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Dynamical and structural self-organization : a study of friction, liquid-crystal nucleus growth, and supramolecular polymers through simple models

Huisman, B.A.H.

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7

The self-assembly of patchy particles

7.1 Introduction to self-assembly

Many of the nano-scale devices, as well as structures and materials found in nature consist of collections of molecules bound together by noncovalent interactions. While some of these supramolecular structures are carefully put together by complex mechanisms involving for example templates or chaperons, an important part assembles without any external help. The challenge in supramolecular self-assembly is not only to understand how these molecules self-assemble into such very precise supramolecular structures, but ultimately also learn how to design molecular building blocks in such a way that they self-assemble into useful novel materials and devices.

Because of the noncovalent nature of supramolecular interactions the intermolecular bonds are often weak enough to break at biological conditions, i.e. the bond energy is somewhere between 1 and 20 $k_B T$. This makes most of the supramolecular self-assembly reversible, and in that case there is a thermodynamic equilibrium between the self-assembled structure, the monomeric building blocks, and sometimes intermediate or wrongly assembled structures. The energy of many of these intermolecular interactions depends on outside factors such as the salt-concentration or the pH of the solvent, and the fact that the stability of the final structure can be tuned by these outside structures, makes self-assembly very flexible. However, the final structure must also be robust, i.e. the desired outcome must be by far the most stable structure, for self-assembly to be an effective tool for building on the nano-scale.

A designer of molecular building blocks has a large set of interactions he can use, and here I will only mention a few. Ring structures, such as aromatic rings, tend to stack because of the interaction between their π -orbitals, an interaction known as π - π stacking. Depending on the pH of the solvent, or its salt concentration, parts of the molecule may be charged, causing repulsion or attraction based simply on Coulomb's law of electrostatics. Furthermore, molecules can interact via series of intermolecular hydrogen bonds, where the hydrogen donors and acceptors are often ordered in such a way that the interaction site has a lock-and-key like specificity and a higher binding

energy. Some parts of the molecular building blocks may have a different solubility in the solvent than others. In the case of water as a solvent, the difference between the hydrophobic and the hydrophilic parts of the molecules creates an effective attraction between parts with a similar solubility, and an effective repulsion between dissimilar ones. Also, molecules have an excluded volume, which is the result of the electron shell repulsion between atoms at close distances.

Molecules that self-assemble often have a large molecular weight, and to study the thermodynamic equilibrium between the final self-assembled structure and its individual building blocks by means of e.g. Monte Carlo simulations, we need to simulate a large number of building blocks at the same time. If we wish to do this with full atomic detail we not only have to describe the atoms of all the molecular building blocks, but also that of the solvent molecules, which outnumber the building blocks by many orders of magnitude at low building block density. At the moment, this is computationally intractable for all but the simplest building blocks and solvents. Fortunately, when atomic detail is not required or too expensive, we can use coarse grained methods that lump multiple, functionally similar atoms of a molecule into a single (often spherical) bead with approximately the same physical characteristics.

7.2 Patchy particles

Geometrically, the building blocks of self-assembly can be viewed as excluded volumes, where the specific attraction and repulsion can be regarded as patches of interaction, distributed over the excluded volume of the molecule, mainly at its surface. Attractive patches represent for example series of hydrogen bonds, oppositely charged parts, ring-structures, or hydrophobic parts, while repulsive patches represent hydrophilic parts or equally charged parts. This defines the patchy particle, a geometrical object dressed with specifically interacting patches, that I will use as a coarse grained model to study self-assembly.

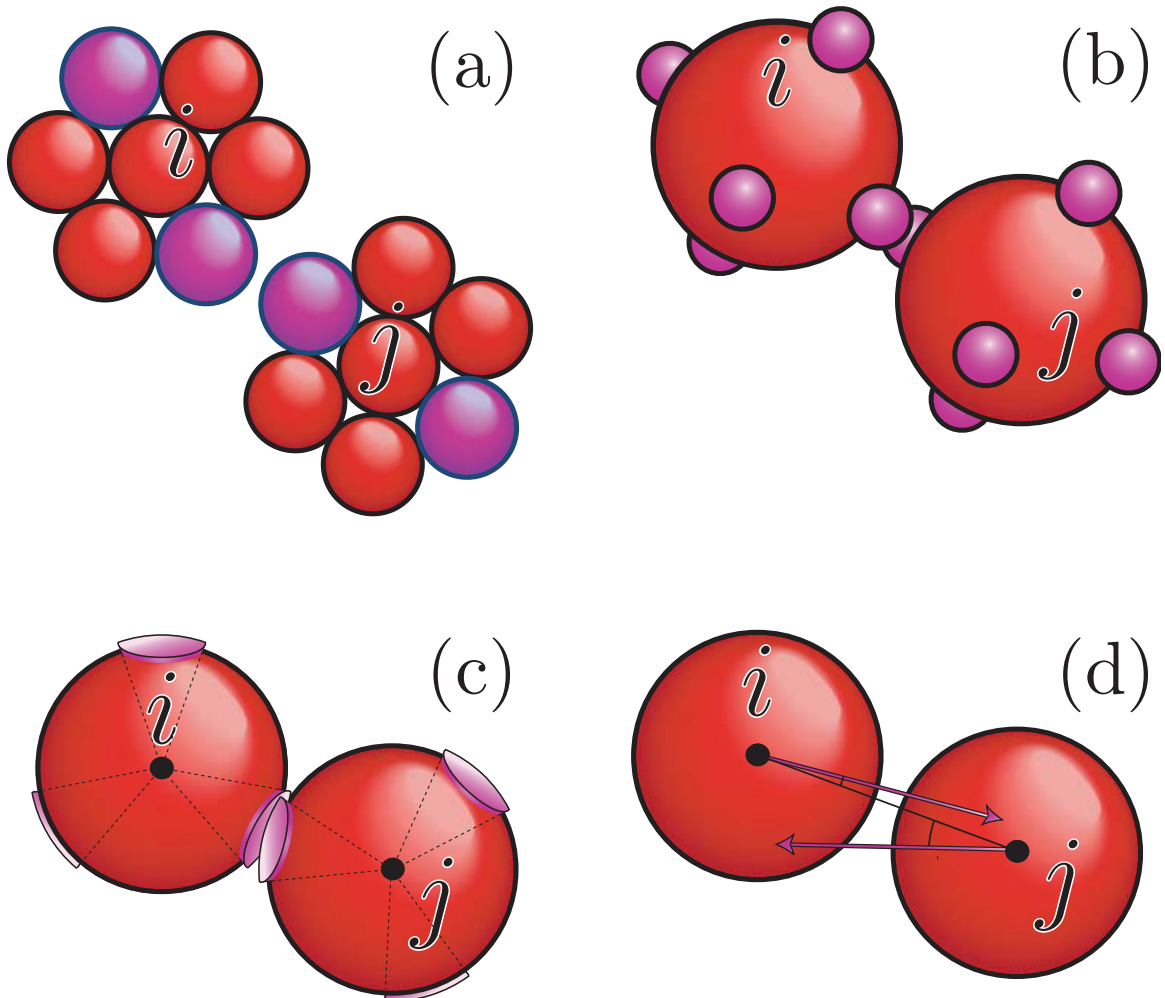


Figure 7.1: Four ways of creating a patchy particle. Red spheres represent beads which are hard, impenetrable volumes. Purple depicts an attractive patch. (a) Rigid clusters of hard sphere beads, where a few beads also have a supplementary attractive part. (b) Square well patchy particles: hard sphere dressed on the surface with spherical square well potentials. For any overlap of the purple volumes, each particle gains an energy $\epsilon/2$. (c) Sticky spheres: hard spheres with cones of interaction. The cone originates at the particle center. For any overlap of the purple cones, the particles gain an energy $\epsilon/2$. (d) Smoothly varying, directionally dependent patches. Patches originate from the center and have a maximum attraction when their directions (depicted by arrows) are aligned along the inter-particle vector. Attraction diminishes when the patches become less aligned.

As a first approximation one usually starts with a spherical volume. In some cases, e.g. for self-assembling globular proteins this is a reasonable approximation. There are several ways of modeling the interacting patches, illustrated in Fig. 7.1, and one can even combine them on a single patchy particle

- One can build a basic shape formed by several smaller spheres (Fig. 7.1(a)), and assign different potentials to some of the spheres at the surface[1]. This basic shape is made of hard spheres, i.e. spheres with a potential

$$V_{\text{HS}} = \begin{cases} 0 & r > R_{\text{HS}} \\ \infty & r \leq R_{\text{HS}} \end{cases} \quad (7.1)$$

where r is the distance between two spheres, and R_{HS} is the hard-sphere radius. Then, at the specific positions at the surface of the basic shape, a hard sphere is supplemented by a patch, a spherically symmetric attractive or repulsive potential. This approach has the advantage that one can make a range of base shapes, and that one only needs spherically symmetric potentials. The disadvantage is that you need many particles to describe a single molecule.

- The square well patchy particle (Fig. 7.1(b)) consists of a hard sphere, with smaller spheres, with the origin on the surface of the larger sphere[2; 3]. The smaller spheres interact via a square well potential

$$V_{\text{SW}} = \begin{cases} 0 & r > R_{\text{SW}} \\ -\epsilon & r \leq R_{\text{SW}} \end{cases}, \quad (7.2)$$

where ϵ is the energy gain (or loss in the case of a repulsive patch) of making a bond between patches, and $R_{\text{SW}} \ll R_{\text{HS}}$ is the square well radius. This is a very useful model, as it has only a few, very well defined parameters, i.e. the number and position of the patches, the ratio between the hard-sphere radius and the square well radius, and the energy of a bond.

- The sticky patchy sphere (Fig. 7.1(c)) consists again of a hard sphere base, but instead of a spherical square well potential at the surface of the sphere, this has a conical square well potential[4]. The apex of the cone is positioned at the center of the hard sphere, and the central axis of the cone pierces the surface of the hard sphere at a fixed position. If patches on different molecules overlap the molecules gain an energy ϵ . By changing the apex-angle, and the amount the cone extends beyond the hard sphere, one can change the patch size.
- Real interactions are never on-off like the square well potential. A smoother potential, such as the Lennard-Jones potential, can be used as a more realistic approximation of the true interaction potential[5]. In this way one can extend the square-well patchy particle, by placing a spherically symmetric, attractive potential on the surface of a hard sphere, or one can extend the sticky patch

potential, by placing a spherically symmetric potential at the center of the hard sphere, and modifying it such that it attracts maximally when the patch-directions are aligned perfectly along the inter-particle vector (Fig. 7.1(d)). A smoother potential is more realistic, as it allows for a temperature dependent average bonding energy. Furthermore with a smooth angular potential one can tune the flexibility of a bond, which is useful to describe for example semi-flexible polymers.

The structures that can be formed by self-assembly fall into two categories, open or closed. The structures are closed if they are limited in size, because additional interactions are geometrically impossible. Virus capsids[6; 7], rings[8] and vesicles[9] all fall into this category. The simplest form of closed self-assembly is a dimer, created by a patchy particle with only one attractive patch, allowing only one interaction. Open self-assembly is found in bundles[10; 11], in photonic crystals[12] and in open membrane sheets[13], and its simplest form is linear supramolecular polymerization[2]. The simplest model for linear supramolecular polymerization is a spherical bead with two diametrically opposed, attractive patches on each side of the bead. The length of the polymers they form is not fixed, nor geometrically limited. The supramolecular polymers themselves can sometimes aggregate into bundles.

The equilibrium polymer length distribution of spherical beads with two diametrically opposed, square well patchy particles has already been solved analytically, and recently these theoretical predictions have been confirmed by numerical simulations[2]. However, the theoretical predictions for more realistic, smoothly varying patchy particles have not been tested previously. Also, the bundling of these supramolecular polymers by sideways interactions of the constituent molecules has never been observed computationally, nor can it be described by polymerization theory.

In chapter 8 I will study this simplest form of open self-assembly, and the subsequent bundling, of a smoothly varying patchy particle that forms semi-flexible polymers. The size of the patch determines not only the polymer flexibility, but also the polymer length distribution at a certain temperature. I show that the aggregation at low temperatures and densities can be described by the simple theory of the ideal free association (IFA) model, and that the more involved Wertheim Thermodynamic Perturbation Theory predicts the extend of polymerization without any fitting parameters, even at higher temperatures. In this model, above a certain patch-size, a patch also interacts sideways with molecules from other polymers, and I show that this attraction between polymers causes a bundling transition. I define a simple thermodynamic model of polymer sublimation to create a qualitative phase diagram between monomers, polymers and bundles. In Appendix 8.A I derive the polymer length distribution that results from the IFA-model, and calculate the chemical potential of a particle in a polymer gas. Then, in Appendix 8.B I equate this chemical potential to the chemical potential of a particle in an Einstein crystal, to derive the polymer sublimation line between an ideal gas of polymers and an Einstein crystal. In Appendix 8.C I show how the bending rigidity of a polymer chain can be derived from

the patch potential, and finally, in Appendix 8.D I show how quaternions can be used to perform rigid particle rotations in Monte-Carlo simulations.

7.3 References

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