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In this work, we use an evolutionary design strategy to design polymer-grafted nanoparticles for targeted self-assembly. While the work is fundamental in nature, it could have large impacts in the self-assembly of nano- and colloidal particles for optical applications. There is a clear molecular design component to this work since we apply the evolutionary optimization strategy to the chemistry of the molecules on the nanoparticles' surfaces to achieve a targeted structure.

1 Introduction

Self-assembly of nanoparticles can give rise to a spectrum of two dimensional lattices in both organic and inorganic materials. By tuning the lattice structure, it has been demonstrated that enhanced or new functionalities including light conversion,¹ optical,^{2,3} and electronic^{4,5} properties can be observed in the materials. In most of cases, to achieve and maintain lattice structures other than beyond simple closepacked forms (*e.g.*, hexagonal packings) requires exquisite control of the interparticle interactions. This task can become particularly complex when it comes to nanoparticle lattices in functional polymeric composites, where the interactions between nanoparticles and polymers are relatively

Inverse design of grafted nanoparticles for targeted self-assembly

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Two dimensional nanoparticle lattices can exhibit unique optical, electrical, and chemical properties giving rise to emerging applications for photovoltaic conversion, electronics and optical devices. In many applications, it is useful to be able to control the particle spacing, the crystal lattice formed, and the local composition of the lattice by co-locating nanoparticles of varying chemistry. However, control over all of these variables requires exquisite control over the interparticle interactions, and a large number of degrees of freedom affect the interactions. Achieving a particular structure by design requires solving the inversedesign problem, where one must optimize the chemistry to meet the structure or property that is desired. In recent years, a variety of examples have shown that one can finely control the interactions between nanoparticles through the use of polymers grafted onto the nanoparticle surface and by controlling the grafting density and the distribution of molecular weights on the nanoparticle surface. In this work, we take the first steps on solving the inverse design problem using an approach that explicitly accounts for the chemistry on the surfaces of the particles. Using two-dimensional hybrid particle/field theory calculations and an evolutionary design strategy, we design polymer grafted nanoparticles that self-assemble into targeted square, honeycomb, and kagome lattices. We optimize both the length and grafting density of the polymers grafted to the nanoparticles, and we show that our design strategies are stable over a range of nanoparticle concentrations. Finally, we show that three-body interactions are critical for stabilizing targeted structures

> weak, typically a few k_bT , and either multi-body or anisotropic effects become important. In this scenario, the design of the interactions between nanoparticles can be quite challenging and involves optimizing a number of degrees of freedom to finely control the interparticle interactions.

> One popular strategy to tackle the design challenge is to use inverse design approaches.⁶⁻¹⁴ In this approach, a specific ordered structure is designated as the target. Then an optimization approach is developed to vary the intermolecular potential between the particles such that the particles with the optimized potential will obtain the targeted structure at equilibrium. Pioneering studies by Torquato, Stillinger, and co-workers established an optimization framework that searches for isotropic, pair-wise potentials where the objective function is defined as the difference between the ground state potential energies for the target structure and other candidate structures.⁶ Their approach was

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successful in searching for isotropic pair-wised potentials for particles self-assembled into two dimensional and three dimensional lattices.^{7,8} More recently, Truskett and coworkers have utilized simulated annealing techniques to optimize the potential such that the stable density range over which the target structure exhibits the lowest ground state potential energy against other candidate structures becomes maximized,⁹ and the form of the potential was restricted to purely-repulsive, convex forms. The method has been demonstrated in potentials that stabilize both two and three dimensional particle lattices against finite variations in the particle density.^{13,14} However, one challenge that remains outstanding in this field is providing direction for achieving a specific interaction between particles in an experimentally-accessible manner. In other words, it remains unknown what specific chemistry should be used to induce a precise interparticle interaction.

Grafting polymers to the surfaces of particles has long been used to stabilize colloidal and nano-particles against aggregation by effectively rendering the interparticle interactions repulsive.¹⁵ For nanoparticles with monodisperse grafting, previous studies have shown that at high grafting density the potential of mean force (PMF) is purely repulsive when long grafted polymers are wetted by short matrix polymers and screen depletion forces between the nanoparticles. In contrast, the PMF can become attractive when the grafted polymer is shorter than the matrix polymer and dewets the brush layer.^{16,17} When the grafting density becomes sparse, studies show that the interactions between the nanoparticles become anisotropic due to the open surface areas uncovered from the grafted polymer.^{18,19} The anisotropy can be further tuned by changing the grafted polymer length and density giving rise to a series of nanoparticle assemblies.²⁰⁻²² Jayaraman and coworkers have shown how polydispersity in the molecular weight of the grafted polymer would affect the PMF between polymer-grafted nanoparticles in a polymer matrix that is chemically identical to the brush. By combining polymer reference interaction site model (PRISM) theory and Monte Carlo simulation, they found at high grafting density condition the short range repulsion is enhanced by the crowing of monomers from both long and short grafted polymers while the attractive well in the intermediate range can be suppressed by the steric repulsion between the long grafted polymers.^{23,24} The enhanced repulsion between nanoparticles in this grafting strategy has been demonstrated by experimental studies, where inorganic nanoparticles with bimodal PDMS grafts show strong miscibility in polymer matrices with high molecular weight PDMS.^{25,26} Varying the graft architecture and using either semi-flexible polymers, mixed polymer brushes, Janus-grafted polymers, or block polymer brushes are other alternative routes for tuning the interparticle interactions.17,27-31

Evolutionary design optimization schemes, in particular the covariance matrix adaptive evolutionary strategy (CMA-ES),^{32,33} have recently emerged as a route for solving complex optimization problems in soft matter research. CMA-ES has been used in both the design of granular particles with tailored mechanical properties¹⁰ and in the guided pattern design of self-assembling block copolymers.^{11,12} In both applications, the method has been demonstrated to have efficient convergence despite the complicated function that is optimized. In this method, variables (denoted as a vector, $\vec{\lambda}$) to be optimized are updated iteratively via a stochastic process mimicking natural evolution. In an optimization trial denoted as j, mutations of variable $\vec{\lambda}_i$ are generated. The quality of each mutation is quantified by a predefined fitness function $G_i(\vec{\lambda})$. Then, the values of $\vec{\lambda}_{i+1}$ for the next generation are determined both upon the covariance matrix of the fitness function of the current mutations and the evolution path of the previous generations. This process is then iterated until convergence, which is typically taken when the fitness function becomes smaller than some threshold value.

In the manuscript, we employed CMA-ES as the optimization method to establish an inverse design framework of grafted nanoparticles based upon a polymer field theory model. In our approach, rather than tuning the non-bonded interactions between the nanoparticles to achieve a particular self-assembled structure, we change the length and number of grafted polymers on the surface of the particle, which in turn modifies the interactions between the nanoparticles. In this first demonstration, the CMA-ES method is applied to a series of two-dimensional lattices by searching for optimized grafting designs that minimize the free energy of square, honeycomb, or kagome lattice unit cells. These optimized designs are then validated using hybrid particle field theory (HPF) simulations where a number of nanoparticles with the optimized designs are sampled and shown to self-assemble into the targeted lattice. After validating our approach, we analyze the role that each grafted chain length plays in the assembly, and we demonstrate that the many-body interactions play a key role in the assembly of the nanoparticles into the targeted structures.

2 Theory and numerical methods

2.1 hSCFT model of polymer grafted nanoparticle

The field theoretic model of polymer grafted NP implemented in the CMA optimization scheme closely follows HPF.³⁴ Here, we briefly describe the key ingredients in the model. Each system contains *n* nanoparticles, and each nanoparticle is grafted with a set of polymer chains that are only distinguished by the number of monomers per chain; each polymer of length N_i has a grafting density of σ_i . The grafted polymer is modeled as a Gaussian chain linked by a harmonic bonds, $u_b(\mathbf{r}) = \frac{3\mathbf{r}^2}{2b^2}$, where *b* is the average bond length. Then the total bonded potential in the model is defined as

$$U_{b} = \sum_{i} \sum_{j}^{n\sigma_{i}} \sum_{k=1}^{N_{i}-1} u_{b} \left(\mathbf{r}_{j,k+1}^{i} - \mathbf{r}_{j,k}^{i} \right),$$
(1)

where i sums over the chains of unique lengths, j sums over all of the individual chains of length i, and k is over the monomers on each chain.

The mass of each monomer is distributed about its center using a unit Gaussian function, $h(\mathbf{r}) = \left(\frac{1}{2\pi a^2}\right) \exp\left(-\frac{\mathbf{r}^2}{2a^2}\right)$, where *a* is the smearing size of the Gaussian function. In a similar manner, the mass of a single NP is distributed about its center according to a complimentary errors function, $\Gamma(\mathbf{r}) = \frac{\rho_0}{2} \operatorname{efrc}\left(\frac{|\mathbf{r} - R_{\rm p}|}{\xi}\right)$, where the density decays from bulk value, ρ_0 , within the particle radius, $R_{\rm P}$, to zero away from the particle surface over a width controlled by ξ . The creating

particle surface over a width controlled by ξ . The grafting sites are distributed homogeneously over the nanoparticle, and the distribution of grafting sites is given by

$$\Gamma_{\sigma}(\mathbf{r}) = \frac{1}{\sigma_0} \exp\left[-\frac{(\mathbf{r} - R_{\rm p} - \xi)^2}{\xi^2}\right],\tag{2}$$

where σ_0 is the normalization factor that enforces the normalization $\int d\mathbf{r} \Gamma_{\sigma}(\mathbf{r}) = \mathbf{1}$. In a multi-NP system, the distribution of the grafting sites is defined as the convolution between Γ_{σ} (**r**) and the NP center distribution, $\hat{\rho}_n(\mathbf{r}) = \sum_{i}^{n} \delta(\mathbf{r} - \mathbf{r}_i)$, which has the form,

$$\hat{\sigma}_{g}(\mathbf{r}) = \frac{1}{n} \int d\mathbf{r}' \Gamma_{\sigma}(\mathbf{r} - \mathbf{r}') \hat{\rho}_{n}(\mathbf{r}') = \frac{1}{n} (\Gamma_{\sigma} \times \hat{\rho}_{n})(\mathbf{r}).$$
(3)

The NPs are immersed in an implicit θ -solvent to the polymer monomers, which allows us to neglect the pair-wise nonbonded interactions between monomers, and the only nonbonded interactions to be considered are the interparticle interactions and the monomer-particle interactions. We assume that the only interactions between the polymer monomers and the nanoparticles are the excluded volume interactions, which is defined as a convolution between the density distribution functions of the two species,^{35,36}

$$u_{\rm eff}(\mathbf{r}_i - \mathbf{r}_j) = \frac{u_0}{\rho_0} \int d\mathbf{r} \ \Gamma(\mathbf{r} - \mathbf{r}_i) h(\mathbf{r} - \mathbf{r}_j), \qquad (4)$$

where u_0 is the parameter indicating the interaction strength between NPs and monomers and \mathbf{r}_i and \mathbf{r}_j are the centers of NP *i* and monomer *j*, respectively. The total nonbonded potential is therefore

$$U_{\rm nb} = \int d\mathbf{r} \int d\mathbf{r}' \hat{\rho}_{\rm g}(\mathbf{r}) u_{\rm eff}(\mathbf{r} - \mathbf{r}') \hat{\rho}_{n}(\mathbf{r}'), \qquad (5)$$

where $\hat{\rho}_{g}(\mathbf{r})$ is the distributions of monomer centers.

The particle based partition function of the grafted nanoparticle system has the form,

$$\mathscr{Z} = z_0 \int d\mathbf{r}_g^{n \sum_{j} \sigma_i N_j} \int d\mathbf{r}^n \exp\left(-U_b - U_{nb}\right).$$
(6)

To develop the hybrid particle-field theory model, we closely follow the particle-to-field transformation³⁷ to decouple pair-wise interactions between monomers and NPs and transform eqn (8) into the field-based form as

$$\mathscr{Z} = z_1 \int d\mathbf{r}^n \int Dw \int D\rho_g \exp\left(-\mathscr{H}\left[w, \rho_g\right]\right).$$
(7)

Here \mathscr{H} is the effective Hamiltonian with the form,

$$\mathscr{H}[w,\rho] = \int d\mathbf{r} \int d\mathbf{r}' \rho_{g}(\mathbf{r}) u_{\text{eff}}(\mathbf{r}-\mathbf{r}') \hat{\rho}_{n}(\mathbf{r}') - \int d\mathbf{r} w(\mathbf{r}) \rho_{g}(\mathbf{r}) - \sum_{i} n \sigma_{i} \int d\mathbf{r}_{g} \hat{\sigma}_{g}(\mathbf{r}_{g}) \ln q_{g_{i}}(\mathbf{r}_{g}, N_{i}; [w]),$$
(8)

where $q_{g_i}(\mathbf{r}_g, N_i; [w])$ is the single chain partition function of the *i*th type grafted chain terminated at site \mathbf{r}_g . No approximations have been invoked in moving from eqn (6) to (7). The continuous field $w(\mathbf{r})$ can be understood as the chemical potential field conjugate with the continuous monomer density field, $\rho_g(\mathbf{r})$, and it captures the non-bonded interactions of the monomers with the nanoparticles. After invoking the mean-field approximation, the *w* and ρ_g fields can be solved from minimizing \mathcal{H} with respect to both the fields,

$$\frac{\delta \mathscr{H}}{\delta w} = \frac{\delta \mathscr{H}}{\delta \rho_{g}} = 0, \tag{9}$$

which gives rise to

$$w(\mathbf{r}) = (\hat{\rho}_n \times u_{\text{eff}})(\mathbf{r})$$

$$\rho_{g}(\mathbf{r}) = \tilde{\rho}_{g}(\mathbf{r}; [w]).$$
(10)

Here, $\tilde{\rho}_{g}(\mathbf{r}; [w])$ is the density operator of the grafted chains, which can be evaluated as the following,

$$\tilde{\rho}_{g}\left(\mathbf{r}; [w]\right) = \sum_{i} \sum_{j=1}^{N_{i}} q_{g_{i}}\left(\mathbf{r}, j\right) e^{w(\mathbf{r})} q_{g_{i}}^{\dagger}\left(r, N_{i} - j\right), \qquad (12)$$

where q_{g_i} and $q_{g_i}^{\dagger}$ are the propagators of the *i*th type grafted chain form the free end and grafted end, respectively. Note that for brevity we did not include the explicit dependence on the field, $w(\mathbf{r})$. To evaluate the propagators, a Chapman–Kolmogorov equation is iterated according to

$$q_{\mathbf{g}_{i}}(\mathbf{r}, j) = \mathrm{e}^{-\mathrm{w}(\mathbf{r})} \int \mathrm{d}\mathbf{r}' \boldsymbol{\Phi}(\mathbf{r} - \mathbf{r}') \times q_{\mathbf{g}_{i}}(\mathbf{r}', j-1).$$
(13)

 $\Phi(\mathbf{r})$ is a normalized bond transition probability $\Phi(\mathbf{r}) = u_0 e^{-\beta u_b(\mathbf{r})}$, where u_0 is defined so that $\int d\mathbf{r} \, \boldsymbol{\Phi}_\sigma(\mathbf{r}) = \mathbf{l}$. The Chapman–Kolomogorov equation is iterated with the following initial conditions,

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$$q_{g_i}(\mathbf{r}, 0) = e^{-w(\mathbf{r})},\tag{14}$$

$$q_{g_{l}}^{\dagger}(\mathbf{r},0) = e^{-w(\mathbf{r})} \frac{\hat{\sigma}_{g}(\mathbf{r})}{q_{g_{l}}(\mathbf{r},N_{l})}.$$
 (15)

We note that the NP coordinates are retained through the particle-to-field transformation and remain explicit in the effective Hamiltonian. This makes the gNP model in the family of HPF simulation approaches³⁴ and we denote it the hSCFT model of polymer-grafted nanoparticles. We take *b* as the unit length in our simulations, and all energies are scaled by k_bT .

During the optimization phase where we implement the CMA-ES algorithm (described below), we perform our calculations in a unit cell with fixed particles that are not allowed to move. Thus, evaluating eqn (6) for this unit cell gives us direct access to the free energy of our system with a fixed nanoparticle lattice.

2.2 Hybrid particle field theory simulation

In the validation stage of our analysis, the NP coordinates need to be evolved in order to sample their equilibrium positions and test whether our optimized grafted nanoparticles will spontaneously self-assemble into the targeted structures. To that end, we begin with a collection of grafted nanoparticles randomly distributed in a simulation box and equilibrate them using a Brownian dynamics scheme.³⁴ To avoid strong overlap between NP cores during validation, a pairwise extended Lennard-Jones potential is employed to mimic hard core repulsion between NP cores,

$$u_{\rm LJ}(r) = 4 \left[\left(\frac{\xi}{r - 2R_{\rm p}} \right)^{12} - \left(\frac{\xi}{r - 2R_{\rm p}} \right)^6 \right], r_{\rm cut} = 2R_{\rm p} + 2^{1/6}\xi.$$
(16)

Thus, the total inter-particle core potential is

$$U_{\rm nn} = \int d\mathbf{r} \int d\mathbf{r}' \hat{\rho}_n(\mathbf{r}) u_{\rm LJ}(\mathbf{r} - \mathbf{r}') \hat{\rho}_n(\mathbf{r}'), \qquad (17)$$

The equation of motion for the *i*th NP is given as

$$\frac{\mathrm{d}\mathbf{r}_{i}}{\mathrm{d}t} = -\zeta \frac{\partial (\mathscr{H} + U_{\mathrm{nn}})}{\partial \mathbf{r}_{i}} + \theta_{i}(t), \qquad (18)$$

where $\theta_i(t)$ is a Gaussian white noise and has the following statistics,

$$\langle \theta_i(t) \rangle = 0 \langle \theta_i(t) \theta_j(t') \rangle = 2\zeta \delta_{i,j} \delta(t-t').$$
 (19)

The parameter ζ in the above equations is set to unity and a time step of $\Delta t = 2 \times 10^{-3}$ is used here. We would like to note that by tracking the inter-particle forces from U_{nn} we do not observe overlap between nanoparticle cores in all the HPF simulations performed here. This is likely due to the repulsion provided by the grafted polymer chains. We note that the force, $-\frac{\partial(\mathscr{H})}{\partial \mathbf{r}_i}$, experienced by each particle contains con-

tributions from both inter-particle and particle-monomer interactions due to chain grafting.³⁴

In our validation simulations, unlike standard selfconsistent field theory calculations, since the nanoparticle positions are evolving direct access to the exact free energy of the system is no long available. Therefore, we resort to an approximation of the free energy. The expression for $\mathscr{H}[w, \rho]$ given above in eqn (8) contains contributions from the enthalpic interactions between the particles and the polymers as well as the entropy of the grafted chains. The entropy associated with the vibrations of the nanoparticles around their equilibrium positions is absent, and this entropic contribution is approximated by using the classical form of the quasiharmonic approximation

$$F_{\rm qh} = \sum_{i} \ln v_i, \qquad (20)$$

where v_i is the frequency of vibration of the *i*th normal mode of the NP lattice. To obtain the normal modes, we first calculate the displacement correlation matrix of NPs,

$$D_{ab} = \langle \mathbf{u}_a(t)\mathbf{u}_b(t) \rangle, \tag{21}$$

where $\mathbf{u}_a(t)$ is the displacement of the *a*th NP at time *t* and $\langle ... \rangle$ denotes the average over the HPF simulation trajectory. We subsequently diagonalize the 2*n*-by-2*n* matrix *D*, and the frequencies v_i are calculated from the eigenvalues as

$$\nu_i = \lambda_i^{-1/2},\tag{22}$$

where λ_i denotes the *i*th eigenvalues of D_{ab} .³⁸ Finally, we approximate the free energy of the system on a per-nanoparticle basis as

$$\frac{F}{k_{\rm B}T} = \left\{ \mathscr{H} + F_{\rm qh} \right\} / n. \tag{23}$$

2.3 Evolutionary design scheme

The implementation of CMA-ES here requires the definition of two key parameters: the fitness function to be optimized and the set of variables to be updated in the optimization. For the *j*th optimization trial, the set of variables needed to optimized are the lengths of the grafted chains $N_{i,j}$ and the grafting density associated with each grafted chain length $\sigma_{i,j}$, which are denoted as the set of variables as $\lambda_j = \{N_{ij}, \sigma_{ij}\}$. To define the fitness function, we first choose a range of densities, $\rho \in [\rho_{\min}, \rho_{\max}]$, over which we wish to obtain a target structure. At a specific density in this range, we calculate $g(\lambda_j, \rho) = \max [F_{target}(\rho) - F_{competing}(\rho)]$, where $F(\rho)$ is the free energy of a crystal structure calculated using the unit cell hybrid particle-field theory described above, and the maximum is taken over all competing structures. For example, when the target structure is a square lattice, $F_{target} = F_{sq}$, and all of the competing structures are the triangle, kagome, and honeycomb lattices. For the sake of brevity, we use SQ, KG, and HC to denote the square, kagome, and honeycomb lattices, respectively. The fitness function for the *j*th optimization trial

is then defined as $G_j = \sum_{\rho}^{n_{\rho}} g(\vec{\lambda}_j, \rho)$, where the sum is taken over n_{ρ} discrete density values we have used in the range $[\rho_{\min}, \rho_{\max}]$.

With the goal of maintaining as simple of a grafted polymer design as possible, we restrict the design to bidisperse grafted nanoparticles; $\bar{\lambda}_j$ consists of two chain lengths and two grafting densities. The population size (number of mutations for the set of $\bar{\lambda}_j$) is taken as seven times the number of variables we are optimizing, giving a parameter population size of 28. This choice is based on suggestions from previous studies^{11,32} and our own tests for convergence. The larger one of the two chains lengths is initialized randomly from a Gaussian with a mean of $(2R_p)^2$ (so the average end-to-end distance is on the order of the particle diameter) and a variance of $(R_p/2)^2$. The smaller chain length is initialized to one half the longer chain length, and both grafting densities are initialized to $2\pi R_p$.

At each iteration in the optimization procedure, a number of mutations of the current generation of $\bar{\lambda_j}$ are made, we evaluate our fitness function G_j , and we call the CMA-ES routine to update the parameters that comprise $\bar{\lambda_{a,j}}$. The implementation here uses the CMA-ES developed by N. Hansen and co-workers,^{32,33} which is freely available as a Python package. In each trial, the CMA-ES routine continues until the parameters no longer change and the change of G_j within a tolerance of $\Delta G_j/n_\rho n = 10^{-4}k_{\rm B}T$ or the global fitness function G_j is less than $-5k_{\rm B}T$ per nanoparticle in the unit cell. The total optimization process is then repeated to convergence for fifty different trials, $j \in [1, 50]$, and the solution with the lowest G_j is taken as the converged solution and tested using the Brownian dynamics HPF described above.

3 Results

3.1 Validation

We begin by presenting the details of the results of our optimization scheme when we target a square lattice over a range of NP areal densities $\rho \in [0.034, 0.042]$. From the set of optimized grafting densities generated in our CMA-ES implementation, three representative designs denoted as SQ1, SQ2 and SQ3 are selected and plotted in Fig. 1a as $N_i vs. \sigma_i$. The SQ1 shown in the black circles has the minimum global fitness function amongst all the generated solutions. For all of the selected solutions, the two optimized chain lengths are distributed about $N_1 \approx 3$ and $N_2 \approx 16$ (Fig. 1c and d), while the variance in the grafting density is significant amongst the solutions. The inset to Fig. 1a plots the scaled fitness function,



Fig. 1 (a) Three representative designs, SQ1 (black circles), SQ2 (red squares), and SQ3 (green diamonds), are selected from all the solutions generated in the CMA-ES process (with the range of $\rho \in [0.034, 0.042]$). The inset shows the optimization process of the scaled global fitness function of SQ1. (b) The fitness function for the selected designs is presented as a function of ρ . (c) & (d) G_j/n of the trials $j \in [1, 50]$ are shown as the red circles in the heat-maps for the short (c) and the long (d) chains designs ($\{N_{ij}, \sigma_{ij}\}$), where the three designs, SQ1, SQ2, and SQ3, in (a) & (b) are highlighted as red solid circles, red solid squares and red solid diamonds, respectively. The values in the heat-maps are determined using the linear interpolation from G_j/n .

 $G_i(t)$ for the solution in blacks circle as a function CMA iteration, t. The function quickly decreases and reaches a plateau after about 50 iterations indicating a fast convergence rate. We further investigate the quality of the selected solutions over the range of ρ by presenting the fitness function, $g(\lambda_i, \rho)$ as a function of ρ in Fig. 1b. The profiles for the three selected solutions exhibit different non-linear patterns. For SQ1 and SQ3, local minimum can be identified in the profiles at about $\rho = 0.035$ and 0.040, respectively while the profile from SQ2 exhibits a concave shape and a maximum at $\rho = 0.038$. Overall, the profile from SQ1 has the lower values over the range of ρ , as we expected. Finally, the convergence of the optimized designs is examined. According to the heat-maps of G_i/n in Fig. 1c and d, the majority of designs from trials $j \in$ [1, 50] with lowest values of G_i/n concentrates about the SQ1 (the star in the center of dark blue region on each figures), which indicates a good convergence of the proposed optimization scheme, although less stable minima were also located (yellow and green regions) with nearby grafting densities and chain lengths.

We next tested whether the converged solutions were able to spontaneously form the targeted structure by performing HPF simulations with 100 NPs with the grafting design from the solutions. Here, the assembled NP configurations from two types of HPF simulations are presented. The first type coming from simulations with initial NP configurations biased to square lattices (Fig. 2a), exhibits a defect-free square lattice pattern for the NPs with design SQ1 over all the entire range of ρ . For the other two sample converged designs SQ2 and SQ3, the assembled structure become less ordered for the highest density test, where $\rho = 0.042$. Similar results can be observed in the results from simulations with random initial NP configurations (Fig. 2b), though generally speaking more defects are present. The assembled structures from NPs with the design from SQ1 also exhibit square lattice pattern at $\rho = 0.042$, although the defects in the form of grain boundaries begin to appear in the pattern. However, for the NPs with the designs from SQ2 and SQ3, the square lattice pattern can only be observed in the lowest ρ value at 0.034. It is interesting that the defective systems, SQ2 and SQ3, adopt local motifs with five-particle symmetries, though long-range order is clearly lacking.

3.2 Optimization of open NP lattices

Having demonstrated the optimization scheme on the formation of a square lattice, we proceed to apply the scheme to design honeycomb (HC) and kagome (KG) lattices in addition to the square (SQ) lattices described above. The optimized designs are shown in Fig. 3, where we see that the HC design includes two longer grafted chains but much smaller grafting densities. For the KG design, the two grafting chains show the largest disparity in the chain lengths, where the longer chain is about ten times longer than smaller one. The designs shown in the inset are generated from the same optimization scheme, though they were generated at a single value of $\rho = 0.038$. These designs optimized at a single density are found to have similar chain lengths compared to when an extended range of ρ is used.

The above designs are tested using HPF simulations with multiple NPs in the system. The assembled configurations shown in Fig. 4a were produced from HPF simulations with initial configuration biased to the target lattice. The NPs using SQ and HC design are found to assemble into defectfree square and honeycomb lattices at all three values of ρ , while defects are observed in the KG lattice. If the initial condition in HPF simulations is changed to a random configuration, as presented in Fig. 4b the NPs using the SQ design still predominantly show a square lattice, though defects and grain boundaries do emerge. However, the NPs using the HC



Fig. 3 Optimized design for NPs forming SQ, HC, and KG lattices over the range, $\rho \in [0.034, 0.042]$ (main figure) and $\rho = 0.038$ (inset).

design exhibit localized defects at small and intermediate values of ρ . For the NPs using the KG design, we do not observe well-ordered KG structures at all the values of ρ . Both the KG and HC lattices do provide an open structure, which could be advantageous for 2D assemblies.

To quantify the ordering of the above shown assembled structures, we construct a lattice order parameter $S_{\rm L}$ based on the distribution of angles formed by three adjacent NPs in the structures. Briefly, we calculate the ratio of the number of angles ϕ distributed within a small range ($\delta \phi = \pm 5$ degree) about the characteristic angles in the lattices relative to the total number of angles; the ratio of the number centered about their characteristic angles to the total defines $S_{\rm L}$. For example, square lattice has two characteristic angles at 90 and 180 degrees such that angles distributed in [85 95] and [175 185] will be accounted to the numerator of the ratio. This ratio has the limits of 1 when the NPs assemble into a perfect lattice and $2\delta\phi/180$ when the angle distribution is completely random. The analyzed $S_{\rm L}$ values from the above structures are presented in Fig. 5. Amongst all the types of NP designs, the structure coming from biased initial configurations exhibit higher values of $S_{\rm L}$ over the range of ρ compared to these from the random initial configurations. This trend is also observed for the structures coming from NPs using designs optimized just at $\rho = 0.038$. For NPs with SQ design, the $S_{\rm L}$ in the assembled structure coming from random initial configurations reaches highest value at $\rho = 0.038$, in the HC design $S_{\rm L}$ decreases as ρ increases, and for the KG design $S_{\rm L}$ is approximately constant.



Fig. 2 Snapshots from HPF simulations on the three selected designs in Fig. 1a where the simulations were initialized with (a) biased and (b) random initial configurations, respectively. The grafted chains are not shown for clarity.



Fig. 4 Snapshots from simulations where grafted nanoparticles are optimized for targeted lattices ($\rho \in [0.034, 0.042]$). Images are shown where the initial HPF configuration was (a) biased towards the target structure and (b) random. The grafted chains are not shown for clarity.



Fig. 5 Lattice order (S_L) parameters plotted as a function of NP density in assembled structures formed by NPs with SQ (a), HC (b) and KG (c) designs. The open symbols come from the optimization over the NP density range, $\rho = [0.034 \ 0.042]$ while the solid symbols are calculated from the optimization at $\rho = 0.038$.

These results demonstrate that the biased states exhibit fewer defects, and we next provide evidence that these configurations are lower free energy states. To approach this, the free energy per NP of the assemble structures is quantified from three contributions: the entropic energy from the grafted chains, H_g , the enthalpic energy from NP-grafting chain interactions, H_w , and the vibrational free energy from NP configurations, H_q . Fig. 6 plots the per NP free energy, F, of the assembled structures as a function of ρ . We observe that for all lattices considered here the free energy has a smaller value from the simulations with biased initial configuration over the range of ρ . As shown in the insets to the figures here, we also find that the majority of free energy contribution arises from the entropy of the grafted chain, H_g . Based on this set of results we would argue that the assem-



Fig. 6 The free energy per NP is plotted as a function of NP density, ρ , in assembled structures formed by NPs with SQ (a), HC (b) and KG (c) designs. The insets to the figures show the free energy contribution from grafted chains, H_q as a function of NP density.

bled structures from the biased initial configurations are energetically more favored states, and the entropy of the grafted polymers plays a dominant role in driving the system into each configuration.

3.3 Anisotropic grafted chain distributions and multi-body effects

The above free energy analysis indicates the importance of the entropic contribution from grafted chains, which is expected to correlate with the grafted chain conformations. Therefore, in this section we explore the grafted chain distribution about the NP cores and attempt to answer how the distribution would affect the interparticle interactions. We first investigate the density map of the grafted chains around a single NP in the lattice as shown in Fig. 7. The distribution of the shorter grafted chains (denoted N_1) shows three- and six-folds rotational symmetry in the HC and KG designs while in SQ design where N_1 has the shortest length, the grafted chain distributions are generally homogenous around the NP. The anisotropy becomes pronounced in the longer grafted chains, N_2 , where four-, three-, and two-fold symmetry can observed. From the scaled angular density profiles, (θ) , we notice that the two types of grafted chains have a very similar angular distribution in the HC design. In contrast,



Fig. 7 Normalized grafted chain angular density profiles are shown in the left column for SQ (upper), HC (middle) and KG (lower) designs. The dashed green lines and read solid lines come from N_1 and N_2 grafted chains, respectively. These angular profiles are calculated on the grafted chains distributed between R_P to $2.0r_0$ away from the NP center, where r_0 is the equilibrium distance in the lattices. The heat maps on the two right columns show the spatial distribution of the grafted chains. Only the grafted chain attached to the solid grey NPs in the center of the maps are shown here. The NP-NP distance in these calculations is fixed to the equilibrium distance corresponding to the density $\rho = 0.038$.



Fig. 8 The potential of mean force, $w_2(\mathbf{r})$, between two isolated NPs with optimized designs for SQ (black), HC (red) and KG (green) lattices. The distance, \mathbf{r} , is the separation from the two NP centers.

the angular distribution in the SQ and the HG designs are quite distinct.

We next examine the NP-NP interactions through the twobody potential of mean force $(w_2(\mathbf{r}))$ between isolated NPs. As shown in Fig. 8, all the potentials of mean force exhibit a purely convex, repulsive nature when the NP-NP distance, r, is below the equilibrium distance in the lattice, r_0 . Interestingly, we observe that $w_2(\mathbf{r})$ remains finite even at distances where r is approximately two times r_0 . The importance of these long-range effects becomes even more pronounced when we investigate the multi-body interactions. To illustrate this point, the total three-body potential of mean force, $w_3(\mathbf{r})$, is calculated. The results show that $w_3(\mathbf{r})$ exhibits a finite strength beyond $2r_0$ for each optimized design. Specifically, for the $w_3(\mathbf{r})$ from the HC and the KG designs, the interaction range can exceed $4r_0$ (Fig. 9a). We further isolate the three body component of the potential by subtracting off the twobody potential between the three particles involved, $u_3(\mathbf{r}) =$ $w_3(\mathbf{r}) - 2w_2(\mathbf{r}) - w_2(\mathbf{r}_0)$; the result is shown in Fig. 9b. It is interesting to observe that the potential shows a nonmonotonic change when r increases across the equilibrium distance \mathbf{r}_0 . In particular, $u_3(\mathbf{r})$ from SQ design exhibits a peak intensity right at the position where the three particles would form an equilateral triangle. This local maximum in the potential indicates that the three body interaction destabilizes triangle structure in the assembly of NPs, which likely leads to the stabilization of the square lattice.



Fig. 9 (a) The total three-nanoparticle potential of mean force $w_3(r)$ and (b) the isolated three body contribution $u_3(r)$ as a function of distance from the equilibrium positions in SQ, HC and KG lattices plotted in black, red and green curves, respectively. The inset to (a) shows the system setup where two static NPs are fixed with a separation r_0 while the mobile NP is displaced along the direction indicated by the dashed line. The distance *r* is measured from the mobile NP to one of the static NPs.

4 Conclusion

In this manuscript, an optimization approach is presented to solve the inverse design problem for systems with some chemical detail, namely polymer-grafted nanoparticles (gNPs) grafted with two distinct grafted polymer chain lengths. Our approach uses an evolutionary optimization scheme (CMA-ES) on a 2D field-theoretic NP model to search for the optimized NP design on a unit cell of the lattice, and our designs are verified on multi-NP systems where we allow the particles to thermally sample their configurations. We find that in many cases, our gNPs self-assemble into the targeted structure over the range of density, though defects are often present at the edges of the density range. Our investigation on the interactions amongst NPs with the optimized design in the target lattice highlights the importance of many-body effects, which serve to prevent the NPs from assembling into competing lattices and thus might contribute to the formation of the targeted lattice.

We take the methods and results presented here as a promising first step towards designing the chemistry of nanoparticles that could be designed experimentally for targeted self-assembly, but there are several assumptions that need to be relaxed in future work. The first one is the definition of uniform grafting density in the hSCFT NP model, which might become an unphysical assumption when the grafting density is small and the discrete nature of the grafting sites becomes important. It is well-known that grafted particles at low graft densities exhibit anisotropic interactions and assemblies.¹⁸ One strategy for addressing this issue can be to adopt the dynamic mean field framework introduced by the authors³⁹ where the grafting sites on the NP surface are treated explicitly, though this loses direct access to the free energy. In addition, the polymer chain conformations are treated entirely at the mean-field level in a θ solvent, and testing the fluctuation effects and the influence of solvent quality and the effects of other enthalpic interactions remains an outstanding issue.

Conflicts of interest

There are no conflicts to declare.

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