Computational and Theoretical Chemistry 1082 (2016) 41–48

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

# Anisotropy effect of multi-center Lennard-Jones molecular clusters

Rui Gong, Longjiu Cheng *

*Department of Chemistry, Anhui University, Hefei, Auhui 230039, People's Republic of China*

ARTICLE INFO

*Article history:*
Received 28 February 2016
Received in revised form 7 March 2016
Accepted 8 March 2016
Available online 10 March 2016

*Keywords:*
Anisotropy
Structural optimization
Multi-center Lennard-Jones potential
Atomic clusters

ABSTRACT

Models of randomly packed hard molecules of Multi-Center Lennard-Jones (MCLJ) clusters exhibit some features of anisotropy effects. To investigate the anisotropy effect on the structures of molecular clusters, four highly symmetrical molecules are modeled: 4-atom tetrahedron (TLJ), 6-atom octahedron (OLJ), 8-atom cube (CLJ), and 12-atom icosahedron (ILJ). The intermolecular interactions are described using the MCLJ model. Using the funnel hopping algorithm, we located the putative global minimum structures of these four MCLJ molecular clusters up to cluster size $N = 80$. The structural patterns of these MCLJ clusters are much different to that of Lennard-Jones clusters, and some new rules and structures are found. The structures of TLJ clusters are most irregular due to the highest anisotropy effect of the tetrahedral molecule. For OLJ clusters, a new structural pattern, rhombic dodecahedron, is viewed. The structures of CLJ clusters are also interesting, which look like oblique face-centered cubic (fcc) structures. For ILJ clusters, icosahedral motifs are favored at cluster size $N \leqslant 19$, and fcc motifs are favored more at $N > 19$.



## 1. Introduction

Random packing problems of rigid geometries have been studied by biologists, materials scientists, engineers, chemists, and physicists to understand the structure of living cells, liquids, granular media, glasses, and amorphous solids [1–5]. A variety of geometries who are packed are paid attention to, for examples spheres and spherocylinders [6–9]. In the field of chemistry, packing of polygons, molecule and atom are most favored. Such as packing of $C_6H_6$, $C_{60}$, Au, ethane and methane [10–14]. Random packing problems of identical spheres are the largest number of studies. To study the packing of spheres, some models are used, such as Lennard-Jones (LJ) model.

LJ clusters represent one such test system. It is often used to simulate atomic clusters, especially for rare gas atomic clusters [15–18]. It also plays an important role in studying the nonbonding pair interactions in many complex molecular systems. Here the LJ pair potential is

$$E_{LJ}(r) = \varepsilon\left[\left(\frac{r_0}{r_{ij}}\right)^{12} - 2\left(\frac{r_0}{r_{ij}}\right)^{6}\right], \quad (1)$$

where $r_0$ is the equilibrium pair separation between two atoms, $\varepsilon$ is the pair equilibrium well depth, $\varepsilon = 1$, is used in this work. The LJ model is obviously simple to implement, and their optimal structures display a very regular variation [19,20]. Icosahedral motifs are most favored for LJ clusters, and only at some magic numbers, decahedral, face-centered cubic (fcc), and tetrahedral motifs can be global minima. For example, $LJ_{38}$ is fcc; $LJ_{98}$ has tetrahedral symmetry [21].

As a simple model, LJ model is important in the study of multi-center LJ (MCLJ) molecular clusters. For $C_{60}$ molecular clusters with all-atom potential [11], the intermolecular interaction between $C_{60}$ molecules is nearly the sum of C–C LJ interactions between two molecules. This kind of $C_{60}$–$C_{60}$ interaction is somewhat a MCLJ model where realistic molecular anisotropy is considered. The favorite structures are much different from those of the LJ potential, where decahedral and close-packed motifs are more favored for $C_{60}$ molecular clusters [22,23]. Two-center Lennard-Jones (2CLJ) model is a special MCLJ model. The ratio of the diatomic bond length to the LJ equilibrium length is varied to increase the degree of anisotropy [24]. Large ratio means strong anisotropy effect. With the increase of anisotropy effect, the potential range increases at optimal orientation, and the global minima change from icosahedral, to polyicosahedral and to novel irregular structures.

The research of the packing of highly symmetrical molecules is of fundamental interests. In this work, four highly symmetrical molecules, tetrahedron, octahedron, cube, and icosahedron, are modeled. The intermolecular interactions are described using the MCLJ model. Given the general importance of the LJ cluster as a simple model cluster, MCLJ model can provide a straightforward analysis of the effect of molecular shape on the structures of

* Corresponding author.
*E-mail address:* clj@ustc.edu (L. Cheng).

http://dx.doi.org/10.1016/j.comptc.2016.03.008
2210-271X/

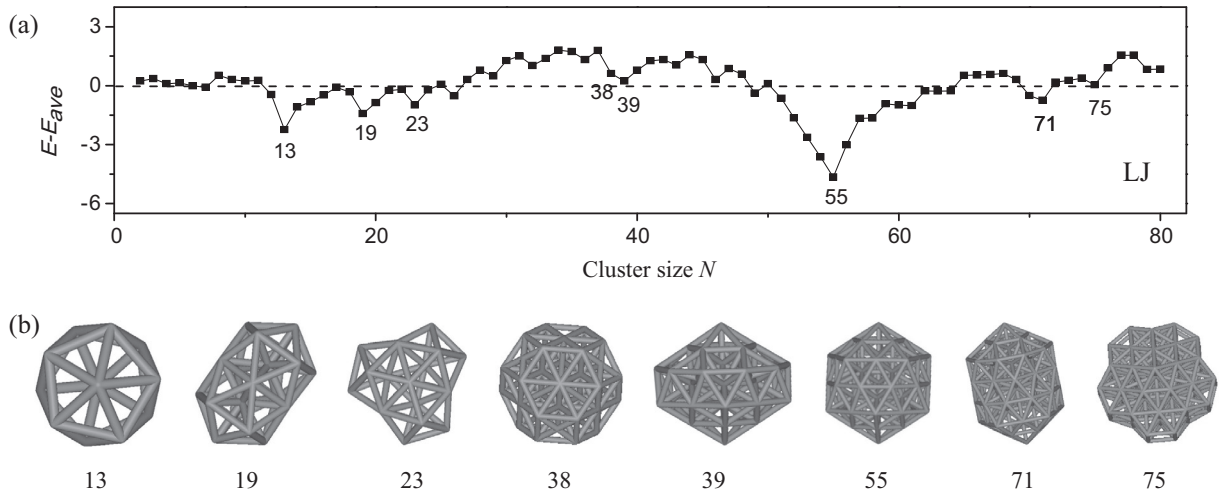


**Fig. 1.** (a) Plots of the relative energies of the global minima of LJ clusters as a function of cluster size $2 \leqslant N \leqslant 80$. $E$ is the energy of the global minima, and Eave is a four-parameter fit to the global minima energy ($E_{ave} = aN + bN^{2/3} + cN^{1/3} + d$) Downward peaks represent the most stable magic numbers compared to the neighbors. (b) Geometries of most stable magic numbers.

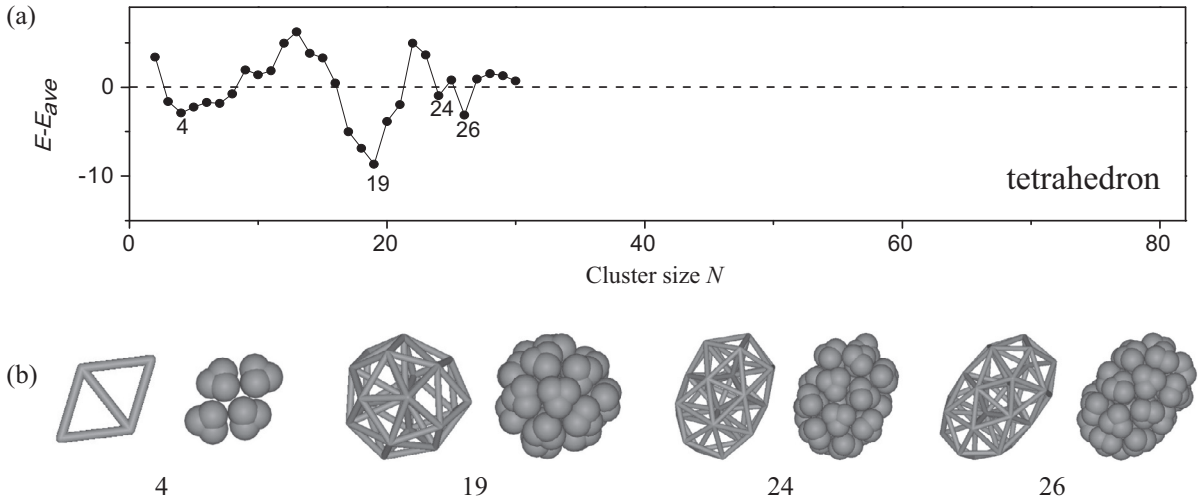


**Fig. 2.** (a) Plots of the relative energies of the global minima of TLJ clusters as a function of cluster size $2 \leqslant N \leqslant 30$. (b) Geometries of most stable magic numbers. For each cluster size, the structures on the left show an overall view of the cluster (each ball means the mass center of each molecule) and those on the right show the real molecular clusters.

clusters. The potential energy surfaces of MCLJ clusters are more rugged than that of LJ cluster, so the highly efficient "funnel hopping" algorithm [25] is employed to carry out this searching on the potential energy surfaces.

## 2. Method

### 2.1. MCLJ model

MCLJ model is important in physics. In this work, as a model study and for simplicity, each molecule is treated as a rigid body and only the LJ interactions are considered. Using the MCLJ model, the energy between two molecules can be written as:

$$E(\alpha,\beta) = \sum_{i=1}^{N}\sum_{j=1}^{N} E_{LJ}(r_{ij}^{\alpha\beta}) \tag{2}$$

where $N$ is the number of atoms in a molecule, and $r_{ij}^{\alpha\beta}$ is the distance between atom $i$ of molecule $\alpha$ and atom $j$ of molecule $\beta$. Tetrahedron, octahedron, cube and icosahedron are studied here since they are highly symmetrical polyhedron models. Clusters of 4-atom tetrahedral molecules are called tetrahedral Lennard-Jones (TLJ) clusters; accordingly, clusters of 6-atom octahedral, 8-atom cubic and 12-atom icosahedral molecules are called octahedral Lennard-Jones (OLJ), cubic Lennard-Jones (CLJ) and icosahedral Lennard-Jones (ILJ) clusters, respectively. In this model study, the bond length in each molecule is set to $0.45r_0$, which is in agreement with the ratio of covalent and van der Waals radius of carbon.

### 2.2. "Funnel hopping" algorithm

Because of the enormous number of local minimum structures of atomic and molecular clusters, it is difficult to locate the lowest energy conformation in the fields of chemistry. The global optimization algorithm [26–32] has been widely used to locate global minimum structures. In the past years, a variety of methods have been developed for global structural prediction, such as "Funnel hopping" algorithm, simulated annealing algorithm [33,34], genetic algorithm (GA) [35,36], basin-hopping and its variants [37,38], particle swarm optimization [39,40], random tunneling