Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for Self-Assembly of Spiral Patterns in Confined System with Competing Interactions

Jakub Pękalski,[1,2,*] Eldar Bildanov,[3] and Alina Ciach[1]

[1]*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland.*

[2]*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA.*

[3]*Belarusian State Technological University, Sverdlova 13a Minsk, Belarus.*

[*]Electronic address: jpekalski@ichf.edu.pl

I. OFF-LATTICE SIMULATION DETAILS

We have verified the main results with Molecular Dynamics (MD) simulations of a continuous model with interparticle potential modeled as a sum of the Lennard-Jones and the Yukawa potentials:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{2\alpha} - \left(\frac{\sigma}{r}\right)^{\alpha} \right] + \frac{A}{r} e^{-r/\xi}, \tag{S1}$$

where $\alpha = 6$, $A = 1.27$, $\xi = 2$, and $\varepsilon = 1.0$, $\sigma = 1.0$ set the unit of energy and length, respectively. Such model parameters were previously used in Ref. [1] and correspond to a SALR potential with the area of the attraction well being 3 times smaller then the area of the repulsive tail. Such potential, was shown in Ref. [1] to lead to formation of lamellar pattern with stripe width similar to those present in the bulk for the used lattice model.

In MD simulations of the symmetric system we have assumed that the confining walls attract particles. For particle-wall interactions we used the Lennard-Jones potential that was cutted at $r_{cut} = 3\sigma$ and shifted in such a way that the acting force was a continuous function of the distance. The low-temperature configurations were obtained with a sequence of simulations with linearly decreasing temperature, usually from $k_BT = 0.4$, to $k_BT = 0.01$, and from $10^7$to 5×10^8 MD moves were run, with $dt = 0.01$.

In the case of the hexagonal system with the symmetry broken by a triangular wedge, the spiral formations occurred only when the particle-wall interactions were set repulsive, i. e. we used Lennard Jones potential cutted at $r_{cut} = 2^{1/6}\sigma$ and shifted in a similar manner as it was in the fully symmetric system. We have also tried different shapes of the wedge and we found that not only equilateral triangle can induce a spiral, but also a right triangle can lead to formation of a spiral.

By means of MD simulations we have reproduced the following results described in the main manuscript: concentric rings at low T (Fig. 1), thermally induced spirals (Fig. 2) and spirals induced by the triangular wedge (Fig. 3).

The off-lattice MD simulations were performed using the HOOMD-blue package [2, 3] and visualized with The Open Visualization Tool (OVITO) [4].

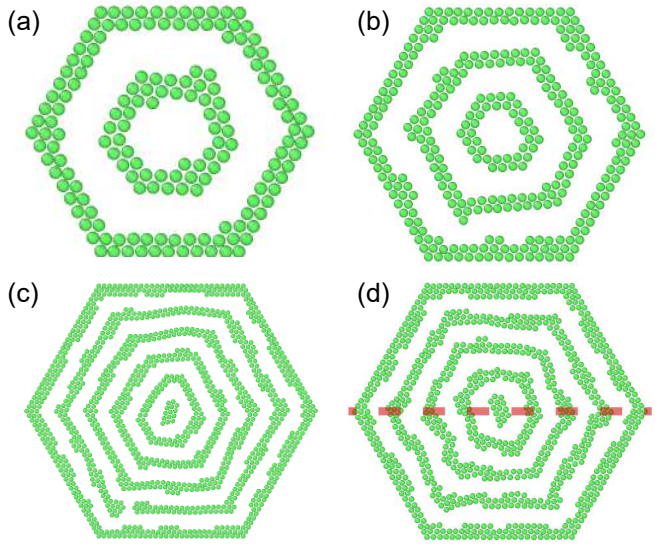

FIG. 1: Low temperature configurations obtained with MD simulations in canonical ensemble. Different panels correspond to simulations with different size of the hexagon, M, and the number of particles N. (a) $M = 12$, $N = 163$, (b): $M = 17$, $N = 324$, (c): $M = 27$, $N = 840$, (d): $M = 32.5$, $N = 1188$. The red dashed line on Panel (d) shows the domain boundary described in the thermodynamic considerations.

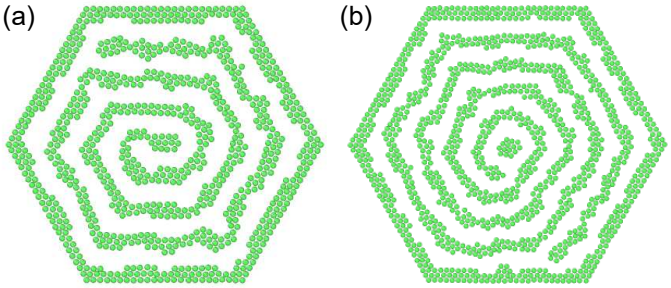

FIG. 2: Spiral conformations in the hexagonal system formed due to thermal fluctuations (a): $M = 27$, $N = 840$, (b): $M = 32.5$, $N = 1188$.

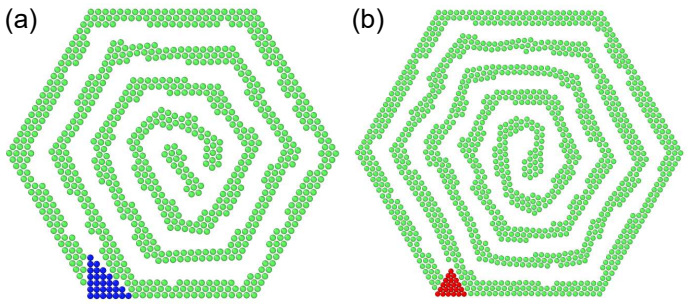

FIG. 3: Spiral conformations induced by a triangular wedge of different shape (a): $M = 27$, $N = 840$, (b) $M = 32.5$, $N = 1188$.

II. DENSITY PROFILES ALONG DIFFERENT SYMMETRY AXES OF THE HEXAGON

The highly symmetric density maps shown in Fig. 4 of the main manuscript result from interference of density waves. An example of the profiles computed along different axes of symmetry is shown on Fig. 4.

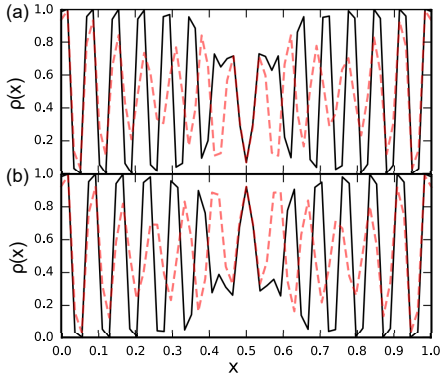

FIG. 4: Density profiles, $\rho(x)$, for (a) $M = 30$ and $T = 0.47$, and (b) $M = 28$ and $T = 0.49$. The black solid lines correspond to the density profiles computed along the diagonal of the hexagon, while the red dashed lines to the density profiles computed along the cross section of the hexagon taken between the sides centers, as shown on Fig. 1 in the main manuscript.

III. APPLICATION OF THERMODYNAMIC CONSIDERATIONS

In what follows we show that the thermodynamic considerations described in the main manuscript indicate stability of concentric rings for the SALR lattice model in the hexagonal confinement when $T = 0$. In order to apply the derived conditions to the lattice system first we find analytical expressions for the energy and the density in the case of concentric ring morphology. The calculations in this section are restricted to $T = 0$, but may be a good approximation for very low T.

A. Density

In order to calculate the density of the ground state, $\rho(M)$, we calculate the contributions from the concentric rings, $\rho_R(M)$, and the defect that is formed in the hexagon center, $\rho_D(M)$, separately.

Firstly, we calculate the number of particles that form rings, $N_R(M)$. Since, increasing the system size, M, by 4 results in a birth of a new ring, the number of rings is $q = \lfloor M/4 \rfloor$, where $\lfloor ... \rfloor$ is the floor function that returns the integer part of the number. Each ring can be treated as composed of straight lines and corners. The number of particles in one ring is $N_{ring} = 6 \times N_{corner} + 6 \times N_{lines}$, where $N_{corner} = 2$, but N_{lines} depends on the size of the ring. However, the increment of N_{lines} when M increases is constant and thus N_{lines} can be computed as a sum of an arithmetic series: $N_{lines} = \sum_{n=1}^{q} 8n - 5 + 2r$, where $r = M \bmod 4$. Thus,

$$N_R(M) = 6(2q + \sum_{n=1}^{q}(8n - 5 + 2r)) = 6q(4q + 2r + 1).$$

The number of particles that form defect in the central part of the hexagon, $N_D(M)$ can be expressed as a sum of the Kronecker delta function: $\delta_{\alpha,\beta}$ which is 1 when $\alpha = \beta$ and 0 otherwise. Namely:

$$N_D(M) = \delta_{1,r} + 7\delta_{2,r} + 18\delta_{3,r}.$$

To get the final expression for the density, one only needs to calculate the number of sites in the system of size M, which is straightforward: $A = 3M^2 - 3M + 1$. Hence, the final expression for the average density at $T = 0$ is:

$$\rho(M) = \frac{6q(4q + 2r + 1) + \delta_{1,r} + 7\delta_{2,r} + 18\delta_{3,r}}{3M^2 - 3M + 1}. \tag{S2}$$

B. Energy

Here, we calculate the grand canonical energy by per site, H/A, where H is defined in Eq. (3). Because the range of particle interaction is 2σ, the particles that form rings and defects do not interact, and their contribution to the total energy can be computed separately:

$$H(M) = H_R(M) + H_D(M) - \mu N,$$

where $\mu = 6$ and $N = N_R(M) + N_D(M)$. The energy contribution from the rings is $H_R(M) = \frac{1}{2}N_R(M)(-4 + 2J)$, where $J = J_2/J_1$, while from the defect it is $H_D(M) = 3\delta_{3,r}(7J - 12) + 3\delta_{2,r}(J - 4)$. Hence, in units of nearest neighbor attraction J_1:

$$H/A = \frac{3q(4q + 2r + 1)(-4 + 2J) + 3\delta_{3,r}(7J - 12) + 3\delta_{2,r}(J - 4) - \mu N}{3M^2 - 3M + 1}. \tag{S3}$$

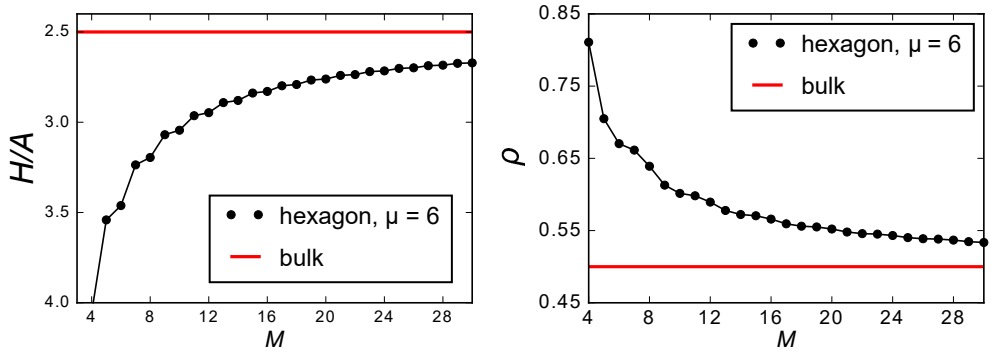

FIG. 5: Energy per lattice site (left panel) and density (right panel) of the hexagonal lattice system at $T = 0$.

C. Stability of concentric rings

We have shown that concentric rings are stable if $\Delta\Omega = 4(\gamma_t - \gamma_{\parallel}) - 6\gamma_{db} - d_c/M > 0$. Thus, to check if this inequality is satisfied, we have to find the values of the surface tensions and d_c. In our lattice model, the stripe turns are not associated with the energy excess, thus $\gamma_{db} = 0$. The surface tension of the stripes tilted to the walls results from the *missing* interactions, when each of the stripes end at the boundary, thus for each stripe $\gamma_t = (3 - 4J)\frac{1}{4}$. What is left, is to determine the values of $\gamma_{\parallel}$ and d_c, which can be computed from comparison of

Eq. (3), with formulas that come from analytical calculations of the energy in the lattice system.

Let $\delta\Omega \equiv \Omega - \omega_b A$, where Ω is the grand potential of the hexagonal system, $\omega_b = \frac{1}{4}(-4+2J-2\mu)$ is the grand potential density in the bulk and A is the area of the hexagon. We have shown that in the case of concentric rings $\Omega = \omega_b A + (6\gamma_{\parallel} + 6\gamma_{db})M + d_c$, and since $\gamma_{db} = 0$, we have $\delta\Omega = 6\gamma_{\parallel}M + d_c$. On the other hand at $T = 0$, the grand potential is $\Omega = H$, thus from Eq. (S3), one can get the following formula for the excess grand potential at $T = 0$:

$$\delta\Omega = (-4 + 2J - 2\mu)\left(3q(4q + 2r + 1) - \frac{1}{4}(3M^2 - 3M + 1)\right) + C(M), \tag{S4}$$

where $C(M) = -\delta_{1,r}\mu + \delta_{2,r}(-12+3J-7\mu) + \delta_{3,r}(-36+21J-18\mu)$. Now we find the value of $\delta\Omega$ for different system sizes:

1. $(r = 0)$

   When $r = 0$, we have $q = M/4$ and $C(M) = 0$, thus $\delta\Omega = 6\omega_b M - \omega_b$. Hence: $\gamma_{\parallel} = \omega_b$ and $d_c = -\omega_b$.

2. $(r = 1)$

   When $r = 1$, we have $q = (M-1)/4$ and $C(M) = -\mu$, thus $\delta\Omega = 6\omega_b M - 7\omega_b + C(M)$. Hence: $\gamma_{\parallel} = \omega_b$ and $d_c = -7\omega_b - \mu$.

3. $(r = 2)$

   When $r = 2$, we have $q = (M-2)/4$ and $C(M) = -12 + 3J - 7\mu$, thus $\delta\Omega = 6\omega_b M - 19\omega_b + C(M)$. Hence: $\gamma_{\parallel} = \omega_b$ and $d_c = -19\omega_b - 12 + 3J - 7\mu$.

4. $(r = 3)$

   When $r = 3$, we have $q = (M-3)/4$ and $C(M) = -36 + 21J - 18\mu$, thus $\delta\Omega = 6\omega_b M - 37\omega_b + C(M)$. Hence: $\gamma_{\parallel} = \omega_b$ and $d_c = -37\omega_b - 36 + 21J - 18\mu$.

From the above calculations it follows that $\gamma_{\parallel} = \omega_b$ for all M as expected. This can be also shown by considering a system with a slit geometry, in which particles are confined between two parallel walls. If the distance between the walls is L and the period of the stripe structure is λ, then the preferable wall separation for a structure with straight, parallel stripes that are adsorbed at the walls, is $L = n\lambda + \lambda/2$, where n = 1, 2, 3, ... In such a case the grand potential per unit length of the walls is $n\lambda\omega_b + \lambda\omega_b$, what indicates $\gamma_{\parallel} = \omega_b$.

We have verified that if $J = 3$ and $\mu = 6$, then $\Delta\Omega > 0$, when $M > 2$ (for $r = 0, 2$) and $M > 11$ (for $r = 1, 3$). In particular we got that $d_c = 2.5$ for $r = 0, 2$ and $d_c = 11.5$ for $r = 1, 3$. The large energy cost of the central defect for $r = 1, 3$ is consistent with spiral formation for such sizes of the hexagon found in simulations.

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