

# Dynamic Monte Carlo simulation of aggregation of nanoparticles in the presence of diblock copolymer

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## Abstract

The aggregation of hydrophobic nanoparticles in the presence of diblock copolymers is investigated using dynamic Monte Carlo simulation on a simple cubic lattice. One nanoparticle occupies one lattice site, one block copolymer ( $A_mB_m$ ) occupies  $2m$  sequentially linked sites with  $m$  segments of A and  $m$  segments of B, and solvents are represented by any unoccupied sites. All of them are self-avoiding and nearest-neighbor interactions are considered. A compact big aggregate, dispersed aggregates wrapped by polymer chains, and an ordered lamellar structure are obtained by varying the concentration of copolymer. The structures are seen to be controlled by competing forces between the interaction of copolymer with nanoparticles and the self-assembly of copolymer in solution. The critical concentration of copolymer needed to form the lamellar structure,  $C_{p,L}$ , decreases with the chain length. It is also found that  $C_{p,L}$  decreases roughly linearly with the concentration of nanoparticles  $C_n$ , which can be approximately expressed as  $C_{p,L} = 0.764 - 0.857C_n$  when  $m = 2$ . The simulation demonstrates that addition of diblock copolymer can effectively control the aggregation of nanoparticles and lead to the formation of a variety of nanostructures.

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**Keywords:** Diblock copolymer; Nanoparticle; Dynamic Monte Carlo simulation

## 1. Introduction

Biomaterials found in nature, such as seashell, pearl, and bones, exhibit a remarkably intricate structure with patterning organized from the nanoscale to the macroscale. These natural systems provide inspiration to synthetic chemists trying to produce biomimetic systems and/or nanostructured inorganic materials [1]. During the past decade, exploration of novel bioinspired strategies for self-assembling or surface-assembling molecules or colloids to generate materials with controlled morphologies is among the hottest research subjects [2]. Through selective adsorption on the inorganic building blocks and stabilization of building blocks at the nano- and mesoscales, block copolymers (or surfactants) have exhibited excellent abilities in controlling the morphology of various inorganic materials [3–5]. Inorganic lamellar nanofillers [6], manganese oxide nanotubes [7], urchin-like architecture and snowflake-like pattern

CuS [8], and ordered mesoporous materials [9] have been prepared by making use of appropriate block copolymers. It has been shown that not only the shape of primary nanocrystals, but also the complicated superstructure, can be effectively controlled by surfactant or block copolymers. However, despite a large number of data that show altered morphologies of crystals in the presence of block copolymers, mechanistic understanding of copolymer-controlled or -directed crystallization is still lacking.

Computer simulations can provide fundamental insight into block copolymer-controlled/directed crystallization and knowledge of important parameters governing the fabrication of inorganic particles with complex structures. So far, however, the reported simulations have mainly focused on the phase behavior of block copolymer/nanoparticle composites and the distribution of nanoparticles in the microdomains of lamellar block copolymers [10–14]. The Glotzer group [15,16] studied the ordering and packing of tethered nanoparticles of different shapes and observed a rich variety of structures. When we address the topic of the formation of inorganic crystals in solution, we know

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that such a crystallization process contains two major steps: nucleation and subsequent growth. During the nucleation the solute molecules disperse in the solvent and form aggregates (i.e., nuclei). However, these nuclei are unstable because of their high surface energies and grow subsequently after their formation to form stable structures. The growth of crystals is influenced by many factors; among these, the surface energy is an important factor. Not surprisingly, then, surfactants or surface-active polymers can strongly influence the crystallization process [17]. However, modeling the crystallization process in solution at the molecular level is very challenging. In the present study, we approximate the crystallization process by simple aggregation of insoluble nanoparticle, and use dynamic Monte Carlo simulations to study how the diblock copolymers affect the aggregation of nanoparticles. We find that the aggregation of nanoparticles strongly depends on the concentration of copolymer  $C_p$ . It changes from a big aggregate at low  $C_p$  to dispersed small aggregates at moderate  $C_p$ , and at high  $C_p$  it forms a lamellar structure. The simulation results may provide new information for better understanding the polymer-controlled/directed crystallization process at the molecular level.

The paper is organized as follows: in Section 2, we describe the lattice model and simulation method. In Section 3, we present the results and discussion of the aggregation of nanoparticles in the absence and in the presence of diblock copolymers. A brief conclusion is given in Section 4.

## 2. Model and simulation method

Dynamic Monte Carlo simulations are carried out in a cubic simulation box with size  $40 \times 40 \times 40$ . Periodic boundary conditions are used in all three dimensions. In this model, each nanoparticle is represented by one bead, and each  $A_m B_m$  chain is denoted by sequentially linked  $m$  segments of A and  $m$  segments of B. Here A and B represent hydrophilic and hydrophobic segments in the chain, respectively. The bond length of a polymer chain equals the lattice parameter and is set to be 1. Every bead occupies one lattice site and obeys self-avoiding.

Pairwise nearest-neighbor (NN) interaction is considered. The hydrophilic and hydrophobic properties of  $A_m B_m$  and the hydrophobic properties of nanoparticles, as well as the interaction between copolymer segments with nanoparticles, are specified by the interaction energy  $\varepsilon_{ij}$  for species  $i$  and  $j$  at NN sites. A typical series of interaction energies is

$$\varepsilon_{ij} = \begin{pmatrix} & \text{A} & \text{B} & \text{n} & \text{v} \\ \text{A} & 0 & 1.0 & 0.5 & -0.8 \\ \text{B} & 1.0 & 0 & -2.0 & 0 \\ \text{n} & 0.5 & -2.0 & -1.0 & 1.0 \\ \text{v} & -0.8 & 0 & 1.0 & 0 \end{pmatrix}, \quad (1)$$

where label n represents the nanoparticle and v represents the vacancy, which is modeled as solvent. The unit of  $\varepsilon_{ij}$  is  $k_B T$ , where  $k_B$  is the Boltzmann constant and  $T$  is the system temperature. A positive value of  $\varepsilon_{ij}$  means a repulsive interaction between two NN species, whereas a negative  $\varepsilon_{ij}$  means an attractive interaction. Thus according to the interaction specified

by Eq. (1), the nanoparticles are hydrophobic and they precipitate from the solution in the absence of block copolymer.  $\varepsilon_{AV}$  is attractive whereas  $\varepsilon_{AB}$  is repulsive, which ensures that the solvent is good to beads A and the immiscibility between beads A and B. Meanwhile nanoparticles and bead A are repulsive; however, nanoparticles and bead B are attractive. We intend to investigate general rules governing polymer-controlled aggregate formation; thus at present we will not map these energies to any particular system.

Concentrations of  $A_m B_m$ ,  $C_p$ , and nanoparticles,  $C_n$ , are defined as  $C_p = 2mN_p/V$  and  $C_n = N_n/V$ , respectively; here  $V$  is the total sites of the simulation box,  $N_p$  is the number of  $A_m B_m$  chains, and  $N_n$  is the number of nanoparticles. First,  $N_n$  nanoparticles and  $N_p$  polymer chains are randomly put in the box. The equilibrium state is achieved by a long period of dynamic Monte Carlo simulation. The simulation includes local movement of all the beads in the system. With this method, we randomly choose a bead and try to move it to one of its NN sites. If the bead belongs to a polymer chain, one of the three elementary motions, the end-segment, normal-segment, and  $90^\circ$  crankshaft motions, is tried. This kind of movement was discussed in detail by Gurler et al. [18] and extensively used in simulations in many aspects [19–21]. This trial move will be accepted if the following two conditions are satisfied: (1) self-avoidance is obeyed, which means it can only exchange with a vacancy; (2) the Boltzmann factor  $\exp(-\Delta E/k_B T)$  is greater than a random number uniformly distributed in the interval (0, 1), where  $\Delta E$  is the change in energy due to the trial move. The second criterion, i.e., the Metropolis criterion, ensures that the system obeys Boltzmann statistics at a specific temperature [22,23]. Each trial move is called a bead cycle;  $(2mN_p + N_n)$  bead cycles consist of one Monte Carlo step (MCS).

## 3. Results and discussion

### 3.1. Aggregation of nanoparticles in the absence of diblock copolymer

First, we investigate the aggregation of nanoparticles in the absence of copolymer. Since nanoparticles are modeled as hydrophobic, they favor staying with themselves to avoid solvent contact. Fig. 1 presents the equilibrium configurations obtained at the end of  $5 \times 10^6$  MCS, when the concentration of nanoparticles  $C_n$  is 0.1. Here the attractive energy between nanoparticles  $\varepsilon_{nn}$  is fixed at  $-1.0$ , while the repulsive energy between nanoparticle and solvent  $\varepsilon_{nv}$  is tunable. At  $\varepsilon_{nv} = 0$ , we observe nanoparticles randomly dispersed in the box (see Fig. 1a). When  $\varepsilon_{nv}$  increases to 1.0, a big compact aggregate is formed to avoid solvent contact (see Fig. 1b). However, with a further increase of  $\varepsilon_{nv}$  to 1.3, relatively small aggregates emerge, as shown in Fig. 1c. Here five or more nanoparticles contacting together are said to form an aggregate.

We have monitored the growth of the big aggregate at  $\varepsilon_{nn} = -1.0$  and  $\varepsilon_{nv} = 1.0$  as a function of simulation time. Initially, nanoparticles randomly disperse in the simulation box, where the simulation time is set as  $t = 0$ . When the simulation time reaches  $0.2 \times 10^6$  MCS, 21 aggregates are formed (see Fig. 2a).

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