameters were chosen as $\epsilon = 1$, $\epsilon_{bp} = 10\epsilon$ and the temperature is reported in reduced units k_BT/ϵ. Provided that $\epsilon_{bp} >> \epsilon$, the particular value of ϵ_{bp} is not critical. NP are built by positioning repulsive beads on a spherical surface of radius $R = 3\sigma$. ssDNAs are distributed uniformly across the NP surface and attached with harmonic springs. Rigid body dynamics are used for the NPs, which have been implemented in HOOMD-blue[5].

For simplicity of the model, we use three CT bead complementary pairs (A-T, C-G, K-F). The additional K-F pair served the purpose to eliminate the artifact of linker curling, where a linker may curl to attract itself. The order of CT beads on the different linkers is A-C-K and F-G-T.

Double Stranded DNA are modeled as ssDNA except for a harmonic angle bond with k= 120 between spacer beads to enforce rigidity. Additionally, every four spacer beads the harmonic angle bond is set to a smaller k= 30, to mimic experiments. The harmonic angle between the spacer and linker group is set to k= 0. The rigidity of the dsDNA can be tuned by changing the k parameter.

DNA linkers are modeled as a string of spacer beads where both ends have linker beads. These are, essentially, ssDNA bonded together. the number of spacers in a linker is identified as n_{la} and the number of linker dna in the simulation is N_{linker}.

0.1 Technical aspects of the simulation

Simulations were started with an initial random configuration generated using packmol [2] and further randomized at high temperature (T=4.0). The time step is $\Delta t = 0.005$ (units of $\sqrt{m\sigma^2/\epsilon}$). The integration used NVT with a Noose-Hover thermostat as implemented in HOOMD-blue edition [3][4]. Simulations were then run at a constant Temperature T. Simulations which were cycled, started from T_{intial}, were heated to T_{high} and then cooled to T_{final}. Simulation runs typically included between 100-200 million timesteps.

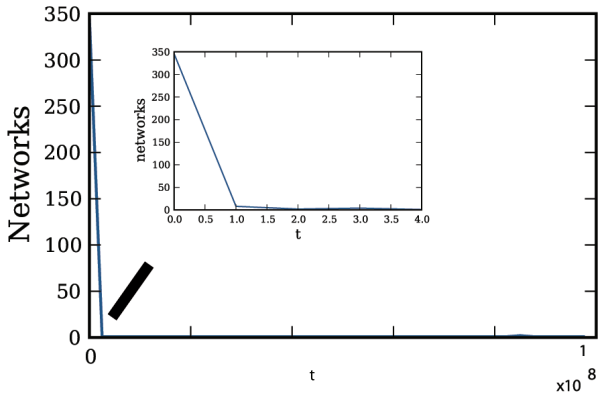

Figure 2: Number of different percolated networks as a function of time. The number quickly drops to 1 and remains stable for the duration of the simulation. N=432, $\eta = 0.675$ and T=1.19

References

[1] Knorowski, C, Burleigh, S, & Travesset, A. (2011) Dynamics and statics of DNA-programmable nanoparticle self-assembly and crystallization *Phys. Rev. Lett.* **106**, 215501–215504.

[2] Martinez, L, Andrade, R, Birgin, E. G, & Martinez, J. M. (2009) Packmol: A package for building initial configurations for molecular dynamics simulations *Journal of Computational Chemistry* **30**, 2157–2164.

[3] Anderson, J. A, Lorenz, C. D, & Travesset, A. (2008) General purpose molecular dynamics simulations fully implemented on graphics processing units. *Journal of Computational Physics* **227**, 5342–5359.

[4] **http://codeblue.umich.edu/hoomd-blue/**.

[5] Nguyen, T. D, Phillips, C. L, Anderson, J. A, & Glotzer, S. C. (2011) Rigid body constraints realized in massively-parallel molecular dynamics on graphics processing units. *Computer Physics Communications* **182**, 2307 – 2313.

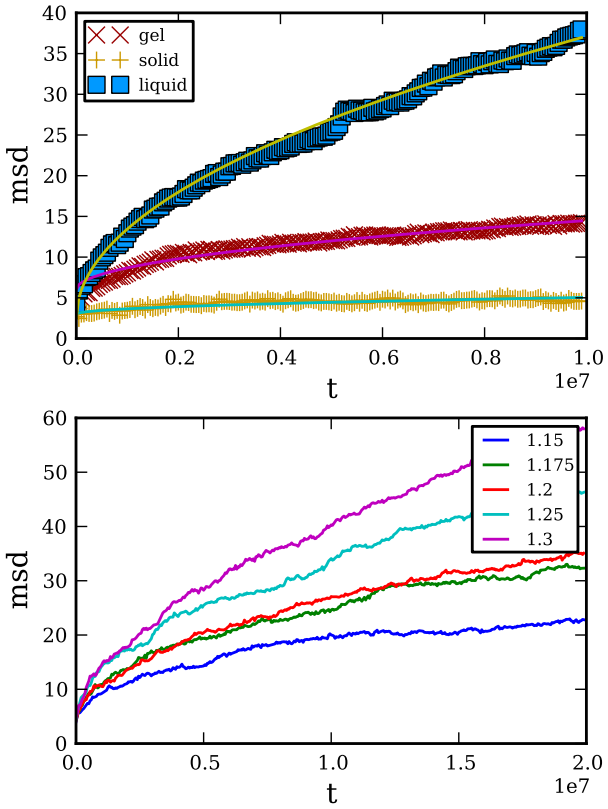

Figure 3: (Top)MSD of particles in liquid, amorphous gel and solid phases. The msd is fit to $\sqrt{6Dt}$, where D is the diffusion coefficient. $D_{liquid} = 2e^{-5}\sigma^2/\Delta t$, $D_{gel} = 1.2e^{-6}\sigma^2/\Delta t$ and $D_{solid} = 2e^{-7}\sigma^2/\Delta t$. Simulations of the liquid are performed for a system of N=432, $\eta = 0.675$, T=1.195 but with FT beads removed. For the gel and solid N=432, $\eta = 0.675$, T=1.19. (Bottom) MSD of particles for various temperatures. These results show the strong temperature dependence of diffusion. Simulations are for N=128, $\eta = 0.675$.

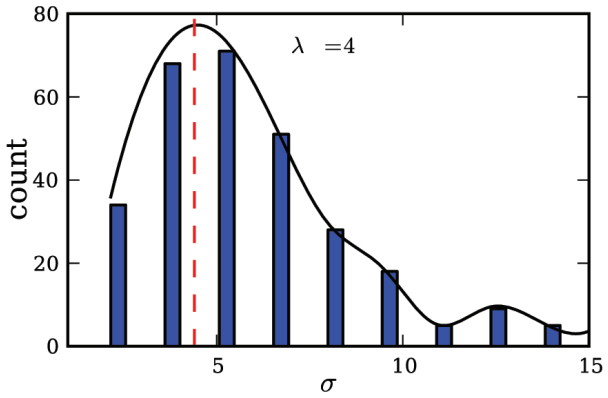

Figure 4: λ is calculated as the average jump distance of a NPs from surrounding gel to crystal. Δt, the characteristic jump time, is chosen as a compromise between time scales of crystal growth and NP diffusion. N=432, $\eta = 0.675$, T=1.19

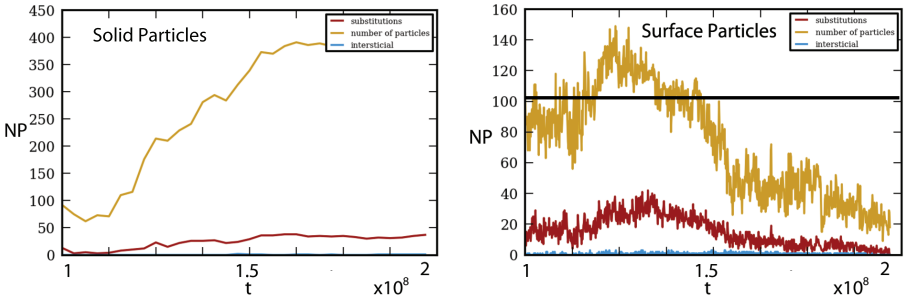

Figure 5: (Left) Solid particles as identified by local bond ordering. The number of substitutionals as well as interstitials are calculated for each solid particle through the same method described in methods and materials. (Right) The number of "surface" particles surrounding the crystal. These are NP which are in the gel, but have > 2 nearest neighbors in the solid.

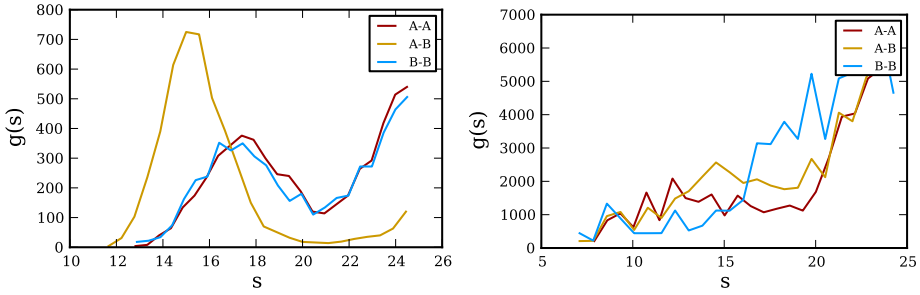

Figure 6: Radial distribution of A-A, A-B and B-B particles in solid (left) and amorphous (right) gel phases at timestep 1.1e8. For N=432, $\eta = 0.675$, T=1.19 and s is in units of σ.

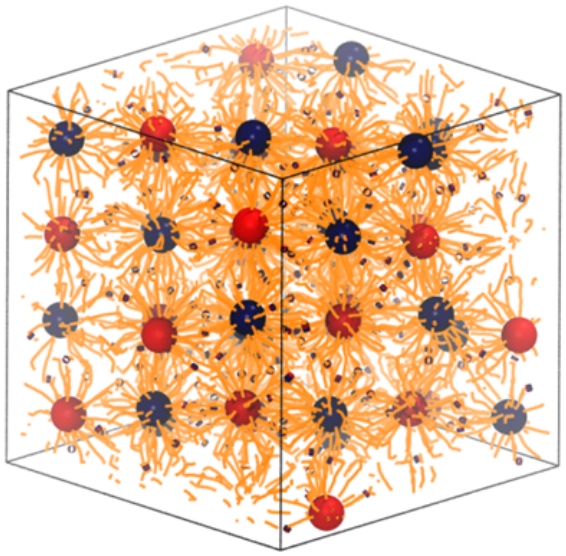

Figure 7: Snapshot of a CsCl-bcc phase with rigid (ds DNA). DNA is drawn as yellow, hybridization as small circles. N=54, $n_s = 8$, T=1.225, $\eta = 0.675$.

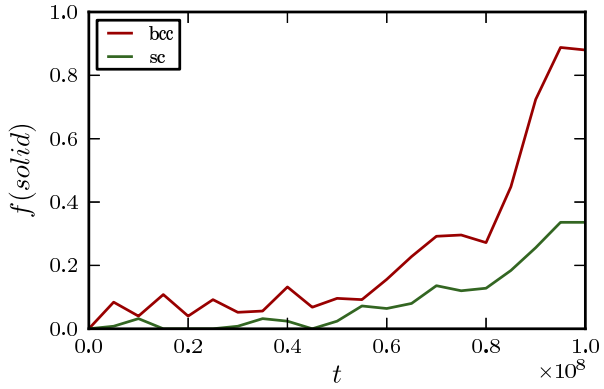

Figure 8: Dynamics of a rigid system with N=250. The simulation is for N=250, $n_s = 5$, T=1.225, $\eta = 0.675$.

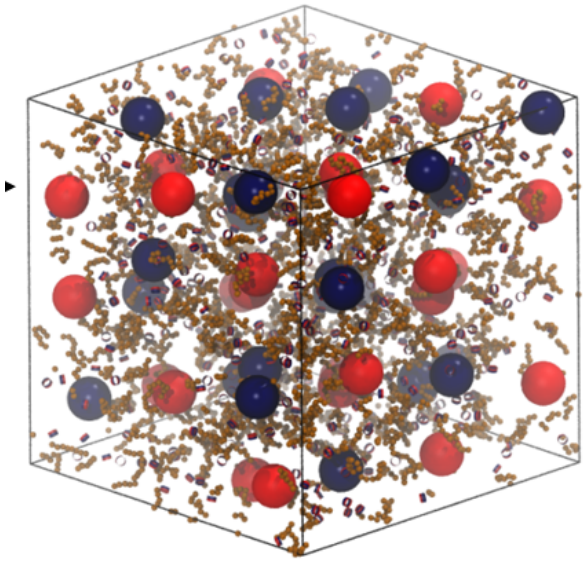

Figure 9: CsCl-bcc phase for linker mediated systems. Linker DNA are drawn as yellow, locations of hybridizations are drawn as small circles. N=54, $n_s = 8$, T=1.15, $\eta = 0.5$, $N_{linker} = 800$(number of linker dna), n_{la}=14 (linker spacer length).

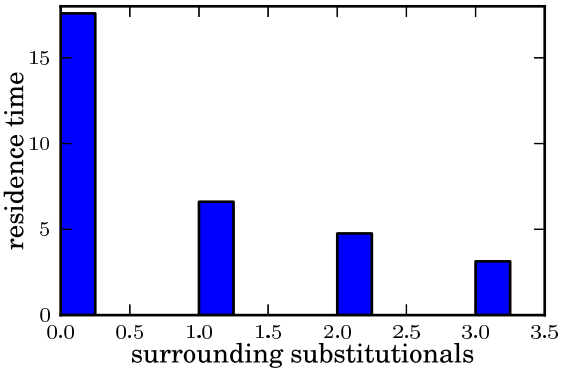

Figure 10: Residence time of a vacancy as a function of the number of surrounding substitutionals. The shorter residence times of the vacancy implies that there is an attractive substitutional-vacancy force and the motion of the vacancy is directed towards higher density of substitutional regions. The simulation is for direct hybridization at N=127, T=1.225, $\eta = 0.7$ $n_s = 8$ where an vacancy was introduced by removing a single NP.

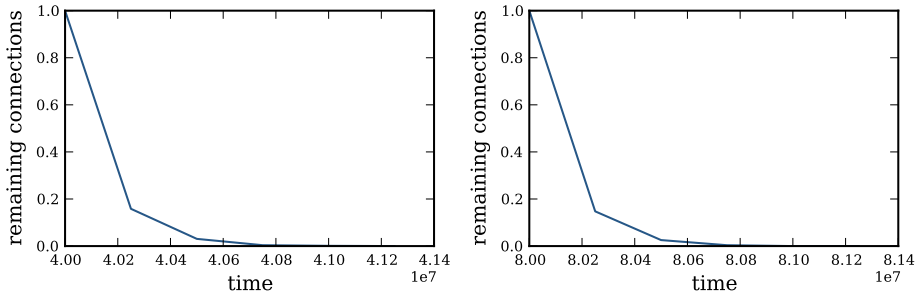

Figure 11: Average hybridization lifetime of ssDNA for a gel(Left) and crystal(Right) for a system of N=432, $\eta = 0.675$ and T=1.195. These results show that hybridization lifetime remains constant within the gel and crystal. These results are general to all other simulations.