Computational and Theoretical Chemistry 1107 (2017) 82–93

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

Low-energy structures of clusters modeled with competing repulsive and either long- or moderate short-range attractive interactions

S.M.A. Cruz, J.M.C. Marques *

CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form 13 January 2017
Accepted 14 January 2017
Available online 14 February 2017

Keywords:
Morse potential
Yukawa repulsion
Evolutionary algorithm
Bernal spiral
Beaded-necklace structure
Binary clusters

ABSTRACT

We have employed an evolutionary algorithm (EA) to study the low-energy landscape of clusters modeled with a potential which is composed by an attractive Morse function and a repulsive Yukawa component. Since the range of the Morse potential is controlled by a single parameter (ρ), this has been varied between 3 and 14 to study its influence on the lowest-energy structure. The present results show that shorter-ranged attractive potentials tend to magnify the effect of the repulsive Yukawa function on the global minimum structure. Due to the higher energy-barriers, the short-range attractive interactions produce low-energy dissociated structures at smaller cluster sizes than long-range potentials. As a consequence of this, global minimum structures of clusters involving short-range attractive potentials tend to be elongated in order to reduce the number of second nearest-neighbor particles that usually correspond to a very repulsive contribution for the interaction energy. In addition, Bernal spirals and beaded-necklace motifs are often observed for potentials with a short-range attractive component, while long-ranged interactions can hardly support such structures. We have also searched for the global minima of the $N = 13$ binary clusters formed by various combinations of the ρ-parameter in the Morse potential. Most of such binary clusters are unstable in relation to the corresponding $N = 13$ homogeneous aggregates, and the structure tend to assume the usual icosahedral shape (especially for the cases involving the longer-range potentials) with particles associated to lower ρ-values preferentially located on the surface.

1. Introduction

Clusters resulting from the balance between attractive and repulsive interactions can be found in several systems, including supercooled liquids [1,2] and solutions of proteins [3–6], cells [7–11] or colloidal particles [12–14]. In turn, a great diversity of systems may be studied with purely attractive potentials of different ranges. While very short-ranged potentials have been employed to model colloidal aggregates [15–18], long-range interactions are present in metal clusters [19,20]. In addition, moderate short-range interactions are involved in the aggregation of C_{60} molecules [21–23].

The Morse pair-potential [24] is a convenient model for studying such a variety of cluster systems, since it has a single parameter (usually designated as ρ) which accounts for the range of the potential. It has been also shown [25] that, for $\rho = 6$, the Morse function is similar to the popular Lennard-Jones potential [26], which is widely used for modeling rare-gas clusters. Because of its relevance, the low-energy structures (including the putative global minimum) of Morse clusters have been exhaustively explored for different potential ranges [18,27–30]. Despite the extra complexity of the energy landscape of binary aggregates (mainly due to the presence of homotops [31]), there are also some work [32,33] reporting putative global minima of Morse clusters involving two types of particles that interact through different potential ranges.

We should stress at this stage the role of several groups in developing optimization methods that have been employed for discovering low-energy structures of atomic clusters (see Refs. [34–52] and references therein). In general, this is a huge computational task, mainly due to the roughness of the energy landscape, the exponential growth of the number of minima with the cluster size and the high potential barriers that connect different funnels [53–55]. In particular, short-ranged cluster systems are very difficult to global optimize, because the number of low-energy minima increase with the potential range [25,29,30]. Thus, algorithms based on random-search or gradient-following (or both) have

* Corresponding author.
E-mail address: qtmarque@ci.uc.pt (J.M.C. Marques).

http://dx.doi.org/10.1016/j.comptc.2017.01.035
2210-271X/

shown small efficacy to discover the global minima of such clusters [30] and, hence, they are essentially useless as the size of the system increases.

In the past few years, global optimization methodologies have been successfully employed to discover low-energy structures of colloidal clusters [17,18,56–59]. Recently, we have faced the difficulty of searching the lowest-energy structure of colloidal systems involving competing attractive (short-range) and repulsive (long-range) interactions [59,60]. This kind of clusters tend to dissociate as the number of particles increase, which difficults the global optimization task of searching for stable structures. To overcome such problem, we have proposed [60] an improved evolutionary algorithm (EA) where the local optimization is only performed for bound clusters and it stops as far as a threshold for dissociation is reached. The new algorithm was able to obtain putative global minima of charged colloidal clusters up to $N = 25$. We noticed [60] that the Bernal spiral is the global minimum for intermediate sizes, while more elongated lowest-energy structures (designated as "beaded-necklace") arise for $N \geqslant 19$. The formation of elongated structures and the tendency of charged clusters to dissociate is reminiscent of the behavior encountered in the dynamical studies of multicharged Morse [61,62] and sodium [63] aggregates. Such works [61–63] established that clusters modeled with short-range (long-range) potentials tend to produce small ionic fragments (large multicharged aggregates) by Coulomb explosion (fission).

In this work, we aim to investigate the effect of the range of the attractive potential on the structure of clusters involving also a long-range repulsive component. While colloidal clusters studied in our previous works [58–60] display very short range attractions, we want to explore here the effect of long- and moderate short-range potential regions. Besides the variation of the lowest-energy structure with the range of the attractive component of the potential which is achieved by using our EA, we also investigate whether it is possible to have Bernal spiral and beaded-necklace structures (and how stable they are) for the interaction models employed. Furthermore, the effect on the global minimum structure of combining two types of particles that are modeled by attractive potentials of different ranges is studied for all compositions of the 13-particle binary cluster.

The plan of the paper is as follows. In Section 2, we present the interaction potential used to model clusters in this work. Also described in Section 2 is the EA employed in the global geometry optimization. The main results are presented and discussed in Section 3. Finally, conclusions are summarized in Section 4.

2. Methodology

We want to study the low-energy landscape of clusters whose interaction potential is modeled with competing attractive and repulsive components. To achieve such goal, we have applied the following methodology: (i) the structures of the putative global minima were obtained by employing our own EA, which has been recently improved to deal with sub-optimal solutions formed by dissociated clusters; (ii) the stability of relevant structural motifs, like the Bernal spiral, that have shown to be the global minima in charged colloidal clusters was investigated by employing the geometries previously obtained [60] as starting points to perform local optimizations with the potential functions described below.

On the remaining of this section, we present the potential model that establishes the interaction among the particles forming the cluster in Section 2.1, while the main features of the EA are described in Section 2.2.

2.1. Potential model

The energy of the cluster has been calculated by assuming a sum over all pair-potentials, *i.e.*,

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

where r_i designates the distance between two particles. In Eq. (1), each pair-potential is composed by an attractive ($V_{attract}$) and a repulsive (V_{repuls}) contributions. The latter is modeled by the long-range branch of the Yukawa function

$$V_{\text{repuls}}(r_i) = \epsilon_{\text{Y}} \frac{\exp\left[-\kappa\sigma(r_i/\sigma - 1)\right]}{r_i/\sigma} \quad (2)$$

We note that such potential has been used in the context of charged colloidal clusters, where σ represents the diameter of each particle and κ is the inverse Debye length; as in previous works [58,59,64], it has been assumed the value 0.5 for the product $\kappa\sigma$. In turn, ϵ_{Y} is related to the charge of the particle and, for comparison with our previous studies [58,59], we have used the values 0.5 or 1.0 for this parameter.

The attractive component of the pair-potential in Eq. (1) is modeled by the Morse function [24]:

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

where ϵ defines the well-depth and σ has the same meaning as in Eq. (2); again, we took the same values as in previous works [58,59], *i.e.*, $\epsilon = 2$ and $\sigma = 1$. Moreover, the range of the Morse potential may be controlled by the sole parameter ρ. This study relies on long- and moderate short-range attractions and, accordingly, we have considered $\rho = 3, 6, 9$, and 14. Shortly, we have designated these potentials, respectively, as M3+Y1.0, M6+Y1.0, M9+Y1.0 and M14+Y1.0 when using $\epsilon_{\text{Y}} = 1.0$ in Eq. (2); for $\rho = 6$, we have also considered $\epsilon_{\text{Y}} = 0.5$ and the corresponding potential function is designated as M6+Y0.5. Obviously, the designation of the potential assume the simple Mρ (with $\rho = 3, 6, 9$, and 14) form when one considers only the attractive Morse component, *i.e.*, without the repulsive Yukawa function in Eq. (1).

The potential-energy curves for the pair interactions with $\epsilon_{\text{Y}} = 1.0$ are shown in Fig. 1. Since we want to compare the present results with previous ones [59,60] for $\rho = 30$ and $\epsilon_{\text{Y}} = 1.0$ (also designated as M30+Y1.0), the curve for this potential range is also represented in Fig. 1.

For $N = 13$, we have also studied all possible compositions of binary clusters. In these systems, we have considered that A and B particles were distinguished by the range of the attractive component of the pair-potential; in all cases, we have used $\epsilon_{\text{Y}} = 1.0$. Thus, distinct values of ρ were used in Eq. (3) for A-A and B-B interactions (that is, ρ_{AA} and ρ_{BB}, respectively), while $\rho_{AB} = (\rho_{AA} + \rho_{BB})/2$ has been employed for A-B interactions. The different combinations of (ρ_{AA}, ρ_{BB}) investigated in this work are designated as: M3M9+Y1.0, M6M9+Y1.0, M6M14+Y1.0, and M9M14+Y1.0 for (3,9), (6,9), (6,14), and (9,14), respectively.

2.2. Evolutionary algorithm

The global minima of the clusters studied in this work were located using our own EA [43,46,60,65], which is able to deal with both homogeneous and binary clusters. Indeed, prior to the application of the EA to the title systems, we have tested the algorithm against the results of Calvo and Yurtsever [33] for all compositions of $N = 38$ binary Morse clusters with all combinations of $\rho = 3, 6$, and 9. The results shown in Fig. S1 of the Supplementary Data are really impressing, since the EA reproduced all the minima reported