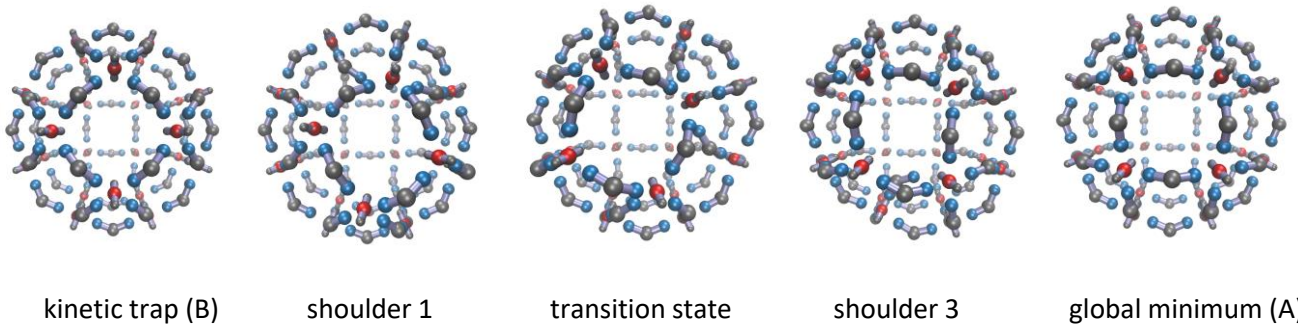
Scientific report 2

Second stage (01.01.2021 – 09.12.2021)

During the second stage of the project, the following activities have been carried out:

1. Selecting single-transition state rearrangements



kinetic trap (B) shoulder 1 transition state shoulder 3 global minimum (A)

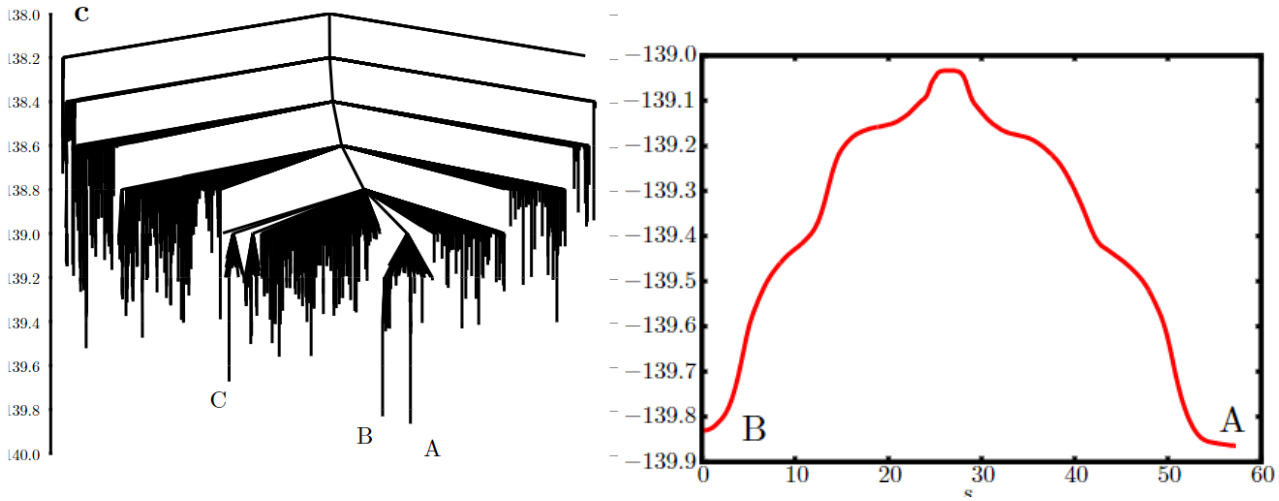


Figure 1. Top panel: snapshots of the single transition state rotatory motion involving two shoulders on each side for the fastest transition pathway between two lowest-energy structures on the landscape. Bottom left panel: extensively sampled low-energy region of the landscape for a ligand bend angle of about 136°. Bottom right panel: the energy profile of the transition.

Single transition state rearrangements that comprise of highly cooperative moves can in theory be exploited as colloidal motors. We therefore explored our previous simulations to see if such rearrangements are a common occurrence or not, when the rigid building blocks feature only Coulomb and excluded volume interactions. Using our model of self-assembling Goldberg polyhedra, we found that these systems are capable of cooperative moves of long path lengths, involving the motion of a large proportion of the cluster particles themselves, but the low-energy single transition state rearrangements are mostly deformations of bistable hollow shells. However, we found an ideal range of bend angles in M_nL_{2n} model systems where the single

transition state rearrangement having a rotatory motion described in page 7 of the project proposal can occur and is the lowest energy pathway: approx. 120-140° for the pseudorhombicuboctahedral-rhombicuboctahedral transition.

The rearrangement shown in Figure 1 can be seen at https://youtu.be/redvzHn34lQ. We attempted to create conditions which are appropriate for spontaneous observation of the same single transition state rearrangement with molecular dynamics using the HOOMD Blue MD environment set up in phase 1. However, for this particular example, only motions leading up to the first shoulder were observed, and on higher temperature the vibrations of the system made observing such rotatory motions extremely difficult. In fact, once the system reached the kinetic trap (which seems to be the entropically most favoured state to reach starting from random building block configurations), we did not observe transition towards the global minimum over the selected range of temperatures. On this landscape, the event is too rare to be observed with the simulation lengths accessible to us. We therefore modified the parameters to lower the barrier for this rearrangement, but that destabilized the structure. Further simulations are ongoing.

2. Finding the basic design of a self-assembling colloidal motor

As the parameter space of the building blocks to be explored is huge, we had to design a somewhat automated framework that can autonomously navigate this parameter space by selecting the fittest set of parameters for a particular task. In this way, a basic rigid body model designed with common sense can be further enhanced to further stabilize the desired structure or enhance its rigidity or self-assembling properties. In this framework molecular dynamics simulations are created automatically by a program from a starting input parameter set and run on the HOOMD Blue MD environment of the group.

Basic notions that will be used in the next sections:

- particle = a basic spherical element with: charge (q), mass (m) and radius (r)
- rigid body = a structure formed from multiple particles, which have fixed position relative to each other
- simulation = the observation of the interaction between multiple rigid bodies confined to a simulation box
- mutation = a random change in any of the characteristics of the studied element
- mutation distance = a measure to somehow quantify the difference between two elements of the same type
- fitness = a measure of how well the simulation result adheres to the desired configuration

All structure data is stored in a database, the simulations are saved in gsd format.

Mutations

The program is designed to create new simulations from existing ones by mutating them. There are multiple mutations which can occur for a simulation, these are:

- increasing the number of a specific rigid body in the simulation

- decreasing the number of a specific rigid body in the simulation
- adding a new type of rigid body to the simulation
- removing a rigid body from the simulation
- mutation of a rigid body type

The possible mutations of a rigid body are:

- adding a new particle
- removing a new particle
- swapping a particle for another one registered in the database
- changing the position of one of the particles

Each of the listed mutations can occur with a given probability, which is defined by the user beforehand. The user can also define a maximum mutation distance, which limits the change of the simulations between generations.

The process is started from an initial simulation (S_0), which will have a fitness, F_0. A new simulation is created by mutating S_0 with a probability of P_M, which can be defined as:

$$P_M(i) \propto \frac{1}{F_i}$$

or

$$P_M(i) = 1 - F_i$$

depending on the range of the fitness function values. If there is no mutation then S_0 will be continued from where it was left off. In further iterations a simulation S_i is started, with probability:

$$P_C(i) \propto F_i$$

Once again the selected simulation is either mutated into a new one or continued based on its fitness value. The process is stopped when the number of desired simulations is reached.

Basic density fitness function

To test the procedure, we chose to implement a simple fitness function based on the density of a subsection of the simulation box. In this approach a fractional box size (α) is chosen (we use α=0.3) and densities are calculated for all the possible fits:

$$\rho_{ijk}(\alpha) = \frac{n_{ijk}}{V(\alpha)}$$

where $V(\alpha)$ is the volume of the cell and n_{ijk} is the number of particles in the cell. The fitness value is given by comparing the maximal $\rho_{ijk}(\alpha)$ value to the theoretical maximum density

$$D(\alpha) = \frac{N}{V(\alpha)}$$

Where *N* is the total number of particles in the simulation. The fitness function will be computed as

$$F = \frac{max(\rho_{ijk}(\alpha))}{D(\alpha)} = \frac{n_{ijk}}{N}$$

Technical details

The program is implemented with the use of Docker containers. There are 3 types of containers:

- *glotzerlab*, these containers run the molecular dynamical simulations
- *head*, this container is responsible for creating new simulations, handing out simulations to the *glotzerlab* containers and writing to the database
- *database*, this container holds data about the structures

The containers communicate between each other on the default docker networks and Python sockets.

Exploring the parameter space of rigid building blocks

To see if we can get further from our original concept of binary charged systems, we considered several rigid body configurations and ran MD simulations to explore their behaviour. Some examples are illustrated below, with their respective MD trajectories:

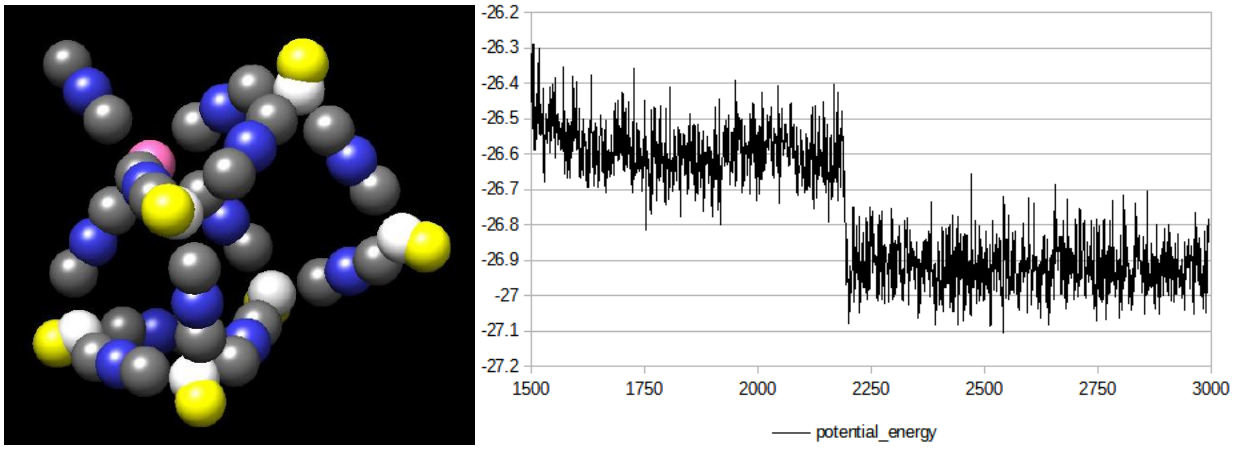


Figure 2. Assembly intermediate of a system preferring face-sharing polytetrahedral arrangement

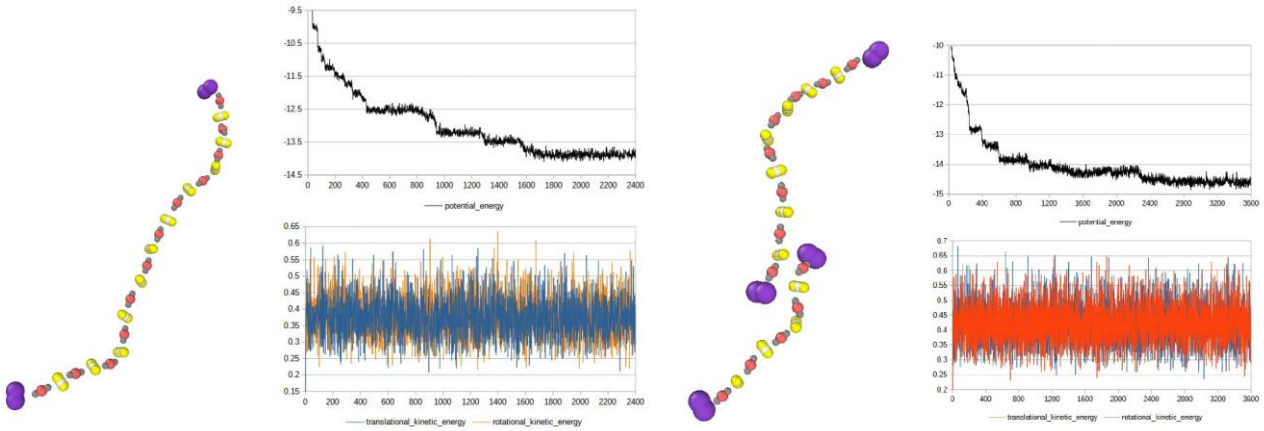


Figure 3. Capped strings which tend to form dimers if the number of caps is increased

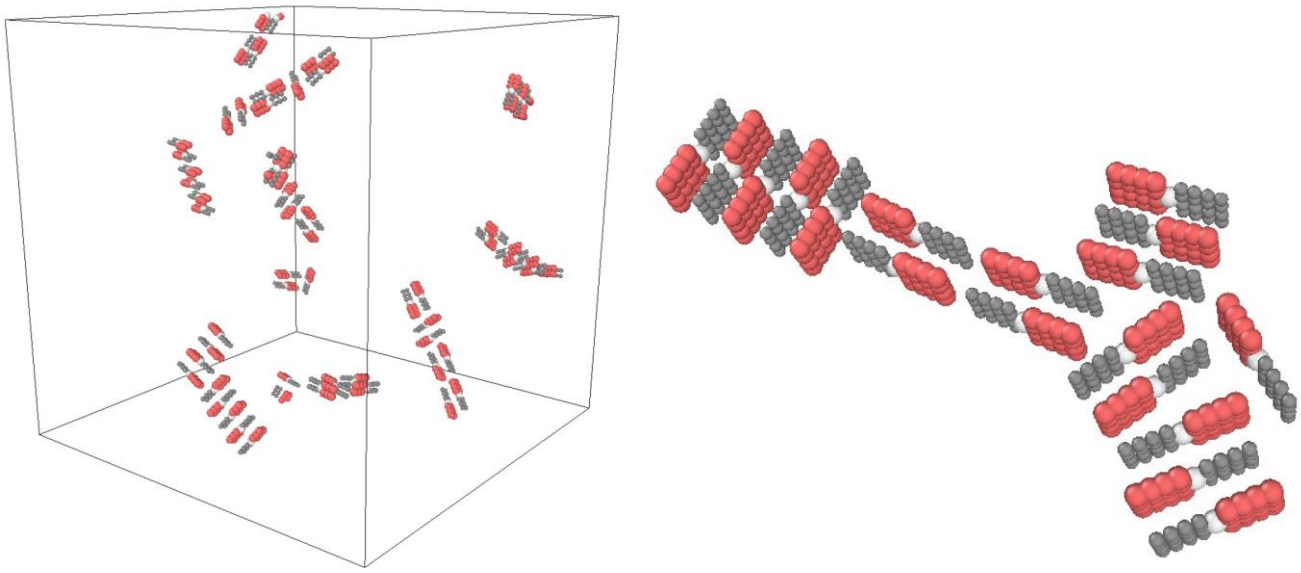


Figure 4. Lennard-Jones interactions with anisotropic plate-like excluded volume areas, having no charges in the system

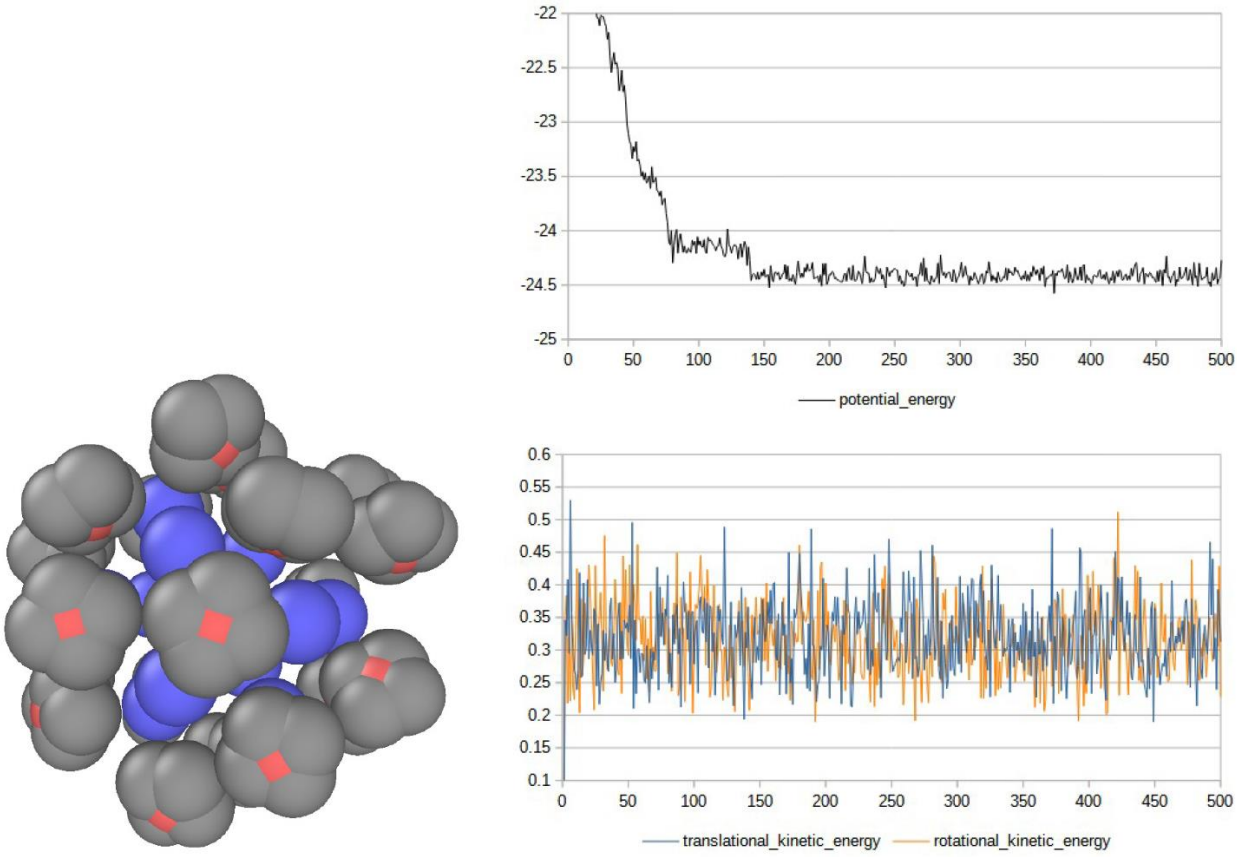


Figure 5. Icosahedral charged particle (+20) with 20 planar counterions

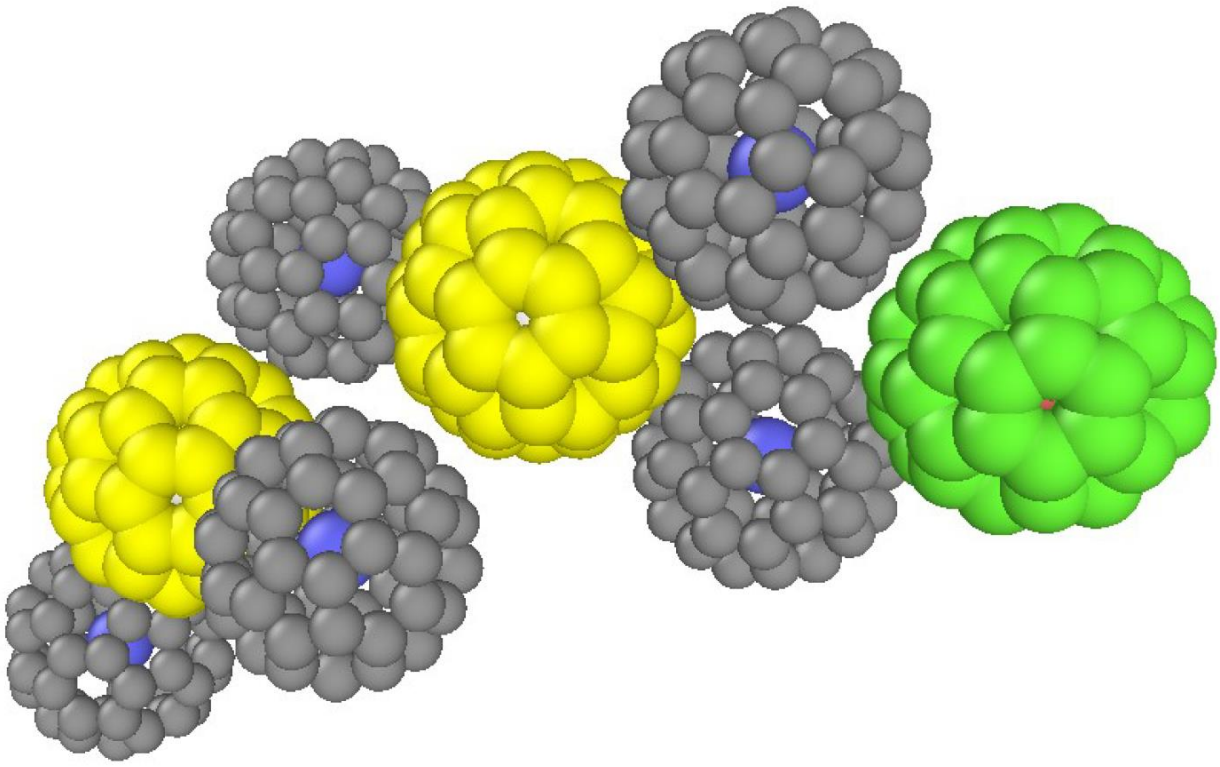


Figure 6. Icosahedral charged particles with various centre charges

The minimal model for a rotating colloidal motor

We found that in order to have self-assembling behaviour of a cluster which can then be capable of a rotational motion easily distinguishable during MD runs, we need to create artificial traps that act on at least two particles so that one axis gets fixed into a position in space, and this will become the axis of rotation. The system contains 3 types of particles: a central charged planar rigid body which will act as an axis (rotation around two sites, one of which is charged +6), two linear rigid bodies with a central charge of +4 and two apex sites with excluded volume interaction, and 7 'ligand' particles (linear rigid bodies with the two apex sites charged -1). If we put these building blocks in a box, they will readily self-assemble into an asymmetric triangle-shaped unit which attaches to the planar rigid body in a tilted manner, like the blade of a fan. The next obvious step was to see how the thermal energy can induce rotatory motion, therefore inert solvent molecules had to be added to the system. For better visualisation, the two axial particles get fixed to a region of the box by using three perpendicular planes that interact only with these particles (basic Lennard-Jones interaction).

3. Adapting the model for explicit solvent

Clearly, one cannot exploit directional rotatory motion using collisions of a blade with solvent molecules undergoing Brownian motion (see also Maxwell's demon). However, we found that starting the simulation far from equilibrium can induce directional rotatory motion, which will obviously turn into rotations in either directions once equilibrium has been reached. The plane perpendicular to the z axis, interacting with one site

of the ‘M’ particle also interacts with the solvent particles (excluded volume, repulsive term of the LJ potential). This plane, together with another one at the bottom of the box is designed to keep the solvent particles on one side of the box so that eventually a pressure difference can be simulated.

Our minimal model building blocks readily self-assembled into the desired asymmetric fan blade structure even in the presence of solvent particles which interact with the rigid body sites using short-range excluded volume interactions. On low temperatures, the self-assembled blade began rotating.

4. Exploring different energy transfer methods to colloidal motors

We are aware of experiments in vacuum chambers where a levitating nonspherical particle was capable of directional rotation due to an anisotropic thermal gradient. In our case, we tried to replicate a similar behaviour by using two different thermostats, a low-temperature thermostat for the rotor, and a higher temperature thermostat for the solvent. However, as the thermostats work by simply rescaling the velocities in simulations, with this approach it is not possible to create an anisotropic temperature gradient and therefore the simulation cannot produce directional rotation. However, we found out that by lowering the temperature of the rotor, the rotation is greatly enhanced, but eventually clockwise and counterclockwise rotations almost cancel out during long simulations.

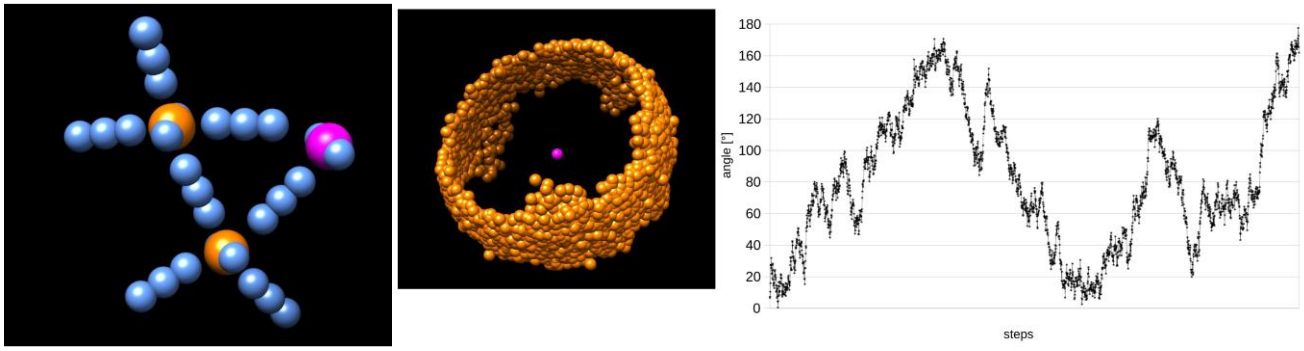


Figure 6. A basic rotor model and the points in space occupied by the rotor vertices during a simulation. The angle variation between a vertex and the rotation axis is also plotted.

A top view of a long simulation of the self-assembled rotor in explicit solvent can be accessed at https://youtu.be/t9GM_H9wXJo. That simulation contains two long, clockwise rotations (5 and 6 full rotations, respectively), while counterclockwise rotations take place on longer timescales but on shorter, more sequential distances. The system therefore has a likely asymmetric activation energy profile for the rotation, but that cannot be investigated with energy landscape methods due to the necessary presence of explicit solvent particles. The charges in that simulation were +12 for the two main ‘M’ particles, +18 for the ‘M’ particle within the axis, and -3 for the two charged sites on the ‘L’ particles.

We are currently exploring how to produce an anisotropic thermal field by running NVE simulations on equilibrated systems with explicit solvent, attached to a low-energy ‘heat sink’ composed of a crystalline configuration of cold particles. An alternative method is explored as well, where there is a pressure difference

between the two sides of the rotor, and therefore a net influx of solvent particles through a hole within the range of the rotor.

5. Dissemination

Due to the ongoing COVID-19 pandemic, no opportunities arose for conference participation in this field, therefore dissemination activities through conferences have been postponed for the next stage of the project.

Sfantu Gheorghe, on 10.12.2021

Dr Szilard Fejer