Chemical Physics Letters 706 (2018) 586–593

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Two-dimensional clusters from the self-assembly of oppositely charged particles

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ARTICLE INFO

Article history:
Received 23 March 2018
In final form 2 July 2018
Available online 4 July 2018

Keywords:
Nanoclusters
Morse potential
Yukawa repulsion
Global optimization
Elongated structures

ABSTRACT

We have employed simple model potentials and an evolutionary algorithm to assess the low-energy landscape of clusters resulting from the self-assembling of oppositely charged particles in two-dimensions (2D). The global minimum structures were obtained by employing an evolutionary algorithm (EA), which has been adapted to deal with planar clusters. The present results show that various families of structures, including linear- and ring-type motifs, arise in a relatively small energy-window.

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1. Introduction

The self-assembly of colloidal particles has a major importance for the fabrication of new functional materials [1–6]. Several techniques are usually employed to perform the assembly of the particles in specific structural arrangements, including the agregation induced by the application of external fields. By increasing the strength of an external magnetic field, it is possible to change the global minimum structure of magnetic colloidal clusters from a ring shape to a linear chain of particles [7]. Also, the aggregation of magnetic spheres in two-dimensions leads to the formation of chains and assembly of chains under the application of strong magnetic fields [8,9]. Dense structures of ring and hexagonally-shaped (onion-like) motifs are formed by 2D self-assembling of magnetic particles in the absence of the external field [10].

In turn, due to long-range dipolar interaction induced by the electric field, dielectrophoresis causes the directional assembly of charged particles to form chain-type morphologies [11–13]. Nonetheless, particles with the same charge sign disassemble imediatelly after the external electric field is removed. Conversely, co-assembly of both positive and negative charged particles conducted by dielectrophoresis may lead to the formation of stable structures corresponding to long-range organized chains [14]. It turns out that the length of such chains is related to both the size ratio and the number ratio of the two oppositely charged species [14].

Theoretical and computational work on colloidal systems becomes useful for the interpretation of measurements as well as for a guide to design new insightful self-assembling experiments. Perhaps the most interesting colloidal systems for creating novel materials require modeling with anisotropic-interaction potentials which complicates numerical calculations. However, it has been shown [15] that, though not quantitatively accurate, simple pair potentials are able to capture the essential features of colloidal clusters and, hence, are extremely useful to give qualitative insight about the experimental behavior of these complex systems. As an example, Demirörs and collaborators [15] have created binary colloidal clusters, that in general require the use of patches or directional bonding, by employing an isotropic potential formed with competitive attractive (long-ranged) and repulsive contributions due to the interactions between particles of opposite charge.

A particular relevant piece of information, which can be obtained by the application of state-of-the-art computational methods, are the most stable structural motifs of the clusters. Indeed, the development of global optimization algorithms has allowed to explore the energy landscapes of cluster systems [16], which is mandatory to treat several problems in chemical physics. In a recent paper [17], we have reviewed the work carried out by several groups in the development of global optimization strategies for searching low-energy structures of atomic clusters that can be also applied to study aggregates of colloidal particles. In particular, we have proposed an unbiased EA [18,19], which has shown to be suitable for exploring the low-energy landscape of charged colloidal clusters [20,21].

In this work, we made use of our EA to discover low-energy structures of colloidal clusters composed by oppositely charged

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https://doi.org/10.1016/j.cplett.2018.07.003
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particles in 2D. We aim to showcase the main families of structures and their relative stability that may arise by tunning the relevant parameters of the inter-particle potential. This elucidates about possible key potential-parameters that may stabilize or destabilize relevant structural motifs. The Letter is organized as follows. The computational methodology is described in Section 2, while the results are presented and discussed in Section 3. Finally, the main conclusions are summarized in Section 4.

2. Computational method

2.1. Potential model

In this work, we study clusters formed by two different types of particles (designated as A and B), where the interactions between unlike particles are attractive while the remaining ones are repulsive. Although one may consider point-charges and use Coulomb law to model the attractive/repulsive interactions, such potential function has the disadvantage to diverge as the inter-particle distance approaches zero. This is a relevant drawback when employing derivative-based minimizers and global optimization methods, because the potential shows numerical instabilities for small inter-particle distances that lead to wrong results. Instead, the interaction between opposite charges may be viewed in the context of colloidal systems, that can be treated in a similar way as it has been prescribed in previous works for 3D clusters [19–21]. Thus, the energy of the cluster has been calculated by assuming a sum over all pair-potentials, *i.e.*,

$$V_{cluster} = \sum_{i=1}^{N^2/4} V_{attract}(r_i) + \sum_{i=1}^{N(N-2)/4} V_{repuls}(r_i) \quad (1)$$

where r_i designates the distance between two particles. In Eq. (1), the first (second) summation applies to the attractive A-B (repulsive A-A and B-B) interactions that are modeled with the $V_{attract}$ (V_{repuls}) pair-potential. The repulsive pair-potential is described by the Yukawa-type function

$$V_{\text{repuls}}(r_i) = \epsilon_Y \frac{\exp\left[-\kappa(r_i - \sigma)\right]}{r_i} \quad (2)$$

where the inverse Debye length, κ, is assumed to be 0.5, *i.e.*, in accordance with the Yukawa repulsive model employed for other studies on colloidal systems [22,17,20]. In addition, ϵ_Y is related to the charge of the particle and, as in our previous studies [17,20], we have used the value 1.0 for this parameter. In turn, σ is the average of the radius of the interacting particles (r_A for particle A and r_B for particle B). Since Eq. (2) only applies for A-A and B-B interactions, one has either $\sigma = r_A$ or $\sigma = r_B$.

The short-range depletion interaction between two colloidal particles can be described by the Asakura-Oosawa potential [23,24], which is well-fitted [25,26] by the simpler Morse function [27]. In the context of the present study, we assume that the Morse function may further account for the attraction between oppositely charged particles. Accordingly, the pair-wise attractive component of the potential in Eq. (1) is modeled by the Morse function [27]

$$V_{attract}(r_i) = \epsilon \exp\left[\rho\left(1 - \frac{r_i}{\sigma}\right)\right]\left\{\exp\left[\rho\left(1 - \frac{r_i}{\sigma}\right)\right] - 2\right\} \quad (3)$$

where ϵ defines the well-depth and $\sigma = (r_A + r_B)/2$. In this study, we have used $\epsilon = 1.0$, 2.0 (for most of the cases) and 2.5. In general, we have considered $r_A = r_B = 1$, although different r_B values have been also employed in order to study the effect of the relative size of the oppositely charged particles. We further note that σ establishes the geometry for the minimum of the attractive potential given by Eq. (3). Hence, the minimum of the interaction energy arises at $r = 1$ when $r_A = r_B = 1$. Moreover, the range of the Morse potential is controlled by a single parameter, ρ. The results shown in this Letter are for $\rho = 6$, but we have also tested $\rho = 14$ and $\rho = 30$.

The effect of crowding due to the presence of non-interacting rigid-sphere-like particles may be simulated by adding a long-range repulsive potential to the attractive A-B interactions. To model such effect, we have employed a Yukawa function like the one reported in Eq. (2). In this case, calculations were performed for $\epsilon_Y = 0.5$ and $\epsilon_Y = 1.0$.

2.2. Global geometry optimization

We have employed a hybrid-type EA to discover the global minimum structure of the binary clusters of oppositely charged particles. The EA has been developed in our group over the years [18,19,28–30] and, hence, only the main ingredients of the method are given here; see Ref. [17] for a recent review on this methodology.

Basically, the EA combines both global exploration of the searching space by using genetic operators (namely, crossover and mutation) and local exploitation through the application of the quasi-Newton L-BFGS method [31]. For this, an initial random population of structures with a given number of A- and B-type particles is generated. After relaxation to local minima, each structure in the pool constitutes a possible solution encoding the type of the particles (A or B) and the corresponding Cartesian coordinates, which allows for the evaluation of the energy by using Eq. (1). Subsequently, the EA uses a tournament strategy to select the best individuals (among the possible solutions in the pool) to be combined through a generalized version [29] of the Cut & Splice crossover [32] that is quite effective and specially appropriate to handle binary clusters. In turn, the sigma mutation introduces some modification in the offspring structures by performing the displacement of a randomly selected particle of the clusters, whose amplitude is controlled by a Gaussian distribution with predifined features. The new structures are, then, submitted to local optimization and the energy evaluated. Because this is a steady-state algorithm, the number of solutions in the pool is kept constant during the optimization process. Accordingly, the substitution of parents

Table 1
Energy of the global minimum structures modeled with potentials whose attractive part has $\epsilon = 2.0$ and different values of the range parameter (ρ). For the repulsive Yukawa function, we have employed $\epsilon_Y = 1.0$. The values in parenthesis represent the repulsive contribution from the Yukawa function.

Cluster size	Morse potential range		
	$\rho = 6$	$\rho = 14$	$\rho = 30$
2	−2.00000000 (0.00000000)	−2.00000000 (0.00000000)	−2.00000000 (0.00000000)
4	−6.85372620 (1.14284258)	−6.85095803 (1.14841859)	−6.85047360 (1.14939176)
6	−11.11269548 (2.87774360)	−11.09670830 (2.90069885)	−11.09470226 (2.90473976)
8	−15.16188102 (4.81733426)	−15.12881161 (4.86571778)	−15.12458726 (4.87423949)
10	−19.10323280 (6.86074078)	−19.05003481 (6.94090964)	−19.04305415 (6.95500655)
12	−23.19458267 (10.74463927)	−23.09000273 (10.89311174)	−23.07702166 (10.91937091)
14	−26.86357505 (11.06338238)	−26.76518672 (11.21744181)	−26.75182521 (11.24446286)
16	−30.71812618 (13.18854055)	−30.59579324 (13.38235911)	−30.57900412 (13.41633251)
18	−34.56569526 (15.32007063)	−34.41895429 (15.55462052)	−34.39865588 (15.59570450)
20	−38.40966365 (17.45484278)	−38.23824192 (17.73068900)	−38.21438599 (17.77898896)

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