



Editor's choice

Potential energy landscapes of tetragonal pyramid molecules

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ABSTRACT

Hiraoka et al. have developed a self-assembling system referred to as a nanocube (Hiraoka et al., 2008). In the present contribution a coarse-grained model for this system is analysed, focusing on how the potential energy landscape for self-assembly is related to the geometry of the building blocks. We find that six molecules assemble to form various clusters, with cubic and sheet structures the most stable. The relative stability is determined by the geometry of the building blocks.

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1. Introduction

The potential energy surface (PES) plays a central role in understanding molecular systems, determining structure, thermodynamic and dynamic properties [1]. In general, however, extraction of key information from the PES can be challenging because the landscape is a complex function in multidimensional space, characterised by numerous local minima and the transition states connecting them. In the present contribution we exploit disconnectivity graphs [2], which provide a powerful tool for representing the multidimensional PES and understanding how observable properties are determined by topological characteristics.

In recent years, the process of self-assembly has attracted considerable attention [3], where a particular set of building blocks combines to spontaneously form an ordered complex [4–10]. Knowledge of assembly mechanisms is, however, still rather limited [11]. Hiraoka et al. have recently developed a system described as a nanocube, in which six planar organic amphiphilic molecules self-assemble into a cubic cluster [9,10] through the dispersion interaction between the functional groups [12]. The system is not well understood; a reported binding energy computed by quantum chemical methods is more than ten times greater compared to the

experimental estimates, and the yield of nanocube strongly depends on the solvent environment. It is likely that the geometrical structure of the building blocks, and the anisotropic interactions between them, govern the stability and structure of the cluster. Hence the nanocube offers a good example for understanding a potentially important self-assembly process, especially in terms of the PES.

In the present work, we develop a coarse-grained representation of the nanocube by adapting a pentagonal pyramid model [13–15], which is known to reproduce some geometrical characteristics of viral capsids. The global PES is then investigated to understand the physicochemical principles underlying assembly.

2. Model

The model consists of tetragonal-pyramidal molecules with five interaction sites, as shown in Fig. 1. r_b is half the length of a side of the basal square and h is the height of the pyramid. The interaction potential between two molecules (i, j) is defined as follows:

$$V_{ij} = \varepsilon_R \left(\frac{\sigma}{r_{ax}} \right)^{12} + \varepsilon \sum_{u=1}^4 \sum_{v=1}^4 \{ e^{\rho(1-r_{uv}/r_e)} - 2 \} e^{\rho(1-r_{uv}/r_e)}.$$

The first term represents repulsion between the apices of two pyramids (r_{ax} is the distance between them), and the second term is a Morse interaction between basal points (u, v) in different molecules. r_{uv} is the distance between the basal points of two molecules.

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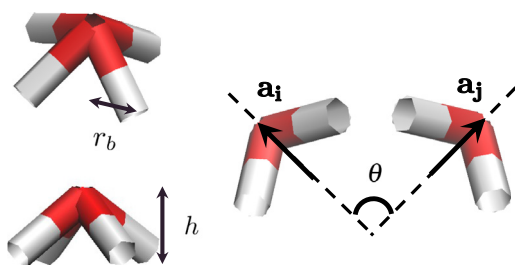


Fig. 1. (Left) The geometrical parameters r_b and h defining the shape of the tetragonal pyramidal building blocks (Right). The orientation angle θ .

σ is set to $2\sqrt{r_b^2 + h^2} + r_b$ to match the apex-apex distance in the cube structure, so that six tetragonal pyramids can be geometrically packed into the cubic hexamer. We have confirmed that molecules beyond the hexamer become less stable, except for the 12-mer. Other parameters are set as follows: $r_c = r_b$, $\rho = 3.25$ and $\varepsilon_R = 0.5\varepsilon$. This is a pyramidal version of a previous viral capsid model [13–15]. We note that this pyramidal molecule does not have a C_3 symmetry axis, so the symmetry is different from the experimental building blocks. Hence, although the present model is inspired by the nanocube, the formation mechanism may not be exactly the same as for the real system.

The PES of the hexamer of pyramidal building blocks was explored using basin-hopping (BH) [16,17] global optimisation, as implemented in GMIN [18] using the L-BFGS minimizer [19]. 10^5 BH steps were employed starting from ten different initial con-

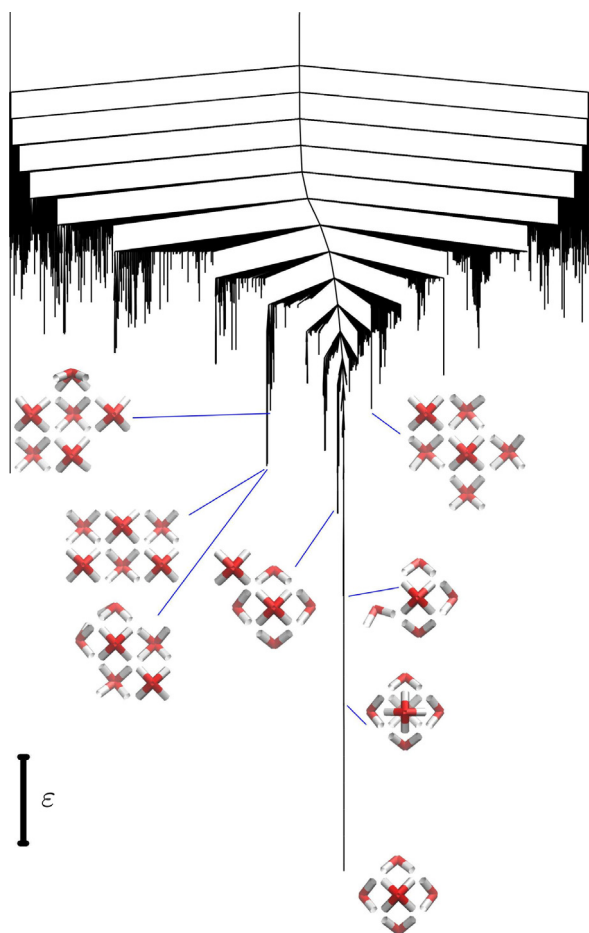


Fig. 2. Disconnectivity graph for six tetragonal pyramidal molecules with $\phi = 0.8$.

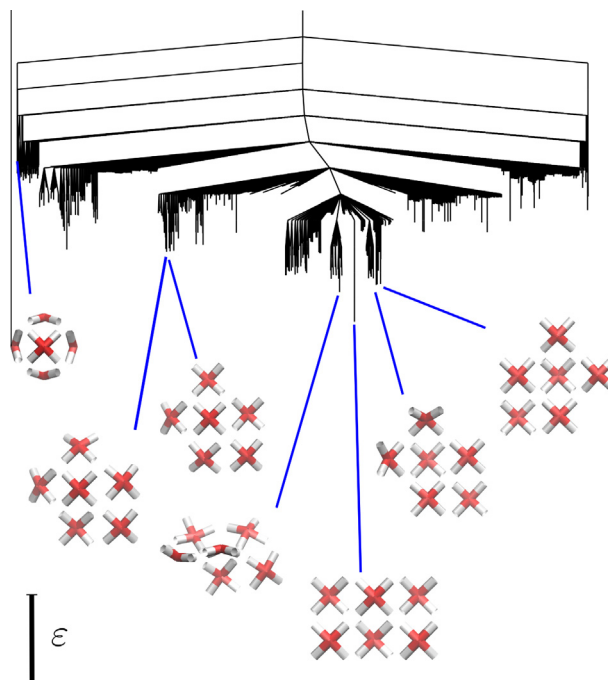


Fig. 3. Disconnectivity graph for six tetragonal pyramidal molecules with $\phi = 0.3$.

figurations. The connections between local minima were then computed by single-ended transition state searches [1,20,21] with OPTIM [22]. The PATHSAMPLE [23] program was used to expand the databases of local minima and transition states, which were distinguished by their energies and moments of inertia. Finally, the databases were visualised using disconnectivity graphs [24,25]. These computations were repeated, changing the geometry of the building block by varying the pyramid height, i.e. $\phi = h/r_b$.

3. Results and discussions

The first disconnectivity graph is shown in Fig. 2, using the 2000 lowest energy local minima. The PES is characterised as a single funnel, in which the global minimum is the cube structure, which lies significantly lower than the other local minima. The second-lowest energy structure is also a cube-shaped cluster, but with one of the six molecules rotated by ninety degrees compared to

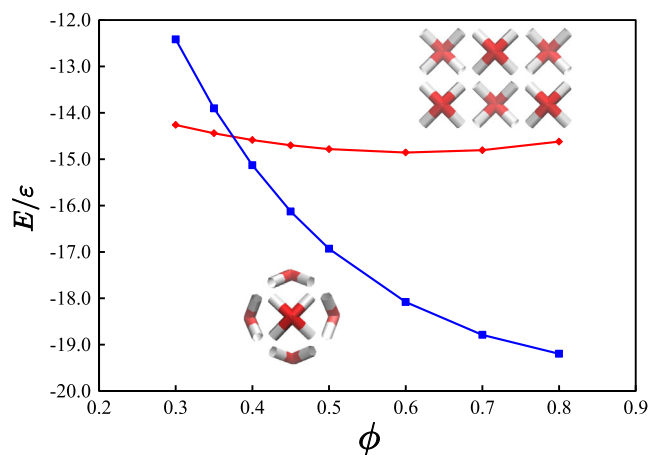


Fig. 4. Potential energy E for the cube (blue line) and sheet (red line) as a function of ϕ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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