## Supplemental Information:

Guiding the self-assembly of colloidal diamond
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## KINETIC PHASE DIAGRAM FOR TETRAHEDRAL COLLOIDAL MOLECULES WITHOUT DNA FUNCTIONALIZATION

To shed light on the effect of DNA on the self-assembly of cubic diamond, we show in Fig. S1 the corresponding kinetic phase diagrams for tetrahedral colloidal molecules, but now without DNA functionalization of the central core particles. The topology of the kinetic phase diagrams resembles that of the ones in the main text for DNA-functionalized tetrahedral colloidal molecules. The kinetic phase diagrams exhibit a fluid phase at small depletant reservoir packing fractions $\eta_{d}^{r}$, corresponding to low interaction strengths $\beta U$ for all core-to-lobe size ratios $s$. Upon increasing $\beta U$, a narrow region is found in which cubic colloidal diamond is formed and another small region where we observe the formation of percolating networks retaining an inner crystalline structure. These two phases are not observed for the largest core-to-lobe size ratio $s=1.28$. Finally, at larger


FIG. S1. Kinetic phase diagram of a system of tetrahedral colloidal molecules without DNA functionalization at a colloid number density $\rho \sigma_{A}^{3}=0.06$ as a function of depletant size $q=\sigma_{d} / \sigma_{A}$ and interaction strength $\beta U$ for varying core-to-lobe size ratios $s=\sigma_{B} / \sigma_{A}:$ (a) 1.18 , (b) 1.22 , (c) 1.24 and (d) 1.28 . Four different phases are identified, namely cubic diamond crystals (dark blue diamonds), percolating cubic diamond gel structures (pink to purple shaded circles), disordered percolating gel networks (blue triangles) and an isotropic fluid phase (light blue circles). Different shades of pink denote different number fractions of cubic diamond $N_{D} / N$ in the percolating structures following the color bar.

[^0]interaction strengths $\beta U$ the system forms a percolating network. The latter is found in a larger region compared to the model where the DNA interaction is considered. This, in general, reinforces the idea that the presence of DNA on the core particles enhances and stabilizes the formation of cubic diamond crystals.

## CLUSTER FORMATION



FIG. S2. Simulation snapshots at initial, intermediate and final simulation times and different $\beta U$ for tetrahedral colloidal molecules with a core-to-lobe size ratio $s=\sigma_{B} / \sigma_{A}=1.24$ and depletant-to-lobe size ratio $q=\sigma_{d} / \sigma_{A}=0.12$ where core monomers only are displayed. Different colors relate to distinct clusters with more than ten monomers arranged in a cubic diamond environment that are formed over the course of the simulation. Colored in gray are particles that are not part of a cubic diamond environment or that are part of a cluster whose size is less than ten units.

In Fig. S2 we show simulation snapshots highlighting the formation of clusters in which particles are arranged in a cubic
diamond conformation over the course of the simulation for varying $\beta U$. As detailed in the main text, for $\beta U=1.05$, a single cluster grows over time forming a compact cubic diamond grain. For intermediate $\beta U$, depending on the degree of arrest of the system, multiple ordered clusters are formed in the beginning of the simulations for then either merging into a single gel-like cluster or leading to structures in which small ordered domains coexist with disordered ones. For $\beta U=4.20$, no crystalline cluster is identified.

## PROBABILITY DISTRIBUTION OF THE ANGULAR STRAIN OF SIX-MEMBERED RINGS

In Fig. S3, we show the probability distribution $P(\xi)$ of the angular strain of six-membered rings for a system of DNAfunctionalized tetrahedral colloidal molecules with a core-to-lobe size ratio $s=1.24$, a depletant-to-lobe size ratio $q=0.12$, and at different values of the interaction strengths $\beta U$ as labelled, corresponding to varying depletant reservoir packing fractions $\eta_{d}^{r}$. At low $\beta U$, the system retains a cubic diamond structure and hence, most of the rings are in a chair-like or staggered conformation. As the interaction strength $\beta U$ increases, the system gets arrested and the probability distribution $P(\xi)$ broadens accordingly. At high $\beta U$, the system fully looses crystallinity and a second peak in the distribution arises at a strain value around -0.35 .


FIG. S3. Probability distribution of the angular strain $P(\xi)$ of six-membered rings for different phases of DNA-functionalized tetrahedral colloidal molecules with a core-to-lobe size ratio $s=1.24$, a depletant-to-lobe size ratio $q=0.12$, and varying interaction strengths $\beta U$ as labeled.

## FRACTAL DIMENSION OF THE GEL-LIKE STRUCTURES

In order to further characterize the nature of the percolating networks, we calculate the fractal dimension $d_{f}$ of our gel-like structures using the box counting algorithm. To this end, we first subdivide the simulation box into cells of varying size $\lambda$, and we count the number of cells $N_{c}$ that contain at least one colloidal particle. We show an example of this procedure in the inset of Fig. S4. The fractal dimension $d_{f}$ is obtained using

$$
\begin{equation*}
\log N_{c}(\lambda)=-d_{f} \log \lambda \tag{1}
\end{equation*}
$$

we discriminate between two regimes by taking a cross-over value $\lambda=8 \sigma_{A}$, and use Eq. 1 to fit the two regimes. In Fig. S4 we show an example of such a fitting for a percolating system of tetrahedral colloidal molecules with a core-to-lobe size ratio $s=1.24$, depletant-to-lobe size ratio $q=0.25$, and depletant reservoir packing fraction $\eta_{d}^{r}=0.20$.

PHASE DIAGRAM FOR $q=0.25$
In Fig. S5 we show the kinetic phase diagram for a system of DNA-functionalized tetrahedral colloidal molecules with a core-to-lobe size ratio $s=\sigma_{B} / \sigma_{A}=1.24$ and depletant-to-lobe size ratio $q=\sigma_{d} / \sigma_{A}=0.25$ as a function of interaction strength


FIG. S4. The logarithm of the number of cells $N_{c}$ with side length $\lambda$ that contain at least one colloidal particle as a function of $\lambda$. The dashed line and dotted line show the fits at small and large length scales usinge Eq. 1 for obtaining the fractal dimension $d_{f}$ for a gel structure of tetrahedral colloidal molecules with a core-to-lobe size ratio $s=1.24$, depletant-to-lobe size ratio $q=0.25$, depletant reservoir packing fraction $\eta_{d}^{r}=0.20$, and at colloid density $\rho \sigma_{A}^{3}=0.06$. The inset shows a schematic of the box counting algorithm in which the simulation box is divided into small cells of side $\lambda$.


FIG. S5. Kinetic phase diagram of a system of DNA-functionalized tetrahedral colloidal molecules with a core-to-lobe size ratio $s=\sigma_{A} / \sigma_{B}=$ 1.24 and a depletant-to-lobe size ratio $q=\sigma_{d} / \sigma_{A}=0.25$ as a function of interaction strength $\beta U$ (left axis) or depletant reservoir packing fraction $\eta_{d}^{r}$ (right axis), and number density $\rho \sigma_{A}^{3}$ (lower axis), or colloid packing fraction $\eta_{c}$ (upper axis). The color bar on the right indicates the fraction of particles in a diamond environment $N_{D} / N$.
$\beta U$ or depletant reservoir packing fraction $\eta_{d}^{r}$ and colloid number density $\rho \sigma_{A}^{3}$ or colloid packing fraction $\eta_{c}$. The phases that we found are consistent with the ones found for a system with smaller depletant size ratio $q=0.12$ shown in the main text.

TYPICAL CONFIGURATIONS AS OBTAINED FROM SIMULATIONS FOR HIGH-DENSITY PHASES

In Fig. S6 we show representative configurations obtained from simulations for the phases observed for DNA-functionalized tetrahedral colloidal molecules at high colloid number densities $\rho \sigma_{A}^{3}$.


FIG. S6. Typical configurations obtained from simulations for phases found for tetrahedral colloidal molecules for a core-to-lobe size ratio $s=\sigma_{B} / \sigma_{A}=1.24$ and depletant-to-lobe size ratio $q=\sigma_{d} / \sigma_{A}=0.12$ : cubic diamond, diamond gel-like network, disordered gel at a colloid number density $\rho \sigma_{A}^{3}=0.2$, and a glass at a colloid number density $\rho \sigma_{A}^{3}=0.4$ (from left to right). Top panels report the full colloidal molecules, while bottom panels display only the core particles.

## CHARACTERIZATION OF THE ARRESTED PHASES

In the regime of high colloid packing fractions $\eta_{c}$ we find a region where the system is completely arrested and present no long-range order. In order to characterize these phases and their dynamical characteristics, we calculate the diffraction patterns and the mean squared displacement at high colloid number densities $\rho \sigma_{A}^{3}$. We show the results in Fig. $\mathrm{S} 7(\mathrm{a}-\mathrm{d})$.


FIG. S7. Diffraction patterns of the different phases for a system of DNA-functionalized tetrahedral colloidal molecules with a core-to-lobe size ratio $s=1.24$, a depletant-to-lobe size ratio $q=0.12$, and depletant reservoir packing fraction $\eta_{d}^{r}=0.12$ a) diamond phase at $\rho \sigma_{A}^{3}=0.06$, b) diamond gel-like structure at $\rho \sigma_{A}^{3}=0.20$ and c) a glass phase at $\rho \sigma_{A}^{3}=0.40$, and d) the mean-squared displacement of the respective system for varying colloid densities as labeled.

## VIDEOS REPORTING THE CLUSTER FORMATION PROCESS

In the attached videos (Video S1-S5) we show the evolution and grow of the initial diamond clusters for a cubic diamond, diamond-gels with different degree of arrest and a disordered gel. Videos correspond to systems with core-to-lobe size ratio $s=1.24$, depletant-to-lobe size ratio $q=0.12$, and at a depletant reservoir packing fraction, $\eta_{d}^{r}=0.10$ (Video S1), $\eta_{d}^{r}=0.15$ (Video S2), $\eta_{d}^{r}=0.20$ (Video S3), $\eta_{d}^{r}=0.30$ (Video S4), and a disordered gel at $\eta_{d}^{r}=0.40$ (Video S5). Diamond particles belonging to same cluster are colored equally, meanwhile particles in a disordered state are colored in gray. A frame of the corresponding videos are reported in Fig. S8.


FIG. S8. Frames of Videos S1-S5 showing the evolution and grow of the initial diamond clusters corresponding to systems with a core-to-lobe size ratio $s=1.24$, depletant-to-lobe size ratio $q=0.12$ and depletant reservoir packing fraction a) $\left.\eta_{d}^{r}=0.10 \mathrm{~b}\right) \eta_{d}^{r}=0.15$, c) $\eta_{d}^{r}=0.20$, d) $\eta_{d}^{r}=0.30$ and e) $\eta_{d}^{r}=0.40$. a) corresponding to a crystalline diamond grain, b-d) to gel-diamond structures with different degrees of arrest and e) to a disordered gel. (Multimedia view)


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