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# MICELLISATION AND AGGREGATION OF HARD SELF-PROPELLED CIRCULANGLES

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**Abstract.**

Self-organization in active materials, inspired by biological systems, shows many features, not found in passive materials. Self-propelling Brownian spheres undergo phase separation, rod-like particles show unusual defects behavior. Both types of particles, however, have a center of symmetry. In order to explore the influence of shape asymmetry, a new 2D shape, named a circulangle, is introduced. Kinetic Monte Carlo simulations of two-dimensional hard Brownian circulangles are presented. Self-propulsion is introduced by additional MC moves along particles' axes. The system undergoes transition from homogeneously distrubited particles to micellar structures arranged in clusters/networks. Circulangles appear to be the first known particles, which form micelles without attractive forces. The newly discovered phenomenon may have wide implications in design of (meta)materials for energy conversion and storage, sensorics, micromechanics, swarm intelligence and targeted drug delivery.

## 1 INTRODUCTION

The term and main principles of self organization were first formulated by William Ross Ashby in 1947 [1]. Later, work by Ilya Prigogine led to groundbreaking research in the field of dissipative systems, for which he was awarded the Nobel Prize in Chemistry in 1977. The central idea of self-organizing systems is that not all structures and designs are developed with a central authority, but are based on an interplay between rules, dynamic adaptation and an appropriate level of entropy. It is important to note that spontaneous formation of order, can only occur at a certain level of still existing disorder and entropy, and no longer occurs with an over-regulated system [2].

In nature we see a whole series of such examples beginning with bird and fish swarms, ant and bees colonies [3]. In sociology, there are similar patterns with a positive reinforcement effect in the use of new communications technologies, such as telephones or the Internet, as well as in the formation of agglomerations. It is even advocated that almost all processes worldwide are dominated by self-organizing systems, which is known as the Gaia hypothesis [4].

The key advantages of a self-organizing system are [2]:

- Resilience: the ability of systems not to fail completely in the face of partial disruption;
- Robustness: the ability to handle adaptations without letting the internal stable structures become defective;
- Efficiency: ability to use available resources and opportunities sparingly.

Self-organization due to self-propulsion stems from biological systems, composed of living self-propelling entities. Artificial (non-living) particles are manufactured to gain self-motility via self-diffusio-phoresis due to asymmetric chemical reaction [8, 9, 10] or via thermophoresis for Janus particles [11, 15]. There are also macroscopic models of active materials [16, 17, 18].

Self-propelled Brownian spheres undergo phase separation [12], rod-like particles show unusual defects behavior, which was confirmed experimentally [14]. Both types of particles, however, have a center of symmetry.

In order to explore the influence of shape asymmetry, a new 2D shape, named a circulangle, is introduced.

## 2 CIRCULANGLE

A circulangle is composed of a circle, wedged into an angle, such that the angle's sides attach to the circle tangentially thus preserving continuous curvature. It is characterized by an elongation factor $L/R$, which is 1 for a circle (Fig.1). From now on we assume that the radius of the circle is alwas $R = 1$, so $L$ is just directly the aspect ratio. The shape can be continuously varied from a circle ($L = 1$) to a rodlike particle. In order to simulate mechanical behaviour of a circulangle, its center of inertia and the radius of gyration must be calculated. These quanitities can be calculated analytically.

The area of a circulangle as a function of $L$

$$S(L) = \sqrt{L^2 - 1} + \pi - \arccos\frac{1}{L}$$

The center of inertia of a particle as a distance from the circle's center is

$$l = \frac{1}{S(L)}\left[\frac{2\left(\frac{L^3}{6} - \frac{3L^2-2}{6L^3}\right)}{\sqrt{L^2-1}} - \frac{2\,(L^2-1)^{\frac{3}{2}}}{3\,L^3}\right] \tag{1}$$

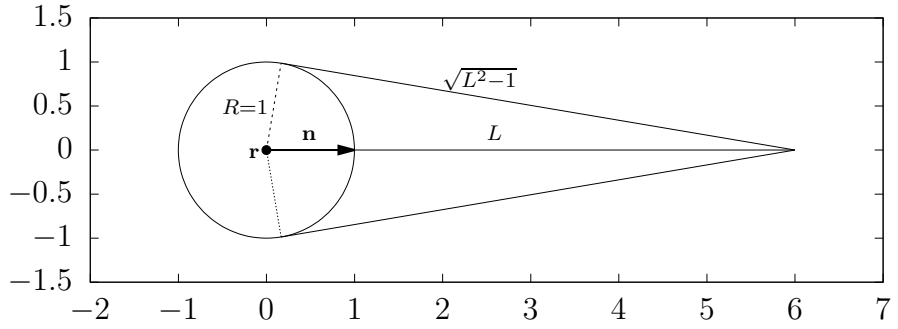


Figure 1: A circulangle with aspect ratio $L/R = 6$. Its position is characterized by the center of the circle $\mathbf{r}$, orientation by the director $\mathbf{n}$ along the axis of length $L$.

The radius of gyration

$$R_g(L,l(L)) = \frac{1}{S(L)}\left[\frac{2\left(\frac{6L^2l^2-4L^3l+L^4}{12}-\frac{\left(12L^4-6L^2\right)l^2+\left(8L-12L^3\right)l+4L^2-3}{12L^4}\right)}{\sqrt{L^2-1}}\right.$$
$$+\frac{\sqrt{L^2-1}\left(6L^2l^2-8Ll+3\right)+\left(L^2-1\right)^{\frac{3}{2}}}{6L^4}$$
$$+\frac{-\left(-24\arccos\left(\frac{1}{L}\right)-24\pi\right)Ll^2-32\sqrt{L^2-1}l-\left(-6\arccos\left(\frac{1}{L}\right)-3\sin\left(2\arccos\left(\frac{1}{L}\right)\right)-6\pi\right)L}{24L} \quad (2)$$
$$\left.+\frac{2\left(\frac{L^4}{4}-\frac{4L^6-6L^4+4L^2-1}{4L^4}\right)}{3\left(L^2-1\right)^{\frac{3}{2}}}+\frac{2\arccos\left(\frac{1}{L}\right)-\sin\left(2\arccos\left(\frac{1}{L}\right)\right)}{8}+\frac{\pi}{4}\right]$$

The dependencies $l(L)$ and $R_g(L)$ given by Eqs.(1) and (2) respectively are depicted on Fig.2

## 3 SIMULATION METHOD

Conventional way to model a system of brownian particles is to use Langevin equations [12]. In this case pairwise interaction between particles must be described dynamically, i.e. either continuously in a form of soft potentials [12], or as a single collision event for hard particles. It is easy for soft isotropic interaction, where one may use LJ, WCA, hard-wall potential, etc. In the case of complex shapes, like circulangles, calculation of pairwise interaction, is not straightforward. Unlike spheres, there are no collision operators calculated yet for hard circulangles.

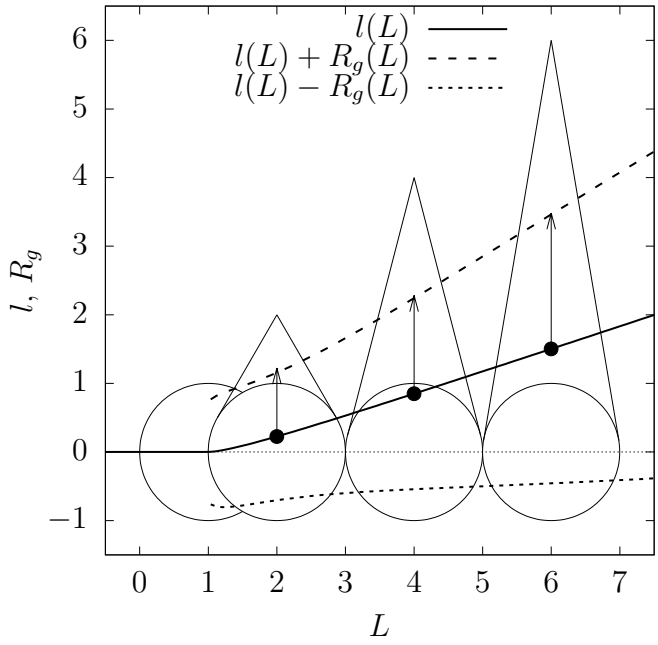


Figure 2: Center of inertia $l$ (Eq. (1)) and radius of gyration $R_g$ (Eq.(2)) as a function of $L$. A set of circulangles with $L = 1$(disc),$2, 4, 6$.

Besides, if we focus only on the structural arrangements of particles, kinetic Monte Carlo for active paricles suffices [20]. Thus, instead of calculating dynamics of pairwise interactions, we may limit ourselves to calculation of overlap condition of two circulangles. The limitation of the MC compared to brownian particles

There are three types of movement in the system: directed self-propulsion, diffusive translation and diffusive rotation. In the originally proposed form, the method has two control parameters: rotational Péclet number and noise-to-persistence ratio, both of which include noise.

We choose different parametrisation pair in order to confine noise to a single parameter: the ratio of rotation to translation and the ratio of self-propulsion to translation.

Consider the overdamped Langevin equation for a single particle

$$\begin{cases} \mathbf{v}_i = \sqrt{2D_t}\boldsymbol{\xi}^T(t) + v_p\mathbf{n}_i \\ \omega_i = \sqrt{2D_r}\xi^R(t) \end{cases} \tag{3}$$

where position and orientation of i-th circulangle is described by the coordinates of its center of inertia $\mathbf{r}_i$ and orientation angle of its axis $\varphi_i$ respectively, having linear velocity $\mathbf{v}_i$ and angular velocity $\omega_i$ respectively. Axis is also described by it director $\mathbf{n}_i = (\cos\varphi_i, sin\varphi_i)$. Where Gaussian white noise variables $\langle\xi_i(t)\rangle = 0$ and $\langle\xi_i(t)\xi_j(t')\rangle = \delta_{ij}\delta(t-t')$ , where $\xi(t)$ is either $\boldsymbol{\xi}^T(t)$ or $\xi^R(t)$, $v_p$ is the self-propulsion velocity. The center of inertia of a circulangle is shifted by $l$ along the axis with respect to the origin of the circle. It depends on $L$, and for our particular case of $L = 6$ we have $l \approx 1.5$, as calculated by Eq.1 and shown on Fig.2.

Initial configuration was generated as a random set of $N = 363$ particles in a periodic boundary box sized $100 \times 100$, and their orientation angle is also randomly generated in the range $(0, 2\pi]$, as depicted on Fig. 3. The generated circulangle was accepted to the ensemble, if no overlaps occured, and rejected otherwise. This corresponds to the surface fraction of 0.278, which remains constant during MC sampling due to fixed number of particles and fixed size of the box. Then we proceed with kinetic Monte Carlo sampling. At each MC sweep each individual circulangle is attempted to be translated and rotated according to the set of overdamped Langevin equations (3). The algorithm might seem like conventional brownian dynamics, but we do not employ pairwise interaction term. Instead, we proceed according to kinetic MC scheme [20] with hard particles: the move is either accepted if no overlap between particles occur, or rejected otherwise. We use Langevin equations just to show physical meaning of our parametrisation as opposed to parametrisation used in [20]. Therefore the time variable in Eq.3 can only be considered as an MC sweep counter, and not as a real time. Here we are interested only in a final stable structure and not in its time evolution.

Precisely speaking, for anisotropic particles, which circulangles are, diffusion coefficient will also be anisotropic and orientation-dependent. We simplify it in this work to a scalar $D_t$. Translation and rotation is coupled for both, conservative and dissipative effects. Ballistically, they are coupled by particle's mass and its moment of inertia, which can be parametrised using the radius of gyration. Dissipative effects, i.e. drag and torque, are coupled by the particles' shapes, and its relative distrubution can be parametrised using the aspect ratio $L$. For this work we simply use the ratio of scalar rotational diffusion coefficient to translational diffusion coefficient as a control parameter. The results, presented in this work were obtained for $\sqrt{\frac{D_r}{D_t}} = 1$. The second control parameter is responsible for the relative contribution of self-propulsion to translational motion. We characterize it by the Péclet number $Pe_L = \frac{Lv_p}{D_t}$, which in our case was 120. Relation of these parameters to persistence length as defined in [20] will be presented elsewhere.

## 4 RESULTS

The system with initial configuration, shown on Fig.3, undergoes MC moves according to the procedure, described above. After $\approx$ 10000 MC moves the system structurally stabilizes as shown on Fig.4, forming partially aggregated micelles. The fundamental difference from the conventional micelle-forming particles [7] is that circulangles do not have to have attractive forces to micellize. Further MC sampling till 25000 MC moves causes no change in global structures, just a few solitary particles travelling between clusters.

Initially homogeneous system develops ordered structures, which we now want to quantitatively characterize. Apparently, we have a coupled orientational and positional order. From one hand, there are widely used orientatioinal orders, e.g. nematic, tetratic, cubatic, etc. However, they do not account for polarity, which clearly present in our case, and are able to describe orientational order only with an expected predefined rotational symmetry. From the other hand, there is the bond orientational order parameter [21].

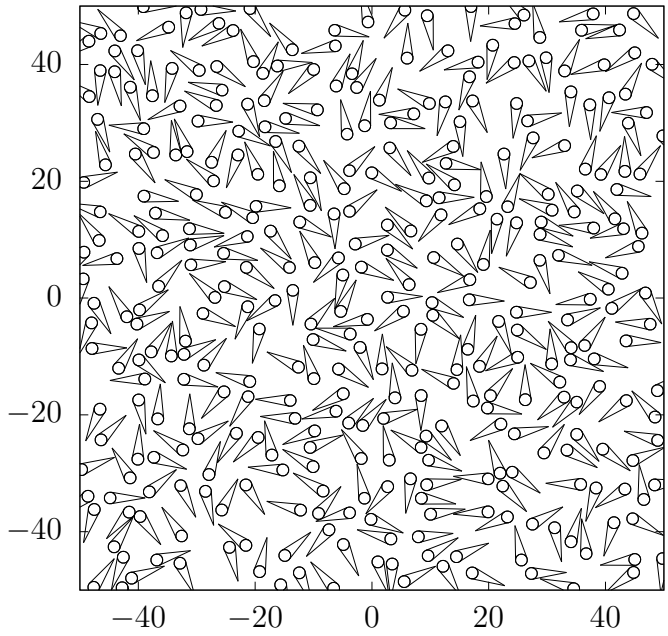


Figure 3: Homogeneously distributed circulangles in a periodic boundary box $100 \times 100$. Initial configuration.

It is quite tempting to use the latter to adopt it for characterization of axes' orientation micellewise. But it makes sense for the cases, where rotational symmetry of bonds is an integer fraction of $2\pi$, so the corresponding Fourier component is peaked. This order parameter may indeed be proper to use for $L$ satisfying the condition, that circulangle's noses stack into a pie with integer number of polarly tight micelle with $\alpha = \sin\frac{1}{L} = \frac{2\pi}{n}$, where $n$ is an integer. But circulangles with $L = 6$ do not satisfy this condition.

So we used the most assumption-free and simple parameter: the average angle between the adjucent circulangles (Fig.5): $s_1 = \langle\cos\Delta\varphi\rangle = \langle\mathbf{n}_1 \cdot \mathbf{n}_2\rangle$, where $\Delta\varphi$ is the angle between the axes of adjucent circulangles. The average is taken over the neighbors, which have their median points $\mathbf{r} + \mathbf{n}\frac{L-1}{2}$ within the vicinity of $2R$.

As can be seen from Fig.6, the order parameter reaches the saturation level of $\approx 0.85$, and then slightly fluctuates around this level. The upper limit of the order parameter yielded by the smallest possible $\Delta\varphi_{min} = 1 - \frac{2}{L^2}$, which in the case of $L = 6$ is $\Delta\varphi_{min} \approx 0.94$ (Fig.6).

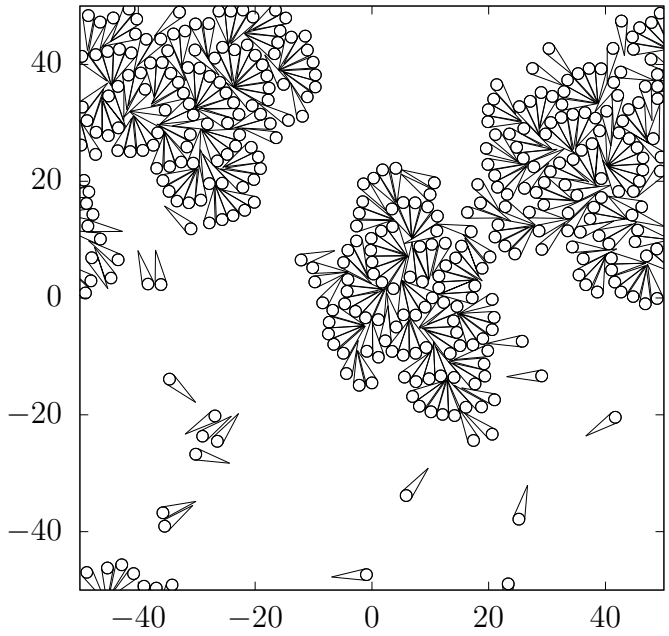


Figure 4: Micellar aggregates/networks in a periodic boundary box $100 \times 100$, formed by MC sampling. Final (stable) configuration.

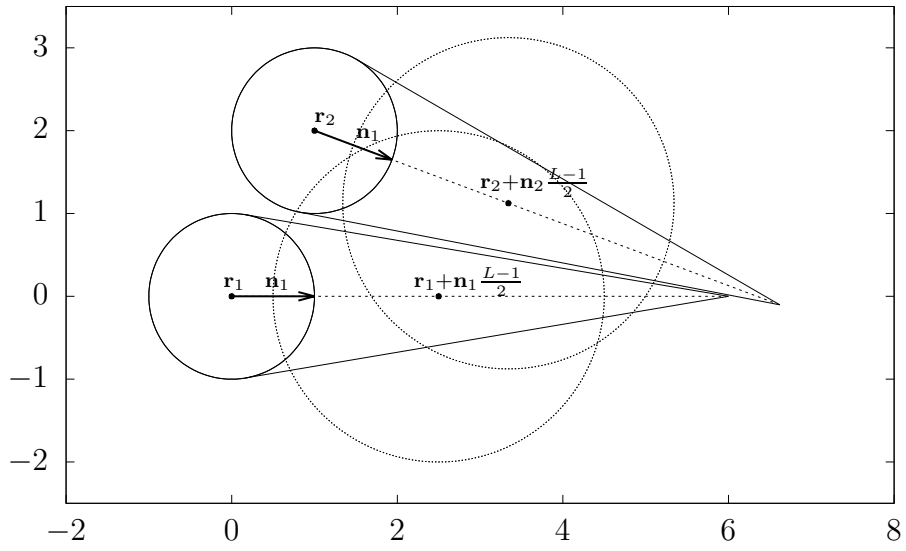


Figure 5: Definition of order parameter $s_1 = \langle \cos \Delta\varphi \rangle = \langle \mathbf{n}_1 \cdot \mathbf{n}_2 \rangle$, where $\Delta\varphi$ is the angle between the axes $\mathbf{n}_1$ and $\mathbf{n}_2$ of adjucent circulangles. The average is taken over the neighbors, which have their median points $\mathbf{r} + \mathbf{n}\frac{L-1}{2}$ within the vicinity of $2R$.

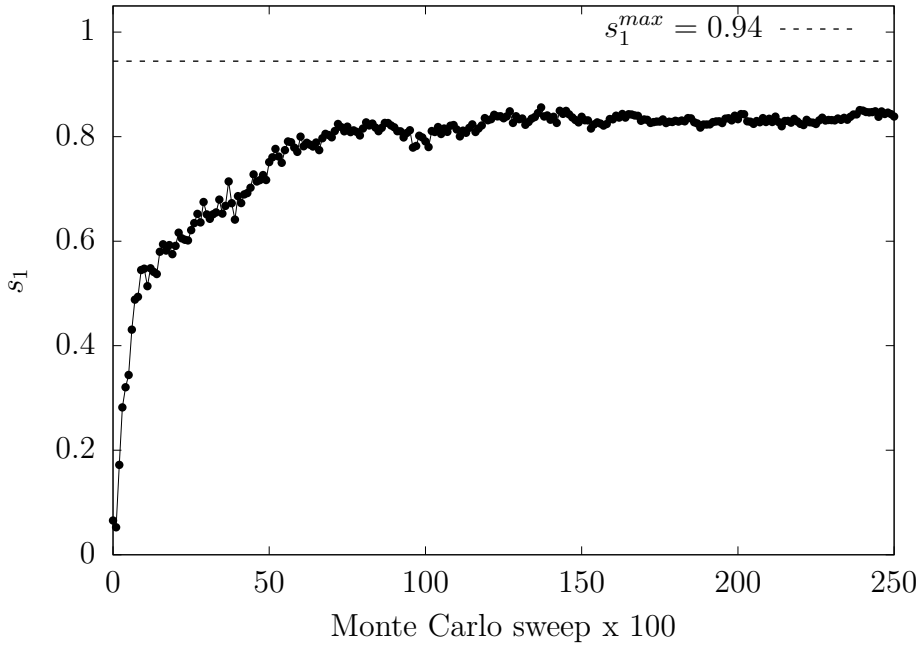


Figure 6: Changle of order parameter $s_1$, defined on Fig.5, with MC sweep. The saturation level of $\approx 0.85$ is reached for the stable structure, shown on Fig.4. Upper limit of order parameter $s_1^{max} \approx 0.94$ for ideally micellized circulangles with $L = 6$.

## 5 CONCLUSIONS AND PROSPECTS

We have introduced a particle with a new shape, which we named a circulangle. A circulangle represents a simplistic particle's model, which belongs to a unique class of shapes, having:

- Only a single curvature singularity
- No center of symmetry
- Analytically integrable geometrical moments (surface, center, radius of gyration)

A system of circulangles, self-propelled along the axis of symmetry, self-organize into aggregated micellar structures. Circulangles are the first known particles, which form micelles without attractive forces, which implies full reversibility of the process. We believe that the properties shown have powerfull implications for fundamental as well as applied research.

From the applied point of view, the discovered phenomenon enables new approaches in numerous applications: design of (meta) materials for energy conversion and storage, sensorics, micromechanics, targeted drug delivery, swarm intelligence, etc.:

- Energy conversion from the source of self-propulsion, e.g. chemical, thermal, photonic etc., to mechanical energy in a macroscopic sense. The process is enabled by entropic energy accumulation via micellisation. Taking into account reversibility of micellisation of circulangles (circulangle-like particles), this opens an entirely new niche in energy storage and conversion technology.
- Targeted drug delivery may be leveraged by micelles, formed by circulangles. They seem to be promising candidates to transport difficult to dissolve drugs and thus reduce the number of necessary particles of a drug and ensure better transportability [5, 6].

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