Electronic Supplementary Material (ESI) for Soft Matter.

Phase diagram for two-dimensional layer of soft particles

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Optimization over Competing Structures for Ground State Calculation

The structures included in the ground state calculations are *n*-particle crystals with periodic configurations containing n particles per unit cell, *n* = 1, 2, 3. Shape deformation of the unit cell is allowed. More complexity can be achieved by including structures with more particles in each unit cell.

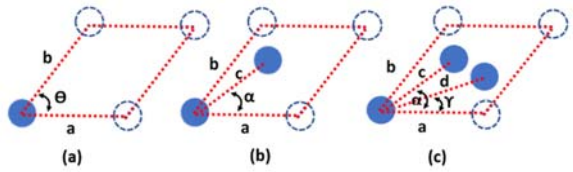

Figure S1 - Unit cell for structures with (a) one particle (b) two particles (c) three particles.

Optimized structures by optimization over competing structures

Five crystal phases are identified in the ground state calculation: triangular phase, stripe (affinely-stretched triangular) phase, honeycomb phase, kagome phase and a second triangular phase. Table S1-S3 gives the optimized lattice parameters for each crystal phases and Figure S2 gives an example crystal structures for each phase mentioned above.

Table S1. Optimized lattice parameters for f = 50

Packing Fraction	0.23-0.88	0.95-1.26	1.31-1.59	1.68-1.87	1.93-2.40
Optimized Structure	Triangular	Stripe	Honeycomb	Kagome	Triangular
a	2.03-3.94	2.10-2.11	2.14-2.45	2.42-2.56	1.23-1.37
b/a	1.00	0.60-0.81	1	1.00	1.00
Θ	60	66-72	53-60	60	60
c/a	-		1.16-1.28	0.5	-
α			25-29	0	
d/a			-	0.87	
ϒ				30	

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Table S2. Optimized lattice parameters for f = 68

Packing Fraction	0.24-0.89	0.99-1.29	1.35-1.61	1.70-1.93	2.01-2.40
Optimized Structure	Triangular	Stripe	Honeycomb	Kagome	Triangular
a	2.02-3.90	2.09-2.13	2.12-2.42	2.38-2.53	1.23-1.34
b/a	1.00	0.58-0.75	1	1.00	1.00
Θ	60	67-73	55-60	60	60
c/a	-		1.16-1.25	0.5	-
α			26-28	0	
d/a			-	0.87	
ϒ				30	

Table S3. Optimized lattice parameters for f = 150

Packing Fraction	0.26-0.89	1.05-1.35	1.43-1.65	1.78-1.92	2.02-2.40
Optimized Structure	Triangular	Stripe	Honeycomb	Kagome	Triangular
a	2.02-3.72	2.08-2.12	2.10-2.29	2.44-2.32	1.28-1.23
b/a	1.00	0.57-0.69	1.00	1.00	1.00
Θ	60	69-73	57-60	60	60
c/a	-		1.16-1.22	0.5	-
α			14-29	0	
d/a			-	0.87	
ϒ				30	

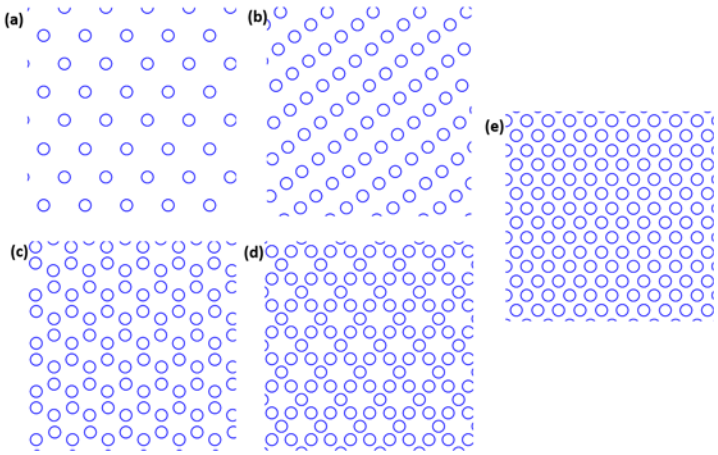

Figure S2 - Optimized ground state structures for f = 150. (a) triangular phase, η = 0.55, (b) stripe phase, η = 1.13, (c) honeycomb phase, η = 1.45, (d) kagome phase, η = 1.82, (e) the second triangular phase, η = 2.08.

Genetic Algorithm Methodology for Ground State Calculation

Gottwald et al. has successfully demonstrated the application of genetic algorithms (GAs) to predict the equilibrium crystal structures for this type of system in three dimensions[1]. The same approach is adapted to 2D systems in our work.

The individual candidates in our case are lattice structures; the target is the lattice structure that gives the lowest u. The unit cell is represented by the primitive vector $\{\boldsymbol{x_i}\} = \{\boldsymbol{x_1}, \boldsymbol{x_2}\}$.

$$\boldsymbol{x_1} = a(1,0)$$
$$\boldsymbol{x_2} = a(x\cos\theta\,, x\sin\theta) \tag{1}$$

where a is determined by the areal packing fraction of the system. The other parameters are limited as follow:

$$0 < x \leq 1,\ 0 < \theta \leq \frac{\pi}{2} \tag{2}$$

The positions of b particles in a unit cell are represented by vector $\boldsymbol{y_i}, \boldsymbol{i} = 1, \dots, b$.

$$\boldsymbol{y_i} = \begin{cases} \boldsymbol{0}, & i = 1 \\ \sum_{j=1,2} c_{ij}\,\boldsymbol{x_j}, & i = 2, \dots, b \end{cases} \tag{3}$$

The value of c is limited by $0 \leq c < 1$. b is set to be 4 in our calculation. An individual is represented by eight variables: $\{x, \theta, c_{21}, c_{22}, c_{31}, c_{32}, c_{41}, c_{42}\}$. Each of the variables are represented by a string of genes of different length $\tilde{b}_i$. $\tilde{b}_i$ are sequences of 0's and 1's in binary alphabet, corresponding to the decimal number $\dot{b}_i$. The value of variables can be given as follow:

$$x = \frac{\dot{b}_x + 1}{\dot{b}_{x,max} + 1}, = \frac{\pi}{2}\,\frac{\dot{b}_\theta + 1}{\dot{b}_{\theta,max} + 1},\ c = \frac{\dot{b}_c}{\dot{b}_{c,max} + 1} \tag{4}$$

Here the $\tilde{b}_\theta$ is represented by a string of 7 genes and all other $\tilde{b}$'s to be a string of 5 genes, such that each individual is represented by 42 genes. Additional genes for each individual force longer simulation time before the system converges. The above choice of b and length of $\tilde{b}_i$ address the complexity and accuracy of potential structures while allowing the system to converge within a reasonable timescale.

GAs require that each individual is represented by a uniquely defined structure: a conversion of all equivalent unit cells to the same $\{\boldsymbol{x_i}\}$ for which the circumference of the cell is minimal. This can be achieved by checking the circumference of the following 4 cells: $\{\boldsymbol{x_1} \pm \boldsymbol{x_2}, \boldsymbol{x_2}\}$, $\{\boldsymbol{x_1}, \boldsymbol{x_1} \pm \boldsymbol{x_2}\}$. The one gives smallest circumference is taken as the new primitive vectors until none of the above four gives a smaller circumference than $\{\boldsymbol{x_1}, \boldsymbol{x_2}\}$. $\boldsymbol{x_2}$ is inverted when necessary so that the vector is positive. The equivalent set of $\boldsymbol{y_i}$ is reduced by sorting vector $\boldsymbol{y_i}$ by $\boldsymbol{x_1}$ coordinate and then by $\boldsymbol{x_2}$ coordinate.

For each individual a positive fitness value F is assigned based on the calculated potential u of the corresponding lattice. As the goal is to minimize u, the fitness function is chosen to be:

$$F = \exp\left(1 - \frac{u}{u_{tri}}^{\varepsilon(i)}\right) \tag{5}$$

Where u_{tri} is the potential of a triangular lattice, $\varepsilon(i)$ is a factor based on the generation i.

$$\varepsilon(i) = 1 + i\,\frac{log(i)}{40} \tag{6}$$

The fitness function ensures a negative correlation between F and u. The exponential factor $\varepsilon(i)$ makes the choice of the fittest individual more selective as i increases, which speeds up the convergence.

The ground state calculation with the genetic algorithm started with 1000 random individual configurations and the population remained unchanged throughout the calculation. The crossover possibility $P_c = 0.1$ and mutation possibility $P_m = 0.05$ were adopted. All trials were carried out with $f = 50, 68, 150$ and packing fraction from 0.1 to 2.4, converging within 1000 generation.

Optimized structures by genetic algorithm

The most complex structure predicted has three particles in each unit cell, showing the choice of b = 4 for GAs is adequate. GA was used at multiple packing fraction to verify the predicted ground state structure by optimizing over a pool of completing structures. This should rule out any complex structures not considered in the pool. As shown in Table S4-Table S6, GA predicts the same ground-state (GS) structures as given in Table S1-Table S3. No new ground state structures are identified.

Table S4. Predicted ground state structures with GA for f = 50

packing fraction	0.60	0.80	1.00	1.20	1.40	1.70	1.80	2.00	2.20	2.40
Predicted GS	T	T	S	S	HC	HC	K	T	T	T
GA results	T	T	S	S	HC	HC	K	T	T	T

Table S5. Predicted ground state structures with GA for f = 68

packing fraction	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00	2.20	2.40
Predicted GS	T	T	S	S	HC	HC	K	C	T	T
GA results	T	T	S	S	HC	HC	K	T	T	T

Table S6. Predicted ground state structures with GA for f = 150

packing fraction	0.60	0.80	1.10	1.20	1.45	1.60	1.80	1.90	2.05	2.20
Predicted GS	T	T	S	S	HC	HC	K	K	T	T
GA results	T	T	S	S	HC	HC	K	K	T	T

Note: T - triangular, S - stripe, HC - honeycomb, K – kagome.

Structure factor

The structure factor $S(\boldsymbol{q})$ is calculated with both isotropic formula (Eq.7)

$$S(q) = \frac{1}{N}\sum_{j=1}^{N}\sum_{k=1}^{N} J_0(qr_{jk}) \tag{7}$$

where $\boldsymbol{q}$ is the scattering vector, N is the total number of particles in system, $\boldsymbol{R}$ is the position of particles $q = |\boldsymbol{q}|, r_{jk} = |\boldsymbol{R}_j - \boldsymbol{R}_k|$. J_n is the Bessel function of the first kind.

While Figure 5. in the manuscript gives $S(q)$ calculated with isotropic formula, it tends to overestimate $S(q)$ for low $\boldsymbol{q}$. The overestimation of $S(q)$ for the experimental data is not as obvious because the system size for experimental data is much larger than the simulation.

Estimation of corona diameter

The corona diameter of PGNCs is estimated from the measured solvent intake by the deposited PS-homopolymer film[2]. And the following experimental data were given. 1) The Fe_3O_4 core radius is r_c = 2.1

nm for the sampled particles with f = 68. 2) The film thickness is measured to be t = 136 nm. 3) If the entire film is composed of selling part, the expected film thickness should be t_{swell} = 99.2 nm, fitted from solvent intake measurements. 4) The particle radius including the non-swelling coat is estimated to be $r_{non-swell}$ = 3.2 nm.

$$\frac{V}{V_{non-swell}} = \frac{t}{t-t_{swell}} = \left(\frac{r}{r_{non-swell}}\right)^3 \quad . \tag{8}$$

With the above data, the radius of the sampled PGNCs with f = 68 is estimated to be r = 4.9 nm, σ = 9.8 nm. The PGNCs with f = 50 contains a Fe_3O_4 core with 3.9 nm diameter. No solvent intake information is available. With the smaller hard core, we are expecting a particle radius slightly smaller than 4.9 nm for f = 50 samples.

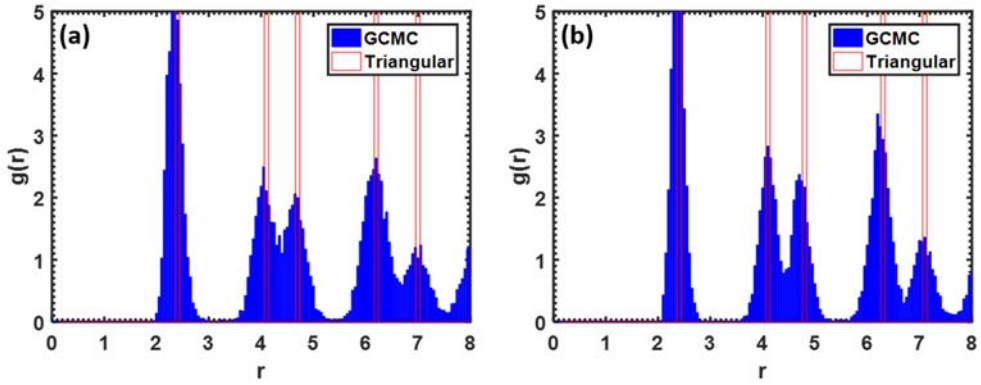

Figure S3 - Radial distribution function from GCMC at (a) f = 50, η = 0.67; (b) f = 68, η = 0.66. Both indicate the triangular ordering.

References

1. D. Gottwald, G. Kahl and C. N. Likos, *The Journal of Chemical Physics*, 2005, **122**, 204503.
2. J. Chen, A. Fasoli, J. D. Cushen, L. Wan and R. Ruiz, *Macromolecules*, 2017, **50**, 9636–9646