TASK QUARTERLY vol. 19, No 1, 2015, pp. 5–13

A NEW, EFFECTIVE METHOD FOR COMPUTING THE INTERACTION POTENTIAL OF HARD CYCLIC MULTIMER SYSTEMS

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(received: 3 November 2014; revised: 12 January 2015;
accepted: 19 January 2015; published online: 13 February 2015)

Abstract: Studies of efficiency of several methods for calculating the interaction potential of a pair of two-dimensional hard cyclic multimers – molecules formed by hard disks (atoms) placed at the vertices of a regular polygon – are reported in this work. Such hard-body particles, known as hard cyclic multimers, constitute a class of important reference systems in modeling structural and thermodynamic properties of molecular systems. A new method is proposed which can be easily implemented to Monte Carlo simulations of two-dimensional cyclic multimers and which is faster than the fastest method used previously.

Keywords: hard cyclic multimer, hard potential, computer simulation, Monte Carlo method

1. Introduction

An efficient method for calculating the interaction potential of any particle is always desirable in computer simulations, especially using the Monte Carlo (MC) method. During the simulation, the potential is calculated at each step of the program and the speed of calculations of the potential has a critical impact on the time needed to carry out the simulation. Thus, in order to be able to perform a sufficiently long run (giving accurate results) of a large number of particles, one needs a very efficient method for calculating the potential.

Particles which are considered in this work, further referred to as hard cyclic multimers (HCM), are composed of n identical hard disks (atoms) of the diameter d with centers forming a regular polygon with side σ (see Figure 1). The considered particles can have different ratios of d/σ, which significantly affects their properties. One of the reasons why HCM systems are of interest is that in appropriate conditions (near close packing) they show auxetic [1] behavior (negative Poisson's ratio [2]), what has been published earlier for $n=3,4,6,7$, *i.e.* for trimers, tetramers, hexamers and heptamers [3–9].

Hard body interaction between particles implies that their potential can result in only two different values: infinity, when any two bodies overlap, and zero otherwise. MC simulations of such a system will therefore proceed in a fairly obvious way – each trial move resulting in overlapping particles is rejected and all others are accepted. Methods created within this paper are in fact designed simply to verify if two neighboring HCM overlap or not.

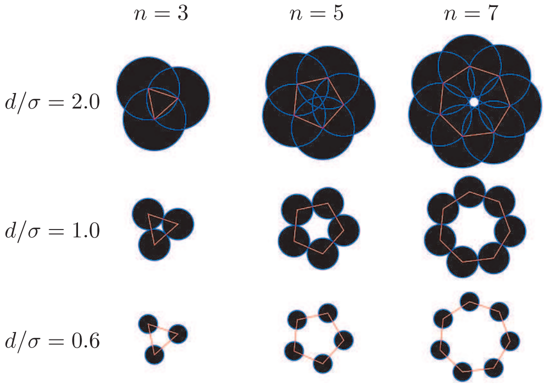

Figure 1. HCM with few examples of n and ratios d/σ

2. The methods

This section describes various possible methods of checking if molecules overlap.

Each method is based on four input parameters: r_a, r_b – positions of two interacting particles on an axis connecting their centers ($r_a < r_b$) and φ_a, $\varphi_b \in \left[-\frac{\pi}{n}, \frac{\pi}{n}\right]$ – angles defining orientations of molecules relative to this axis (see Figure 2).

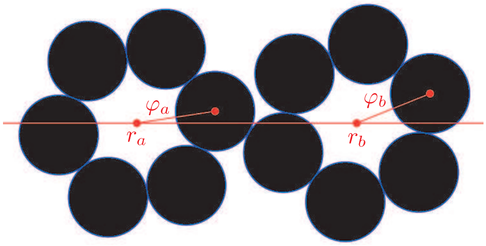

Figure 2. Presentation of input parameters using example of two HCM of $n=6$

- Method #1: calculates mutual distances between pairs of atoms, and stops when a pair of disks of infinite potential energy is found. It takes into account all atoms (n^2 pairs) of both particles.

- Method #2: the same idea as in the case of method #1, but calculations are done for only three atoms ($3^2 = 9$ pairs) which are the closest to the other particle.
- Method #3: further improvement of method #1 – calculations are done for only two atoms of each molecule, hence only the closest four pairs of disks are taken into account.
- Method #4: four closest atoms (two per particle, see Figure 3) are selected as in method #3, and then three mutual distances of centers of molecules are calculated at given angles φ_a and φ_b, assuming that they are in contact by:
  - (a) atoms a_1 and b_1 (r_{11}),
  - (b) atoms a_2 and b_1 (r_{21}),
  - (c) atoms a_1 and b_2 (r_{12}).

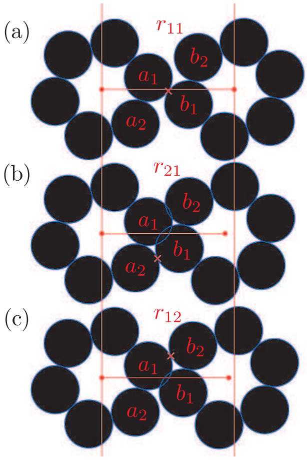

Figure 3. Example of situations a–c using method #4; red crosses indicate locations of considered contacts of two molecules

The largest of these three distances is the minimum distance at which molecules can occur at given angles.

Distances r can be obtained from the following formula:

$$\begin{aligned} r_{ij}(\varphi_a,\varphi_b) = & R[\cos(\varphi_{ai}) - \cos(\varphi_{bj}+\pi)] \\ & + \sqrt{d^2 - \{R[\sin(\varphi_{ai}) - \sin(\varphi_{bj}+\pi)]\}^2} \end{aligned} \tag{1}$$

for pairs of $\{i,j\}$: $\{1,1\},\{1,2\},\{2,1\}$, where: $R = \frac{\sigma}{2\sin(C)}$, $C = \frac{\pi}{n}$, $\varphi_{a1} = \varphi_a$ and $\varphi_{a2} = \begin{cases} \varphi_a - 2C; & \varphi_a > 0 \\ \varphi_a + 2C; & \varphi_a \le 0 \end{cases}$, similarly for φ_{b1} and φ_{b2}, however, one should note that φ_b must be modified for an odd HCM. If the remainder of division $(\varphi_b + 2C)$ by $2C$ equals φ_{bmod}, then:

$$\varphi_b = \varphi_{bmod} - C \tag{2}$$

The minimum distance at which molecules do not overlap at the given angles reads:

$$r_{min}(\varphi_a,\varphi_b)=\max\left\{\begin{array}{l}\mathrm{Re}[r_{11}(\varphi_a,\varphi_b)]\\ \mathrm{Re}[r_{21}(\varphi_a,\varphi_b)]\\ \mathrm{Re}[r_{12}(\varphi_a,\varphi_b)]\end{array}\right\} \tag{3}$$

and the potential energy of two molecules is equal to:

$$U=\begin{cases}0; & r_b-r_a\geq r_{min}(\varphi_a,\varphi_b)\\ \infty; & r_b-r_a<r_{min}(\varphi_a,\varphi_b)\end{cases} \tag{4}$$

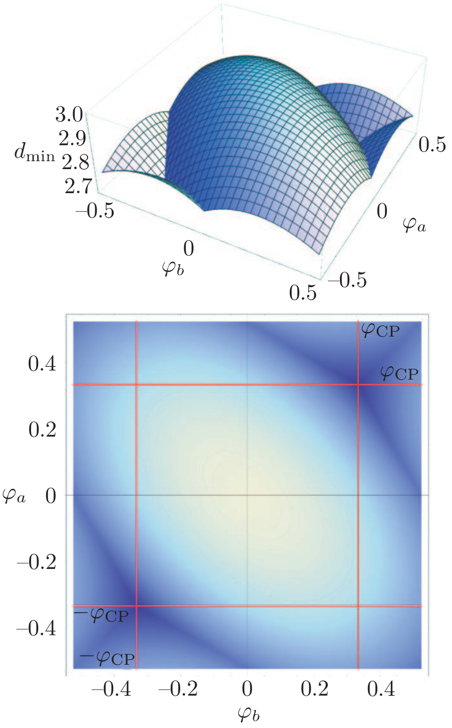

Figure 4. Interaction surface and its projection on (φ_a,φ_b) plane of two HCM molecules of $n=6$ and $\sigma=d=1$

- Method #5: the same idea as in the case of methods #1–#3, but the relative angle between molecules is taken into account. Also a comparison of value of their angles in relation to interval $(-\varphi_{\mathrm{CP}},\varphi_{\mathrm{CP}})$ is made, where:

  $$\varphi_{\mathrm{CP}}=C-\mathrm{arctg}\left\{\left[2\,\mathrm{ctg}(C)+\frac{d}{\sigma}\sqrt{4-\left(\frac{\sigma}{d}\right)^2}\right]^{-1}\right\} \tag{5}$$

  is the angle at which two molecules are located at the absolute minimum distance [10]. The main idea of this method follows from the analysis of Figure 4. It can be seen that when orientations of both molecules are in the range of

$(-\varphi_{\mathrm{CP}}, \varphi_{\mathrm{CP}})$, the problem is reduced to one continuous interaction surface. In this case, it is sufficient to consider only one pair of disks (the most protruding atoms toward the other particle) to check any overlap. Otherwise it is necessary to consider an additional pair of disks. In such a case, for one of molecules not one but two disks must be taken into account. Another part of the method determines, for which of molecules the additional disk should be found. This is done by comparing the orientations of particles: the additional disk must be considered for this particle, which has a greater value of $|\varphi|$. The sign of its φ indicates the specific disk of the molecule.

In conclusion, the function finds three disks-atoms (two for one particle and one for the other one), and in situations where the HCM's angles are both in the range $(-\varphi_{\mathrm{CP}}, \varphi_{\mathrm{CP}})$, two disks (one per particle), for which the overlap check is sufficient. The flowchart of the method #5 is shown in Appendix A.

- Method #6: corresponds to the analytical approach described in the literature [10].
- Method #7: the approach introduced in method #5 is implemented in method #4. The maximum value in formula (3) is selected not among three distances (1), but only two or even one (automatic selection). This modification additionally increases the efficiency of method #4.

3. The efficiency tests

The efficiency of the described methods was examined by the tests discussed below.

Sets representing large numbers of twōmolecule HCM systems were generated, each characterized by four parameters as in section 2, *i.e.* r_a, r_b, φ_a, φ_b. Then, the time required by a particular method for calculations of the potential of all systems generated in a given set was measured. Sets were identical for each method, and the calculations were made on a processor of the same computing power.

The correctness of all methods were checked on the basis of the analytic approach [10]. For each of the considered systems, each method always returned the same value of the potential, as method #6.

Parameters were generated randomly, assuming:

- $r_a = 0$,
- $r_b \in [r_{min}(\varphi_{\mathrm{CP}}, \varphi_{\mathrm{CP}}), 2R + d]$,
- φ_a, $\varphi_b \in [-C, C]$.

It is only the selection of the r_b range that requires a comment. This parameter determines the distance between centers of particles (since $r_a = 0$), therefore its minimum value is defined by formula (3) assuming that $\varphi_a = \varphi_b = \varphi_{\mathrm{CP}}$. Lower values of r_b would obviously result in an infinite potential energy (overlapping particles). Considering the upper limit, for r_b greater than the presented above, each system would have zero potential energy. The described range of r_b guarantees that, depending on orientations, the generated systems can always take any of two possible values of the interaction potential.

Two tests were carried out: (1) using all the created methods except #6; (2) using only the fastest methods from (1) and method #6. In the first case particles of $n=6$ and ratio $d/\sigma=1.0$ were considered. In the second case, series of tests were carried out for $n=4,5,6,19,20,21,97,98,99$, in each case for three different ratios $d/\sigma=0.6,1.0,2.0$.

4. Results

The results of the first test for a set containing $5\cdot10^6$ systems are shown in Table 1. The advantage of methods #4, #5 and #7 over the rest of the methods is clearly seen.

Table 1. Mean computation times of the described methods and their standard errors for $5\cdot10^6$ randomly generated configurations of two molecules; HCMs with $n=6$ and $d/\sigma=1.0$ were considered

Method	Time [s]
#1	21.1541(35)
#2	7.8023(21)
#3	3.8312(14)
#4	2.2516(16)
#5	1.8544(11)
#7	2.1909(12)

The main aim of the experiment was to compare the efficiency of different methods for calculating the interaction potential of two HCMs. However, the computations gave also a certain result concerning the frequency of configurations of zero energy against all the generated configurations. The fraction describing this contribution is approximated by 42.2. This result can be interpreted in such a way that the average probability of a non-overlapping state in which two HCMs ($n=6$) are located within the range $\left[\sigma\sqrt{7},3\sigma\right]$, equals approximately 0.422. Obviously, the probability that identical hexamers have zero energy at a distance larger than 3σ is equal to unity as the hexamers cannot overlap. With the distance reduction below 3σ, the probability of occurrence of a state without an overlap decreases and at distances smaller than $\sqrt{7}\sigma$ the haxamers always overlap so the probability of zero energy is then zero.

In the second part of the efficiency test in each case method #5 turned out to be the fastest one, while methods #6 and #7 occupied different positions depending on n. For small n (4, 5, 6) method #7 was faster than #6, but with increasing n, method #6 began to overtake it. Examples of dependences obtained in the test are shown in Tables 2 ($n=4$, $d/\sigma=2.0$) and 3 ($n=21$, $d/\sigma=2.0$). The results obtained during other tests, for other combinations of n and d/σ, roughly revealed the same character.

Table 2. Mean values of duration of calculations of created methods and their standard errors for $5 \cdot 10^6$ randomly generated systems; considered HCMs: $n = 4$, $d/\sigma = 2.0$

Method	Time [s]
#5	1.6693(17)
#6	2.2159(8)
#7	1.8362(15)

Table 3. Mean values of duration of calculations of created methods and their standard errors for $5 \cdot 10^6$ randomly generated systems; considered HCMs: $n = 21$, $d/\sigma = 2.0$

Method	Time [s]
#5	1.8757(8)
#6	1.9336(6)
#7	2.1466(11)

5. Summary

On the basis of the efficiency tests performed, it can be concluded that method #5 is the fastest, faster than the analytic approach – method #6 published previously [10]. Method #5 is particularly advantageous at small n (4, 5, 6). For large n the difference between the efficiency of methods #5 and #6 decreases.

It is worth adding that for small n (6 and less) also method #7 is found to be better than the analytic approach described in the literature.

Appendix A

Flowchart of method #5 are shown in Figures 6–5. Variable names coincide with those used in this paper.

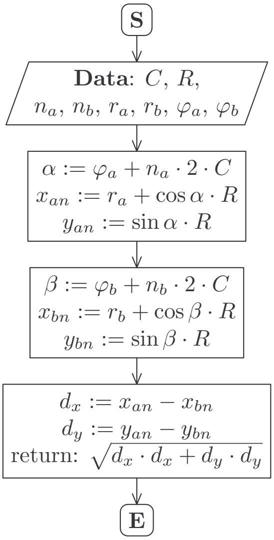

Figure 5. Flowchart of procedure 'getDisksDistance' (used in subsequent flowchart)

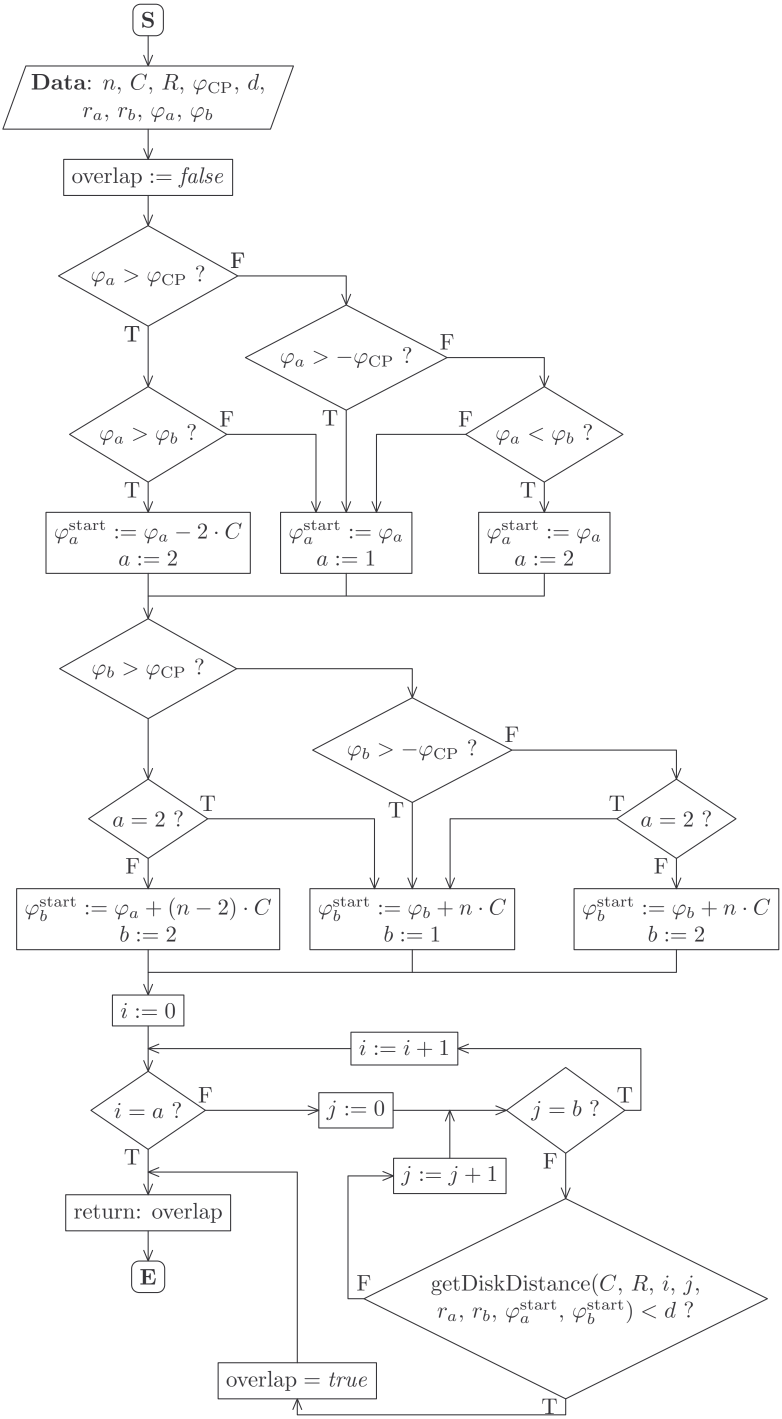

Figure 6. The flowchart of the method #5

Acknowledgements

I would like to thank Prof. K. W. Wojciechowski for sharing his thoughts about the study of HCM systems and also for his valuable comments and remarks.

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