Self-Assembly of Patchy Particles into Diamond Structures through Molecular Mimicry

Zhenli Zhang\textsuperscript{1}, Aaron S. Keys\textsuperscript{1}, Ting Chen\textsuperscript{1}, and Sharon C. Glotzer\textsuperscript{1,2}\textsuperscript{*}

\textsuperscript{1} Department of Chemical Engineering and \textsuperscript{2} Department of Materials Science Engineering, University of Michigan, Ann Arbor MI, 48109-2136

Fabrication of diamond structures by self-assembly is a fundamental challenge in making three-dimensional photonic crystals. We simulate a system of model hard particles with attractive patches and show that they can self-assemble into a diamond structure from an initially disordered state. We quantify the extent to which the formation of the diamond structure can be facilitated by “seeding” the system with small diamond crystallites or by introducing a rotation interaction to mimic a carbon-carbon antibonding interaction. Our results suggest patchy particles may serve as colloidal “atoms” and “molecules” for the bottom-up self-assembly of three-dimensional crystals.

I. INTRODUCTION

The diamond structure is one of the most desirable structures from which to make photonic crystals because it provides a three-dimensional, complete photonic band gap that allows the crystal to diffract light efficiently\cite{1}. The current methods of fabrication of these structures involve direct drilling\cite{2} and layer-by-layer lithography\cite{3}, which are both top-down approaches and are usually expensive and inefficient. Thus the current fundamental challenge to the materials community is how to fabricate the diamond photonic-band gap structure in an economically feasible and controllable way that is capable of being scaled up to industrial scales. Bottom-up self-assembly is a promising strategy, given the right interactions among the building blocks. There has been substantial interest in assembling 3D crystals from colloidal particles\cite{4,5,6,7,8,9}. However, self-assembling a diamond crystal using a one-component system of colloids has not yet been achieved\cite{11}. Decorating the surface of colloids with attractive “patches” suggests a promising approach to assemble more complex structures, in a potentially controllable and predictable way due to the precise interactions between the patches\cite{12}. Many natural and synthetic molecules and particles, such as protein capsomers in virus shells and nanoparticles with binding ligands\cite{13}, can be viewed as patchy particles which may serve as programmable building blocks for tomorrow’s materials\cite{14}.

Here we propose a model system of patchy particles that, soon, may be possible to fabricate based on recent experimental findings and theoretical analysis\cite{15,16}. By performing Monte Carlo simulations, we show that these model patchy particles are capable of assembling from a disordered state into a diamond lattice, and we quantify the extent to which seeding the system, or adding a rotational interaction, can dramatically facilitate the formation of diamond structured assemblies.

\textsuperscript{*}Corresponding author. E-mail: sglotzer@umich.edu

FIG. 1: Model of patchy particle in our simulations (right). Sticky “patches” are shown in pink. Dotted circle indicates fourth sticky patch on far side of particle. Related models described in text (left). Nelson model in upper left based on similar schematic in ref \textsuperscript{15}.

A. Model and Simulation Method

The model system we consider is illustrated in Figure 1 (right), which shows a spherical particle with four circular patches arranged in a tetrahedron on the particle surface. A pairwise attraction is assigned between the patches\cite{12}. Many natural and synthetic molecules and particles, such as protein capsomers in virus shells and nanoparticles with binding ligands\cite{13}, can be viewed as patchy particles which may serve as programmable building blocks for tomorrow’s materials\cite{14}.

Here we propose a model system of patchy particles that, soon, may be possible to fabricate based on recent experimental findings and theoretical analysis\cite{15,16}. By performing Monte Carlo simulations, we show that these model patchy particles are capable of assembling from a disordered state into a diamond lattice, and we quantify the extent to which seeding the system, or adding a rotational interaction, can dramatically facilitate the formation of diamond structured assemblies.

*Corresponding author. E-mail: sglotzer@umich.edu
within the cluster protrudes slightly beyond the radius of
the outer sphere, providing circular “patches” of material
different from that of the outer sphere. To first approxi-
imation, both types of building blocks can be modeled
by a sphere with four circular patches arranged tetrahe-
drally.

The spherical shape of our model patchy particle allows
the use of a pair potential between patches expressed
as a hard sphere, square-well potential modulated by an
angular term [17]

\[ U_{ij}(r_{ij}; Q_i, Q_j) = u_{\text{hsw}}(r_{ij}) \cdot f(Q_i; Q_j), \]

where \( u_{\text{hsw}} \) is the regular hard sphere square well potential
with reduced range

\[ u_{\text{hsw}}(r_{ij}) = \begin{cases} 
\infty & \text{for } r < \sigma \\
-\epsilon & \text{for } \sigma \leq r < \lambda \sigma \\
0 & \text{for } r \geq \lambda \sigma 
\end{cases} \]

Here \( \sigma \) is the diameter of the particles and set to be
unity, and \( \epsilon \) is the depth of the square well potential.
The function \( f(Q_i; Q_j) = 1 \) only if particles \( i \) and \( j \) are
oriented so that the vector joining their mass centers in-
tersects an attractive patch on both particles; otherwise
\( f(Q_i; Q_j) = 0 \). The angle \( \delta \), shown in Figure 1(right),
represents the patch size, and \( \lambda \) represents the interac-
tion range. The two values in combination determine the
directionality and preciseness of the interaction between
any two patches. In this study we fix the location of the
patches and choose \( \delta = \pi/6 \), \( \lambda = 1.1\sigma \) which, for a 1 \( \mu \)m
diameter particle corresponds to a patch size of 0.26 \( \mu \)m
and an interaction range of 0.1 \( \mu \)m. We leave the effect
of size, interaction range and disorder in the location of
the patches for future investigation.

We perform Monte Carlo simulations using this model
in a cubic box of fixed size with periodic boundary con-
ditions. Since we are interested in the diamond struc-
ture (density \( \rho_d = 0.6495 \) for a perfect, box-spanning
diamond crystal), we limit our study to \( \rho < \rho_d \). All
simulation runs begin from a disordered state at high
temperature \( T \) and are subsequently cooled to the target
temperature. We investigate three types of systems: sys-
tems without small diamond crystal seeds, systems with
seeds, and systems with a modified potential to induce
the rotation of particles relative to “bonded” neighbors.
The details of the potential used for the third system will
be discussed later.

B. Results and Discussion

1. Systems Without Seeds

For the unseeded system, we examine the effect of two
different cooling rates on assembly. In the “fast” run, \( T \) is
decreased by \( \Delta T = 0.001 \) over cycles of 1 million Monte
Carlo steps (MCS), where \( T \) is defined in units of \( \epsilon/k_B \). A
MC step is defined here as one attempted MC move per
particle. In the “slow” run, \( T \) is decreased by \( \Delta T = 0.001 \)
over cycles of 10 million MCS. A Monte Carlo move for
a randomly selected particle is randomly chosen to be
either a translation or a rotation with equal probabil-
ity. The maximum values of the translation and rotation
are variable to keep the acceptance ratio at 0.5. De-
pending on the density, the maximum translation varies
from 0.02 to 0.04 particle diameters and the maximum
rotation ranges from 0.05 to 0.09 rad. Although there
is no simple and direct connection between the number
of Monte Carlo steps and the physically relevant time
scales of the system, the purely local, physical moves of
the simulation provide a reasonable approximation to lo-
cal diffusive motion. Eleven or twelve independent runs
are performed to obtain the statistical results shown for
each density. For the fast cooling rate, only kinetically
arrested, disordered structures are obtained. However,
at the slow cooling rate we observe the formation of di-
}
FIG. 2: Simulation results of the system without seeds. (a) Diamond structure obtained at slow cooling rate for $\rho = 0.40$, $T = 0.11$. (b) Pair correlation function $g(r)$ for disordered structures obtained with fast cooling rate and diamond structures obtained with slow cooling rate. Note absence of characteristic third peak for disordered structure. (c) Bond-angle distribution $g(\theta)$ for the diamond and disordered structures.

FIG. 3: Structural information for all systems. S1 corresponds to system without seeds, S2 corresponds to the seeded system, and S3 corresponds to the system with “antibonding” rotational interactions. (Top) Degree of crystallinity $\varphi_c$. (Bottom) Bond-angle correlation function $C_b$.

It is well-known that introducing small crystalline seeds of the desired structure into a liquid can accelerate crystallization in molecular and colloidal systems[19]. Therefore, it is of interest to ascertain to what extent this approach facilitates the formation of the desired diamond structure. To introduce the seeds, we freeze eight of the 512 particles in the simulation box into a single unit cell of a perfect diamond structure and let them remain immobile throughout the simulation. Prior to cooling, all other particles except the seed particles are randomly distributed in the simulation box. We investigate the same two cooling rates as for the unseeded system.

With the introduction of the seeds, we observe diamond structures for the fast cooling rate, which did not permit crystallization on the time scales of our simulations in the absence of a seed (Table 1). A typical structure at $\rho = 0.40$ is shown in Figure 5a. The fraction of times the diamond structure is obtained in 11 independent runs at a fast cooling rate increases from 0% for the systems without seeds to 64% for the systems with seeds. The same trend is observed for the slow cooling rate; although the fraction increases less dramatically from 55% to 64%, the facilitation is still evident. Table 1 shows that seeding facilitates crystallization at nearly all den-

2. Seeded Systems

responding ideal values of 100% and 1.0, respectively, for a perfect diamond crystal. The calculated values are much higher than those of the disordered structures, as shown in Figure 3, which includes data from several densities.

Figure 4a shows the time evolution of $\varphi_c$ and $C_b$ for the slowly cooled system in Figure 2a. We see that both quantities consistently show a sharp transition near $T = 0.133$, which indicates the occurrence of a structural transition. In contrast, no obvious change in the corresponding curves is found in the systems formed via the fast cooling rate. A plot of the “phase boundary” be-
TABLE I: Probability of Observing Diamond Structure for Various Systems.\(^a\)

|                | S1        | S2        | S3        | S1        | S2        |
|----------------|-----------|-----------|-----------|-----------|-----------|
| \(\rho = 0.10\) | 0\% (0/12)| 25\% (3/12) | 75\% (9/12) | 25\% (3/12) | 58\% (7/12) |
| \(\rho = 0.20\) | 0\% (0/12)| 42\% (5/12) | 100\% (11/11)| 25\% (3/12) | 50\% (6/12) |
| \(\rho = 0.30\) | 0\% (0/12)| 33\% (4/12) | 100\% (12/12)| 50\% (6/12) | 75\% (9/12) |
| \(\rho = 0.40\) | 0\% (0/12)| 64\% (7/11) | 100\% (12/12)| 55\% (6/11) | 64\% (7/11) |
| \(\rho = 0.50\) | 0\% (0/12)| 50\% (6/12) | 100\% (12/12)| 75\% (9/12) | 67\% (8/12) |

\(^a\)S1, S2, and S3 are defined in the caption of Figure 3. The percentages in the table correspond to \(N_d/N_r \times 100\%\), where \(N_d\) is the number of runs in which diamond structure is observed and \(N_r\) is the total number of total runs. \(N_d\) and \(N_r\) are indicated in parentheses.

3. Systems with Particle-Particle “Bond” Rotation

If we consider the attractive interaction between a pair of patches as a type of “bonding”, then all of the bonds in our colloidal diamond structure are rotated by 60° or 180°, as are the carbon-carbon bonds in the staggered conformation of ethane. Inspired by this atomistic feature of chemical bonding, we introduce an additional potential energy \(u_{ij} = \Delta U \cos(\theta)\) between pairs of bonded patchy particles, where \(\theta\) is the relative rotation angle and \(\Delta U \approx k_B T\). This additional potential energy term induces a relative orientation between particles that favors the formation of the diamond structure at low \(T\).

This rotation preference facilitates formation of the diamond structure substantially as compared to the first two methods; this is quantified in Table 1. We find diamond structures for all 12 independent runs at the fast cooling rate and density \(\rho = 0.40\). A typical structure is shown in Figure 5b. Further analysis of \(\varphi_c\) and \(C_b\) (Figure 3) indicates the diamond structures have fewer defects than those obtained by the first two approaches. For example, \(\varphi_c = 90.9\%\) and \(C_b = 0.922\) for \(\rho = 0.40\), indicating the formation of a nearly perfect diamond structure. How might such an interaction be induced between patchy particles? The rotation of a chemical bond in molecules such as ethane is due to antibonding interactions between the hydrogen atoms on opposite ends of the molecule. Here we offer two possibilities for mimicking this interaction with particles. The first approach involves the use of charges. Assume the patchy particle modeled here represents a tetrahedral cluster of four spheres fused permanently together. If the colloidal spheres carry a uniform surface charge, the repulsive electrostatic interaction between spheres in different clusters will induce a similar rotation, as shown schematically in Figure 5c. For 1\(\mu\)m-diameter colloidal spheres, we estimate that the surface charge needed on each sphere to induce an energy difference between two different rotation states of \(1k_B T\) at \(T = 298K\) is \(0.011231 C^2/m^2\), based on a model for a solution of charged colloids or proteins in water proposed by Phillips\[20\]. Considering the additional repulsive electrostatic interaction, an attraction energy \(\epsilon\) of a patch-patch interaction or “bond” of roughly \(3.0 \times 10^{-17} J\) should be sufficient to induce formation of the diamond structure.

The second approach uses a “patterned” patch. In the present work, the patches are considered circular and uni-
form, but they could be made to be nonuniform like the linear bi-patch pattern investigated computationally in our previous work, which also induces rotation. Thus by combining an attractive interaction between patches to provide a “bond” between particles with an additional interaction that provides bond rotation, colloidal spheres can be made to mimic tetravalent carbon atoms. It should be noted that the use of seeds and “antibonding” interactions apply to thermal systems as well as to systems where cooling rate is not a factor, as in suspensions of large colloids.

II. CONCLUSIONS

In summary, our simulations predict that patchy particles with small attractive patches located on the particle surface at the corners of a tetrahedron provide a promising route to achieve a diamond structure through self-assembly. Introducing a small amount of seeds or an “antibonding-like” interaction greatly facilitates the formation of the diamond structure. Our simulations demonstrate that atomic and molecular interactions can guide the design of patchy particles as a new generation of “colloidal molecules” to achieve colloidal crystal analogues of atomic and molecular crystals.

Acknowledgments

Financial support was provided by the Department of Energy, Grant No. DE-FG02-02ER46000. We thank M. A. Horsch, J. Mukherjee, M. J. Solomon, and N. A. Kotov for discussions and helpful comments on the manuscript. We thank the University of Michigan Center for Advanced Computing for support of our computing cluster.

[1] M. Maldovan and E. L. Thomas, Nature Mater. 3, 593 (2004).
[2] E. Yablonovitch, T. J. Gmitter, and K. M. Leung, Phys. Rev. Lett. 67, 2295 (1991).
[3] K. M. Ho, C. T. Chan, C. M. Soukoulis, R. Biswas, and M. Sigalas, Solid State Commun. 89, 413 (1994).
[4] P. V. Braun, R. W. Zehner, C. A. White, M. K. Weldon, C. Kloc, S. S. Patel, and P. Wiltzius, Adv. Mater. 13, 721 (2001).
[5] Y. A. Vlasov, X. Z. Bo, J. C. Sturm, and D. J. Norris, Nature Mater. 414, 289 (2001).
[6] A. Van Blaaderen, R. Ruel, and P. Wiltzius, Nature 385, 5.
321 (1997).
[7] Y. Yin and Y. Xia, Adv. Mater. 14, 605 (2002).
[8] W. Lee, A. Chan, M. A. Bevan, J. A. Lewis, and P. V. Braun, Langmuir 20, 5262 (2004).
[9] V. Tohver, J. E. Smay, A. Braem, P. V. Braun, and J. A. Lewis, Proc. Natl. Acad. Sci. USA 98, 8950 (2001).
[10] B. Griesebock, M. Egen, and R. Zentel, Chem. Mater. 14, 4023 (2002).
[11] Y. Xia, B. Gates, and Z.-Y. Li, Adv. Mater. 13, 409 (2001).
[12] Z. Zhang and S. C. Glotzer, Nano Lett. 4, 1407 (2004).
[13] Z. Tang, N. A. Kotov, and M. Giersig, Science 297, 237 (2002).
[14] S. C. Glotzer, Science 306, 419 (2004).
[15] D. R. Nelson, Nano Lett. 2, 1125 (2002).
[16] V. N. Manoharan, M. T. Elsesser, and D. J. Pine, Science 301, 483 (2003).
[17] N. Kern and D. Frenkel, J. Chem. Phys. 118, 9882 (2003).
[18] P. ten Wolde, M. Ruiz-Montero, and D. Frenkel, J. Chem. Phys. 104, 9932 (1996).
[19] A. Cacciuto, S. Auer, and D. Frenkel, Nature 428, 404 (2004).
[20] G. D. Phillies, J. Chem. Phys. 60, 2721?2731 (1974).
[21] S. C. Glotzer, M. J. Solomon, and N. A. Kotov, AIChE J. 50, 2978 (2004).
[22] A. van Blaaderen, Science 301, 470 (2003).