Three-dimensional non-close-packed structures of oppositely charged colloids driven by pH oscillation

Lei, Qun-li; Ren, Chun-lai; Long, Cheng; Ma, Yu-qiang

2018

Long, C., Lei, Q., Ren, C., & Ma, Y. (2018). Three-dimensional non-close-packed structures of oppositely charged colloids driven by pH oscillation. *The Journal of Physical Chemistry B*, 122(12), 3196-3201. doi:10.1021/acs.jpcb.8b00441

<https://hdl.handle.net/10356/90000>

<https://doi.org/10.1021/acs.jpcb.8b00441>

© 2018 American Chemical Society. This document is the Accepted Manuscript version of a Published Work that appeared in final form in *The Journal of Physical Chemistry B*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.jpcb.8b00441>

Downloaded on 26 Apr 2023 17:02:32 SGT

Three-dimensional Non-close-packed Structures of Oppositely Charged Colloids Driven by pH-oscillation

Cheng Long,[†] Qun-li Lei,[‡] Chun-lai Ren,^{*,†} and Yu-qiang Ma^{*,†,¶}

[†] *National Laboratory of Solid State Microstructures and Department of Physics,
Collaborative Innovation Center of Advanced Microstructures,
Nanjing University, Nanjing 210093, China*

[‡] *School of Chemical and Biomedical Engineering,
Nanyang Technological University, 637459, Singapore*

[¶] *Center for Soft Condensed Matter Physics and Interdisciplinary Research,
Soochow University, Suzhou 215006, China*

E-mail: chunlair@nju.edu.cn; myqiang@nju.edu.cn

Abstract

The building of non-close-packed structures in colloidal systems is challenging. Using Brownian dynamics simulations, we study nonequilibrium self-assembly in suspensions of oppositely charged particles, whose charge magnitude is responsive to the pH of the solution. Under the fast pH-oscillating condition, various non-close-packed (e.g., graphite-like and diamond-like) structures are obtained. Here changing the amplitude of the pH-oscillation is an effective way to fabricate colloidal dynamic structures. To clarify the underlying mechanism of the dynamic self-assembly, the analysis of effective potential is adopted. A dimensionless parameter, the ratio of effective repulsion and attraction, is introduced to reflect the subtle interactions in the system. We find that the imbalance between repulsion and attraction is the cause of structural diversity. Madelung energy is used to study the stability of these structures. Our results provide a new way to fabricate non-close-packed structures in colloidal systems, which has potential applications in the synthesis of photonic crystals.

Introduction

With the development of photonic technologies, non-closed-packed diamond lattice, typically consisting of optical wavelength-sized building blocks, has attracted immense interest in scientific community, due to its full three-dimensional photonic band gap.¹⁻³ A multi-decade effort was made to fabricate such non-close-packed structures using conventional lithography,² micromanipulation⁴ or holographic lithography⁵ as well as self-assembly approaches based on block copolymers,³ nanoparticles⁶⁻⁸ or colloidal crystallization.⁹⁻¹⁷ Among those approaches, colloidal self-assembly has been shown to be an efficient way to build photonic crystals not only for the desirable scale around the wavelength of the visible region, but also for the tailorability of colloidal size, shape, and interactions.¹⁸ However, without the help of covalent and hydrogen bonding at the molecular scale, low filling fraction and mechanical instability of the structure announce the notorious difficulty of forming a non-close-packed

lattice using colloidal crystallization,¹⁹ since colloids with short-ranged and isotropic attractive interaction will favor close-packed structures.

Experiments indicated that oppositely charged nanoparticles could self-assemble into diamond-like crystals,⁶ under the condition of charge asymmetry and screening length far more larger than the size of the assembling particles.²⁰ Those harsh conditions limit the component size and make it to be unadaptable to the larger scales required for photonic materials where systems usually present body centered cubic or simple cubic structure.^{21,22} Recent years, dissipative self-assembly via time-dependent interaction was reported promising not only in overcoming kinetic arrest in the process of crystallization,^{23,24} but also in its capability of forming novel structures that equilibrium methods cannot.^{25–27} Here, we investigate three-dimensional self-assembly in suspensions of oppositely charged particles where the magnitude of the charge is responsive to the pH of the solution. Under the condition of fast pH oscillation, various non-close-packed structures are obtained by changing the amplitude of pH oscillation and the volume fraction. Different from the equilibrium self-assembly of opposite charged particles in the previous work,²⁰ more rich structures are realized, and limitations in the equilibrium self-assembly are overcome. Moreover, the underlying mechanism of the dynamic self-assembly is disclosed by the analysis of effective potential. An important dimensionless parameter is introduced to emphasize the importance of the imbalance between repulsion and attraction of the system.

Methods

The system we consider is a binary mixture of equal amount of oppositely charged particles in a continuously pH-oscillating environment. We assume the pH of the solution varies with a sinusoidal function,

$$\text{pH}(t) = 2\mathcal{A} \sin(2\pi t/\tau) + 5 \quad (1)$$

where the parameter τ gives the period and the value of $\mathcal{A}$ is the oscillation amplitude. Moreover, it is postulated that the magnitude of the charge for particles of both positive type (p-type) and negative type (n-type) is responsive to the pH of the solution synchronously, yielding the well-known expression for acid-base equilibrium,

$$q_i(t) = \pm q_0 \frac{1}{1 + 10^{\pm(\text{pH}(t) - \text{p}K_a)}} \quad (i = \text{p}, \text{n}). \quad (2)$$

Here, the maximum absolute charge is set to the same value q_0 for both n-type and p-type. We choose the logarithm of the equilibrium constant $\text{p}K_a = 5$. Due to pH oscillation, the change of particle's charge within a single period is illustrated in Fig 1 (a).

Figure 1: (a) Time evolution of normalized charge on a particle for a single period with $\mathcal{A} = 1$. (b) The effective potential analysis. $\bar{k}_{pp/nn}$ represents the effective repulsion in the system; $\bar{k}_{pn}$ is the effective attraction; λ is the ratio of $\bar{k}_{pp/nn}$ to $\bar{k}_{pn}$. Double y axis is used, including the left y axis for λ and the right y axis for $\bar{k}_{ij}$.

On account of the screening effect from free ions in the solution, Yukawa potential is employed to approximate the Coulomb interaction in a low screening ratio system; Lenard-Jones potential with cutoff radius σ is adopted to manifest the repulsion between colloidal cores. As a result, the interaction potential between particles of i type and j type can be

expressed by

$$U_{ij}(r, t) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + k_{ij}(t)U_m & 0 < r < \sigma \\ k_{ij}(t)U_m \frac{e^{-\kappa(r-\sigma)}}{r} & r \geq \sigma \end{cases} \quad (3)$$

where r is the distance between the particles, κ^{-1} is the Debye-Hückel screening length related to the ionic strength of the electrolyte. $U_m = q_0^2/(4\pi\epsilon_0\epsilon_r k_B T(1 + \kappa\sigma)^2)$ is the maximum interaction strength. $k_{ij}(t) = q_i(t)q_j(t)/q_0^2$ is the normalized time-dependent function due to charge oscillation of each particle. In this work, we set $\kappa = 3$ corresponding to the case where Debye screening length is one third of the particle diameter.

In the limit of the fast oscillations, the time-dependent interaction (3) can be well approximated by a time-averaged effective potential,²⁶

$$\begin{aligned} U_{ij}^e(r) &= \frac{1}{\tau} \int_0^\tau U_{ij}(r, t) dt \\ &= \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \bar{k}_{ij}U_m & 0 < r < \sigma \\ \bar{k}_{ij}U_m \frac{e^{-\kappa(r-\sigma)}}{r} & r \geq \sigma \end{cases} \end{aligned} \quad (4)$$

where

$$\bar{k}_{ij} = \frac{1}{\tau} \int_0^\tau \frac{q_i(t)q_j(t)}{q_0^2} dt. \quad (5)$$

According to Eqs (2), (4) and (5), effective repulsions between the same type of charged particles are equal, i.e., $U_{pp}^e(r) = U_{nn}^e(r)$ (or equivalently, $\bar{k}_{pp} = \bar{k}_{nn}$), where subscript p corresponds to p-type, n is n-type. In terms of effective attraction, two cases should be considered separately. One is $\mathcal{A} = 0$, where the pH of the solution is constant and the system will evolve to its equilibrium eventually with $\bar{k}_{pp} = \bar{k}_{pn}$. The other is $\mathcal{A} \neq 0$. Since we choose the oscillation of pH between 3 and 7 in our calculations, where the repulsion reaches its maximum and the attraction decreases to its minimum, it gives rise to stronger strength for repulsion than attraction ($\bar{k}_{pp/nn} > \bar{k}_{pn}$), which is inaccessible just by a simple

combination of a short-range repulsion and a Yukawa potential in an equilibrium condition.

To characterize such repulsion-attraction imbalance induced by the pH-oscillation, we define a dimensionless parameter

$$\lambda \equiv \frac{\bar{k}_{pp}}{\bar{k}_{pn}}. \quad (6)$$

For the case of $\mathcal{A} = 0$, $\lambda = 1$ represents the equilibrium state. For conditions of $\mathcal{A} \neq 0$, λ deviates from 1. The relationships between $\bar{k}_{pp}$, $\bar{k}_{pn}$, λ and $\mathcal{A}$ are illustrated in Fig 1 (b). It can be seen that effective repulsion is larger than attraction. With the increase of $\mathcal{A}$, λ increases monotonously indicating more severe divergence between $\bar{k}_{pp}$ and $\bar{k}_{pn}$. In the following, we use λ instead of $\mathcal{A}$ to discuss the structural formation of the system for the reason that λ reflects the influence of competition between repulsion and attraction on the self-assembly, which also can be used in other self-assembly systems with the repulsion-attraction imbalance, not only for the charged system.

Results and Discussion

Figure 2: Snapshots with unit cells of self-assembly structures including mixed graphite structure (a), bridged graphite structure (b), hexagonal diamond structure (c), cubic diamond structure (d), shrunken diamond structure (e) and simple cubic structure (f). Red balls represent p-type while blue balls are n-type. For each couple of particles whose distance between them is less than 1.3, a bond is added in snapshots to indicate that they are the nearest neighbor. Snapshot (a) is taken from the direction of $\langle 110 \rangle$, (b) $\langle 010 \rangle$, (c) $\langle 001 \rangle$, (d) $\langle 110 \rangle$, (e) $\langle 100 \rangle$ and (f) $\langle 100 \rangle$. In unit cells, a_1 , a_2 and a_3 specify the lengths of their three translation vectors, and the lattice constants for their unit cells are provided in SI Table S1.

To explore structural formation of the system, overdamped Langevin dynamics simulations are performed in a binary mixture of $N = 2744$ oppositely charged particles where the amount of the n-type is equal to the p-type. We use dimensionless units and set the fundamental quantities mass μ , diameter of the particles σ , and energy $\epsilon = 1$; we also set our simulation temperature $T = 1$. Our parameter choice corresponds to the diffusion coefficient $D_0 = k_B T / \zeta = 0.1$; hence, the characteristic diffusion timescale can be evaluated by $t_d = \sigma^2 / D_0 = 10$. According to the requirement for the emergence of steady-state structures that the period of pH-oscillation τ should be small enough comparing to the diffusional timescale t_d ,²⁵ we set the period of the pH-oscillation $\tau = 0.02 \ll t_d$. Throughout our simulations, the depth of the effective attraction well is kept constant at $\bar{k}_{pn} U_m = 13.68$ by adapting the interaction strength U_m , to provide a strong attraction between particles of different type. More details on our simulations are provided in simulation methods of Supporting Information (SI).

Under the condition of pH-oscillation, a number of distinct structures are found with different λ and volume fraction ϕ . Generally, self-assembly structures can be classified into disordered structures which have no long-range translational order in any direction, and crystalline structures which have long-range translational order in specific directions. When the volume fraction is low ($\phi < 0.2$), systems reside in disordered states. For large values of λ , network structure is formed (see Fig. S1 in SI). With the increase of volume fraction, various crystals may appear. Particularly, non-close-packed structures come into being. At $\phi \approx 0.25$, mixed graphite structure (Fig 2 (a)) occurs. As the snapshot indicates, it has a layered, planar structure as graphite where each layer is arranged in honeycomb lattice. There are two slightly different stacking form inside mixed graphite structure: overlapped graphite (Fig 2 (I)) and staggered graphite (Fig 2 (II)). Although they are very similar in unit cells, particle's distribution in layer is different for these two structures. Denser than the mixed graphite structure, bridged graphite structure (Fig 2 (b)) is found at the volume fraction $\phi \approx 0.29$. From its unit cell, it can be viewed as a direct deformation of the overlapped graphite

structure with additional bridges connecting between adjacent layers. With the increase of volume fraction, a next structure is hexagonal diamond structure (Fig 2 (c)) appearing at $\phi \approx 0.33$. However, with the increase of λ , the mixture of hexagonal diamond and cubic diamond (Fig 2 (d)) is developed. To distinguish these two different diamond lattices, common neighbor analysis²⁸ (CNA) is implemented (see Fig S2 in SI). A ratio of particles in hexagonal diamond structure to total particles N_h/N is used to distinguish different diamond structures. We regard it as the hexagonal diamond structure with $N_h/N \geq 0.8$; the cubic diamond structure with $N_h/N \leq 0.2$; and their mixture at $0.2 < N_h/N < 0.8$. When volume fraction reaches to $\phi \approx 0.36$, shrunken diamond structure (Fig 2 (e)) appears. It has the same coordination number with the diamond structure, but exhibits completely distinct symmetry from the diamond structure. According to the illustration of unit cells, cubic/hexagonal diamond structure has FCC/HCP lattice, while shrunken diamond structure has BCC lattice. With the further increase of particle volume fraction, simple cubic structure (Fig 2 (f)) happens, which has been proved hard to exist stably in the equilibrium self-assembly for the binary mixture of oppositely charged particles.²⁹

Figure 3: Structural diagram of pH-oscillating systems. Thick lines are used to delineate different regions with different structures. Areas connected by horizontal thin lines are disorder-order and order-order phase coexistence regions.

Structural diagram in the plane of $\lambda - \phi$ is given in Fig 3, including different regions for different structures, as well as the phase coexistence region which identifies a first-order

phase transition between adjacent structures. There will be disorder-order and order-order phase coexisting region. A large order-order phase coexistence region can be seen between cubic diamond structure and simple cubic structure, while the region of shrunken diamond coexisting with simple cubic is narrow.

Figure 4: (a) RDF and (b) BOP for the mixed graphite structure. “DT” represents the curve obtained from different type of particles, and “ST” is calculated from the same type of particles. Thicker solid lines are results from our calculations. Dash lines and thinner solid lines are obtained from ideal crystals.³⁰

To specify the crystalline structures quantitatively, radial distribution function (RDF) and bond order parameters (BOP)³¹ are calculated. The former is used to characterize the spatial correlation between particles, and the latter is to reflect the bond distribution for the nearest neighbors of each particle. Fig. 4 (a) shows RDF both for the structure obtained from our simulation and ideal overlapped and staggered graphite structures, implying that the structure in our simulation is their mixture. It should be mentioned that, BOP curves for two ideal structures are same. Fig. 4 (b) indicates a small deviation between our simulation results and the ideal structures, meaning that there will be a little deformation on unit cells

of our simulation results compared with ideal crystals. RDF and BOP for other structures are given in Fig. S3 of SI. All of them consist with ideal crystals, in addition to some small deviations.

Figure 5: Madelung energy calculations for distinct perfect crystals. The inset is the enlarged part of the bridged graphite area. Two dash lines divide the graph into three parts with different stablest structures. Because the Madelung energies for hexagonal diamond and cubic diamond are almost same, data points for these two structures are overlapped in this figure.

To analyze the stability of these structures, Madelung energy³² (potential energy per particle in the perfect crystal) of ideal crystal lattices are calculated in Fig 5, where lattice constants for each perfect crystal are chosen as SI Table 1. Although overlapped graphite structure is stabler than staggered graphite structure in terms of lattice energy, their energy are very similar. That's the reason that these two structures are always mixed. Additionally, the Madelung energies for hexagonal and cubic diamond structures are almost same, which supports the coexistence of these two structures. Furthermore, according to the minimum Madelung energy, three areas can be obtained along the direction of increasing λ , which are simple cubic area, bridged graphite area, and overlapped graphite area. In each area, with the increase of the volume fraction at the fixed λ , the structure with the minimum Madelung energy is the first ordered structure occurring after the disordered state, which can be seen that from the structural diagram in Fig. 3. We find increasing λ drives the

structure toward more non-close-packed cases. In other words, λ is larger, the repulsion dominates the self-assembly, resulting in the more loose structure.

Considering an experimental setup with particle diameter $\sigma = 500\text{nm}$, mass of a single particle $\mu \approx 0.916 \times 10^{-16}\text{Kg}$, environmental temperature $T = 298\text{K}$, and viscosity of the solvent, for example, $\eta \approx 0.89\text{mPa}\cdot\text{s}$ for water, the characteristic diffusion timescale in this system is $t_d = 3\pi\eta\sigma^3/k_BT \approx 0.253\text{s}$. In our simulations, the ratio of the pH-oscillation period to the characteristic diffusion timescale is $\tau/t_d = 1/500$ and accordingly, the corresponding pH-oscillation period in the real world time-scale will be $t_d \approx 0.506 \times 10^{-3}\text{s}$, which might be implemented by photochemical^{33,34} or electrochemical³⁵ technique in experiments. Moreover, applying more viscous solvent in experiments may support larger pH-oscillation period.

Conclusions

In contrast to the research work done by Sherman and Swan on 2016,²⁴ where periodically toggled short-range attraction was applied in a dispersion of nanoparticles to avoid kinetic barriers and to yield well-ordered crystalline domains, we investigate a binary system with periodically oscillating long-range interactions and utilize it to fabricate exotic non-close-packed structures. By introducing the external driving forces, namely, an oscillating pH environment, opposite-charged colloidal particles were found to undergo nonequilibrium self-assembly, forming three-dimensional non-close-packed structures including graphite-like structures and variable diamond crystals. To our knowledge, it is the first report that stable graphite-like and diamond-like structures can form in the colloidal system. Moreover, we introduce a dimensionless parameter λ to reflect the imbalance between repulsion and attraction of the system, which basically can be used in other systems where both repulsion and attraction play important roles on the final structure, not only charged systems. It can be concluded that larger λ , more non-close-packed structure could be, which would be a general conclusion in similar self-assembly systems.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (No. 11774146, 11774147, 91427302, and 11474155), and the Fundamental Research Funds for the Central Universities (No. 020414380045). We are grateful to the high performance computing center of Nanjing University for doing the numerical calculations in this paper on its IBM blade cluster system.

Supporting Information Available

Detailed descriptions of simulation methods (Table S1), the length of basis vectors for the ideal crystal lattices (Figure S1), snapshot of the disordered structure, discriminating hexagonal diamond structure and cubic diamond structure with common neighbor analysis (Figure S2), quantitative structural specification for the remaining crystals (Figure S3). The supporting information is available free of charge.

References

- (1) Ho, K. M.; Chan, C. T.; Soukoulis, C. M. Existence of a photonic gap in periodic dielectric structures. *Phys. Rev. Lett.* **1990**, *65*, 3152–3155.
- (2) Yablonovitch, E. Photonic band-gap structures. *J. Opt. Soc. Am. B* **1993**, *10*, 283–295.
- (3) Maldovan, M.; Thomas, E. L. Diamond-structured photonic crystals. *Nature materials* **2004**, *3*, 593–600.
- (4) García-Santamaría, F.; Miyazaki, H.; Urquía, A.; Ibisate, M.; Belmonte, M.; Shinya, N.; Meseguer, F.; López, C. Nanorobotic Manipulation of Microspheres for On-Chip Diamond Architectures. *Advanced Materials* **2002**, *14*, 1144–1147.

- (5) Ullal, C. K.; Maldovan, M.; Thomas, E. L.; Chen, G.; Han, Y.-J.; Yang, S. Photonic crystals through holographic lithography: Simple cubic, diamond-like, and gyroid-like structures. *Applied Physics Letters* **2004**, *84*, 5434–5436.
- (6) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. Electrostatic Self-Assembly of Binary Nanoparticle Crystals with a Diamond-Like Lattice. *Science* **2006**, *312*, 420–424.
- (7) Cigler, P.; Lytton-Jean, A. K.; Anderson, D. G.; Finn, M.; Park, S. Y. DNA-controlled assembly of a NaTl lattice structure from gold nanoparticles and protein nanoparticles. *Nature materials* **2010**, *9*, 918–922.
- (8) Liu, W.; Tagawa, M.; Xin, H. L.; Wang, T.; Emamy, H.; Li, H.; Yager, K. G.; Starr, F. W.; Tkachenko, A. V.; Gang, O. Diamond family of nanoparticle superlattices. *Science* **2016**, *351*, 582–586.
- (9) Tkachenko, A. V. Morphological Diversity of DNA-Colloidal Self-Assembly. *Phys. Rev. Lett.* **2002**, *89*, 148303.
- (10) Hynninen, A.-P.; Thijssen, J. H.; Vermolen, E. C.; Dijkstra, M.; Van Blaaderen, A. Self-assembly route for photonic crystals with a bandgap in the visible region. *Nature materials* **2007**, *6*, 202–205.
- (11) Hynninen, A.-P.; Filion, L.; Dijkstra, M. Stability of LS and LS2 crystal structures in binary mixtures of hard and charged spheres. *The Journal of Chemical Physics* **2009**, *131*, 064902.
- (12) Marcotte, .; Stillinger, F. H.; Torquato, S. Communication: Designed diamond ground state via optimized isotropic monotonic pair potentials. *The Journal of Chemical Physics* **2013**, *138*, 061101.

- (13) Jain, A.; Errington, J. R.; Truskett, T. M. Dimensionality and Design of Isotropic Interactions that Stabilize Honeycomb, Square, Simple Cubic, and Diamond Lattices. *Phys. Rev. X* **2014**, *4*, 031049.
- (14) Wang, Y.; Wang, Y.; Breed, D. R.; Manoharan, V. N.; Feng, L.; Hollingsworth, A. D.; Weck, M.; Pine, D. J. Colloids with valence and specific directional bonding. *Nature* **2012**, *491*, 51–55.
- (15) Zhang, Z.; Keys, A. S.; Chen, T.; Glotzer, S. C. Self-assembly of patchy particles into diamond structures through molecular mimicry. *Langmuir* **2005**, *21*, 11547–11551.
- (16) Romano, F.; Sanz, E.; Sciortino, F. Phase diagram of a tetrahedral patchy particle model for different interaction ranges. *The Journal of Chemical Physics* **2010**, *132*, 184501.
- (17) Wang, Y.; Jenkins, I. C.; McGinley, J. T.; Sinno, T.; Crocker, J. C. Colloidal crystals with diamond symmetry at optical lengthscales. *Nat Commun* **2017**, *8*, 14173.
- (18) Li, B.; Zhou, D.; Han, Y. Assembly and phase transitions of colloidal crystals. *Nature Reviews Materials* **2016**, *1*, 15011.
- (19) Glotzer, S. C.; Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nat Mater* **2007**, *6*, 557–562.
- (20) Bishop, K. J.; Chevalier, N. R.; Grzybowski, B. A. When and why like-sized, oppositely charged particles assemble into diamond-like crystals. *The journal of physical chemistry letters* **2013**, *4*, 1507–1511.
- (21) Bartlett, P.; Campbell, A. I. Three-dimensional binary superlattices of oppositely charged colloids. *Phys Rev Lett* **2005**, *95*, 128302.
- (22) Leunissen, M. E.; Christova, C. G.; Hynninen, A. P.; Royall, C. P.; Campbell, A. I.;

- Imhof, A.; Dijkstra, M.; van Roij, R.; van Blaaderen, A. Ionic colloidal crystals of oppositely charged particles. *Nature* **2005**, *437*, 235–40.
- (23) Risbud, S. R.; Swan, J. W. Dynamic self-assembly of colloids through periodic variation of inter-particle potentials. *Soft matter* **2015**, *11*, 3232–3240.
- (24) Sherman, Z. M.; Swan, J. W. Dynamic, directed self-assembly of nanoparticles via toggled interactions. *ACS nano* **2016**, *10*, 5260–5271.
- (25) Tagliazucchi, M.; Weiss, E. A.; Szleifer, I. Dissipative self-assembly of particles interacting through time-oscillatory potentials. *Proceedings of the National Academy of Sciences* **2014**, *111*, 9751–9756.
- (26) Tagliazucchi, M.; Szleifer, I. Dynamics of dissipative self-assembly of particles interacting through oscillatory forces. *Faraday discussions* **2016**, *186*, 399–418.
- (27) van Ravensteijn, B. G. P.; Hendriksen, W. E.; Eelkema, R.; van Esch, J. H.; Kegel, W. K. Fuel-Mediated Transient Clustering of Colloidal Building Blocks. *Journal of the American Chemical Society* **2017**, *139*, 9763–9766.
- (28) Maras, E.; Trushin, O.; Stukowski, A.; Ala-Nissila, T.; Jónsson, H. Global transition path search for dislocation formation in Ge on Si(001). *Computer Physics Communications* **2016**, *205*, 13 – 21.
- (29) Hynninen, A. P.; Leunissen, M. E.; van Blaaderen, A.; Dijkstra, M. CuAu structure in the restricted primitive model and oppositely charged colloids. *Phys Rev Lett* **2006**, *96*, 018303.
- (30) Szczygielska, A.; Burian, A.; Duber, S.; Dore, J.; Honkimaki, V. Radial distribution function analysis of the graphitization process in carbon materials. *Journal of Alloys and Compounds* **2001**, *328*, 231 – 236.

- (31) Steinhardt, P. J.; Nelson, D. R.; Ronchetti, M. Bond-orientational order in liquids and glasses. *Phys. Rev. B* **1983**, *28*, 784–805.
- (32) Kittel, C. *Introduction to Solid State Physics, 7th Edition*.
- (33) Nunes, R. M. D.; Pineiro, M.; Arnaut, L. G. Photoacid for Extremely Long-Lived and Reversible pH-Jumps. *Journal of the American Chemical Society* **2009**, *131*, 9456–9462.
- (34) Shi, Z.; Peng, P.; Strohecker, D.; Liao, Y. Long-Lived Photoacid Based upon a Photochromic Reaction. *Journal of the American Chemical Society* **2011**, *133*, 14699–14703.
- (35) Shacham, R.; Avnir, D.; Mandler, D. Electrodeposition of Methylated Sol-Gel Films on Conducting Surfaces. *Advanced Materials* **1999**, *11*, 384–388.

Graphical TOC Entry