



## Dynamic self assembly of confined active nanoparticles

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### ABSTRACT

We report the dynamic self-assembly of chemically propelled nanoscale building blocks (NBBs) under confinement using reactive molecular dynamics simulations. The NBBs are hollow rectangles with one side open (tail) to expose the catalysts inside to the fuel environment. Adjacent NBBs can self assembly into tail–tail or tail–head (the side opposite to the tail) pairs. It was found that chemical propulsion forces unlock many tail–tail pairs but not tail–head pairs. Although the distributions of both tail–tail and tail–head pairs are orientation-dependent with respect to the confining wall, the effect of chemistry seems to be orientation-independent.

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As nature's preferred way to produce its creations, self-assembly refers to the autonomous process in which individual components organize into ordered patterns or structures [1]. This procedure can occur at multiple scales and only depends on the interactions among the components without human intervention [2–4]. Self-assembly offers a practical fabrication method from a bottom-up approach and becomes one of the most active research areas across different disciplines. Various building blocks and synthesis techniques have been explored, for instance, the synthesis of colloidal crystals by the template-directed colloidal crystallization process [5] and the synthesis of nanofibers via pH-induced self-assembly [6]. These works focus on the static self-assembly in which the systems are thermally driven towards a thermal equilibrium state [1]. However, most self-assembly phenomena in nature, such as the swarm of flocks and fish schooling, are dynamic self-assembly (DySA) processes which involve dissipative forces to drive the system to a non-equilibrium steady state [1]. Man-made systems involving various driving forces and different dimensions have been studied to mimic natural dynamic self-assembly processes. Among these research activities, the self-propelled objects which are inspired by the molecular motors in nature have been used as building blocks. The self-propelled plates designed by Whitesides et al. are 1–2 mm in thickness and 9 mm in diameter partially covered by platinum, which can be driven by the catalytic decomposition of hydrogen peroxide [7]. With the edges of these plates patterned with hydrophobic and hydrophilic regions, capillary interactions result in the self-assembly between these objects causing both heterochiral and homochiral dimers to be formed. In a more recent work [8], the surface tension from the dissolution of camphor drives these camphor boats (1 mm in diameter and

500  $\mu\text{m}$  in thickness) to form ordered structures. Ebbens et al. [9] studied the self-assembly behavior of the chemically fueled Janus colloidal beads which are 2  $\mu\text{m}$  in diameter. They observed that several types of aggregates containing two of these Janus particles formed in the system and performed different trajectories depending on the relative orientation of these two Janus particles. Sen et al. investigated the schooling behavior of the light-powered autonomous micromotors system made of micrometer-sized silver chloride particles [10]. As seen from above, due to fabrication and detection limitations, experimental investigations on DySA are so far limited to micron-sized or larger particles.

Computer simulation is a powerful tool to investigate phenomena at the nanoscale and has been used to design building blocks and provide important insights to various self-assembly systems. For example, lattice Monte Carlo simulations have been used to study the self-assembly of functionalized inorganic nanoscale building blocks with recognitive biomolecule linkers [11]. Brownian dynamics simulations reveal that anisotropic structures can form as a result of active packing of microspheres within confined microchannels driven by fluid flow [12]. A coarse-grain model for amphiphilic diblock copolymers was developed by Srinivas et al. to probe the self-assembly of polymersome membranes system driven by the hydrophobic interaction of polyethylene segments with water [13]. Coarse-graining simulations [14] typically used in lipid membrane systems [15,16] are also used in the study of self-folding behavior of multilayer graphene sheets [17], the self-assembly of lipoprotein particles from lipids and proteins [18] and the study in amyloid nanofibrils system [19]. Cheng et al. used the molecular dynamics simulation method to study the self-assembly behavior of the wedge shaped monomers with bonding sites [20]. They observed the formation of the helical microtubules of these monomers. Golestanian et al. [21] used an effective rigid body model to investigate the dynamic collective behaviors of an array of interacting microfluidic rotors via hydrodynamic forces,

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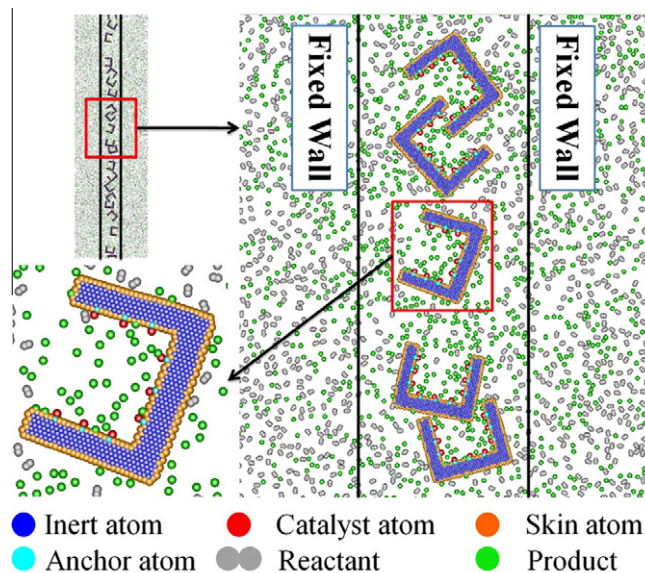
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which showed various dynamical behaviors including the phase ordering and self-proliferating spiral waves. D'Orsogna et al. modeled the self-propelling particles via superimposing a fixed driving force to study the stability and morphology of the particle assembly as a function of their two-body interactions [22]. However, these computational studies either focused on the static self-assembly or focused on dynamic self-assembly with non-chemical driving forces. There are few computational studies looking into the dynamic self-assembly system with nanoscale building blocks which are driven by chemical propulsion forces. For instance, Thakur et al. investigated the collective behavior of self-propelled dimer motors using a hybrid simulation method [23,24].

In this Letter, reactive molecular dynamic simulations are utilized to study the dynamic self-assembly behavior of the chemically propelled nanoscale building blocks (NBBs). Particularly, we wish to investigate to what extent the dissipative chemical force can affect the assembly behaviors of NBBs. The NBBs used here are hollow rectangles with one side open, in order to expose the catalysts inside to the fuel environment. It has been demonstrated that these NBBs exhibit self-propelled motion driven by dissipative chemical forces [25]. We choose to study the simplest self-assembly system, which is composed of 20 self-propelled NBBs confined inside a channel. By turning on and off the chemistry, the role played by the dissipative chemical force on the self-assembly behaviors of the NBBs can be elucidated. Two specific configurations of NBB pairs were observed to form due to their unique structure. By defining the open side of the NBB as the tail and the opposite side as the head, we found that the number of tail–tail (TT) pairs decreases by  $27 \pm 15\%$  overall due to dissipative chemistry. On the other hand, the number of tail–head (TH) interlocking pairs remains the same: a  $6 \pm 20\%$  change with chemistry turned on. Although the distributions of both TT and TH pairs are orientation-dependent with respect to the confining wall, the effect of chemistry seems to be orientation-independent. This Letter sheds lights on how to tune the local packing of NBBs by means of dissipative chemical forces.

We carried out reactive molecular dynamics simulations to study DySA of NBBs. We will use  $\sigma$ ,  $\tau$ ,  $\varepsilon$  as the reduced length, time and energy units. They are roughly the bond length, 0.16 times the vibration period and 0.415 times the bond strength of the diatomic fuel molecules, respectively. The simulation system is constructed as shown in Figure 1. Twenty of the rectangle-shaped autonomous catalytic NBBs [25] are randomly placed in the simulation box with a dimension of  $300\sigma$  by  $1000\sigma$ . The individual NBB is in rectangular shape with a dimension of  $36.4\sigma$  by  $29.6\sigma$ . If the atomic spacing  $\sigma$  can be estimated to be around 0.3 nm, then the NBB is about 10 nm in size. The inner wall of the NBB is composed of 437 inert (I) atoms and covered by 175 skin (S) atoms. The skin layer prevents attraction forces between the NBBs. These atoms are close packed with an atomic spacing of  $1\sigma$ . Nine anchor (A) atoms, which are used to attach 9 catalyst (C) atoms, are embedded in the skin layer. The interatomic distance between the catalysts is  $6\sigma$ . The rest of the simulation box is filled with 10922  $F_2$  molecules as reactants, each with two fuel (F) atoms. The distance between two F atoms in  $F_2$  molecules is about  $0.97\sigma$ . In addition, non-catalytic NBBs without catalyst atoms, which are otherwise identical to catalytic NBBs, are also constructed for comparison purposes. Six independent simulations were carried out for both the catalytic systems (with catalytic NBBs) and the control system (with non-catalytic NBBs) to reduce fluctuations in measurements.

The force field used to describe the interaction between the chemical components in the simulation system is modeled by the reactive state summation (RSS) potential scheme [25–28]. The essential idea of the RSS potential scheme is to model each individual reactive state by a nonreactive force field. The final reactive force field is then obtained from the weighted summation of



**Figure 1.** Illustration of the entire simulation system (top-left pane), zoomed-in view showing a TT pair on the top and a TH pair on the bottom (right pane) and a further zoomed-in view of a single NBB (bottom-right pane). C atoms, I atoms, A atoms and S atoms are red, blue, cyan and orange, respectively. The diatomic reactant molecules  $F_2$  and the monatomic product F are grey and green, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

all nonreactive force fields. Compared with other high-fidelity reactive force fields including the REBO potential [29,30] and ReaxFF potential [31,32], RSS potential is not intended to describe specific chemical reactions with high accuracy. Instead, RSS potential aims to describe generic chemical reaction in a minimalist's approach. The advantages of RSS potential include short development time for formulation and parameterization, and moderate computational demand for simulations.

The chemical reaction utilized in the system is a catalytic exothermic decomposition of a diatomic molecule  $F_2$  into two F atoms:



Note that the presence of a catalyst will significantly lower the reaction barrier for the above decomposition reaction [25]. The formulation and parameterization of the force fields can be found in Ref. [25] and the Supplemental material Section A.

Both the catalytic system and control system are subjected to identical simulation conditions detailed as follows. In order to obtain a steady state with constant temperature and constant chemical composition in the system, two operations are applied in the simulation. First, the F atoms are coupled to a Nose–Hoover thermostat [33,34] to avoid the temperature rise induced by the exothermic chemical reactions. The temperature is set to be  $0.09\varepsilon/k$  ( $k$  is the Boltzmann constant). Other atoms constituting the NBBs (i.e. the inert atoms, skin atoms, anchor atoms and catalyst atoms) do not couple to the thermostat. Second, a Monte Carlo (MC) operation of product-to-reactant conversion is introduced every  $10\tau$  to achieve constant chemical composition in the system [25]. In addition, the NBBs are subjected to confinement via two reflective walls along the Y direction. The reactants and products have no interaction with the walls so that these molecules can diffuse across freely. Initially, those two walls were placed at the simulation box boundaries with randomly distributed NBBs. The confined NBB-chain were formed by moving both walls with a speed of  $0.005\sigma/\tau$  towards the center of the simulation box until the wall-separation reaches  $60\sigma$  (Figure 1). This wall-separation is chosen

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