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Molecular dynamics simulation of trimer self-assembly under shear☆

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ABSTRACT

The self-assembly of patchy trimer particles consisting of one attractive site and two repulsive sites is investigated with nonequilibrium molecular dynamics simulations in the presence of a velocity gradient, as would be produced by the application of a shear stress on the system. As shear is increased, globular-shaped micellar clusters increase in size and become more elongated. The globular clusters are also more stable at higher temperatures in the presence of shear than at equilibrium. These results help to increase our understanding of the effect of shear on self-assembly for a variety of applications.

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1. Introduction

While self-assembly is a promising route to fabricate new materials, practical length scales for fabrication are limited by the formation of defects [1]. In order to exploit self-assembly in technological applications, self-assembly may be directed by external fields, templates or specific chemical interactions in order to promote long-range ordering [2]. One example of directed self-assembly is the application of shear to block copolymer thin films, which has been shown to reduce defects and impose long-range order and alignment of the self-assembled structures as templates for nanolithography [3]. In addition, studies of *de novo* materials design of bioinspired silk fibers find that shear enhances alignment of polymers to improve the mechanical properties of the material [4,5]. Shear may also play a role in extrusion of self-assembled materials for industrial applications [6,7]. Self-assembly under shear has been the subject of many experimental, theoretical and computational studies. Experimental studies of shear-induced self-assembly include block copolymer thin films [3,8–12], worm-like micelles [13,14], carbon nanotubes [15] and colloidal crystals [16,17]. Theoretical and particle-based simulations are useful because they elucidate the mechanism of self-assembly under shear in block copolymers [18–24] and micelles [25,26]. Studies of aggregation under shear also provide insight into the ability of shear to enhance and hinder cluster formation [27,28].

While many of the previous studies of self-assembly under shear involved molecular systems, colloids with anisotropic shapes and interactions under shear are less well understood. Recent advances in colloidal synthesis have led to the creation of a variety of patchy colloids including rods, lock and key colloids, cubic colloids and colloidal clusters [29,30]. Nikoubashman et al. simulated the self-assembly of Janus particles under shear, and found that moderate shear enhances the aggregation of spherical clusters [31,32]. In addition, DeLaCruz-Araujo et al. simulated the aggregation of Janus particles under shear into micelles, wormlike clusters, vesicles and lamellae *via* Brownian dynamics [33]. In this work, we apply shear to trimers consisting of one attractive site and two repulsive sites. The trimers in this work are qualitatively similar to the recently synthesized patchy colloidal trimers consisting of one smooth and two rough beads, where the smooth beads possess an attractive interaction in the presence of depletant molecules in solution [34]. While these trimers have been the subject of thermodynamic studies [34–37], there have been no studies on the dynamics of these particles. In addition, the trimer particles geometrically resemble the Y-shape of monoclonal antibodies, and the study of these particles under shear may aid in understanding aggregation-driven increases in the viscosity of monoclonal antibody solutions, with an application of improving the delivery of biological pharmaceuticals [38,39]. Although the model in this work is not as short ranged as the protein and colloid systems described above, the model may be used to capture basic aspects of

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real systems.

In this work, molecular dynamics simulations of trimers consisting of one attractive site and two repulsive sites are performed in the presence of a velocity gradient, as would be produced by the application of shear stress. These trimers were shown previously [35] to self-assemble into globular-shaped clusters at equilibrium. We find that increasing the shear stabilizes larger clusters, and shear also leads to an increase in tubular structures.

This paper is organized as follows. In Section 2, the model for the trimer particles studied in this work is presented. The nonequilibrium molecular dynamics simulations are described in Section 3. In Section 4, the distribution of cluster sizes, the short range spatial order of the trimers in a cluster, and the potential energy of the system are examined. Finally, conclusions are provided in Section 5.

2. Model

The system consists of 500 rigid trimers. Each trimer is composed of an attractive site and two repulsive sites located at a distance L from the attractive site with bond angles of 60°, as shown in Fig. 1 and described in Ref. [35]. The attractive sites interact via a Lennard-Jones potential $\phi(r)$,

$$\phi(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right]. \quad (1)$$

The Lennard-Jones interaction is truncated at $r = 3\sigma$ in the shifted-force form [35]. The interaction between all other site pairs is through a repulsive interaction $\psi(r)$ of the Weeks-Chandler-Anderson form [40].

$$\psi(r) = \begin{cases} \phi(r) + \varepsilon & : r < 2^{1/6}\sigma \\ 0 & : r \geq 2^{1/6}\sigma \end{cases}. \quad (2)$$

Each of the particles in a trimer has mass m. The units of mass, length and energy used in the simulation have unit values so that $m = 1$, $\sigma = 1$ and $\varepsilon = 1$ with the result that the time unit $\tau = \sqrt{\varepsilon/m\sigma^2} = 1$ as well. The bond length L is set to 1 in these simulations. Unless noted otherwise, reduced units are reported. Note that the solvent is modeled via the effective interaction between the particles. Thus, the effective interaction amounts to a potential of mean force, as could be obtained by integrating over the solvent degrees of freedom. Accordingly, the model simulated here lacks explicit solvent and ignores some solvent mediated phenomena, such as hydrodynamic effects and buffeting due to random forces. Although hydrodynamics can influence dynamical properties in non-equilibrium self-assembly processes [41], implicit solvent simulations allow for the simulation of larger system sizes [42] and have been shown to possess similar self-assembled structural properties as explicit solvent simulations [41].

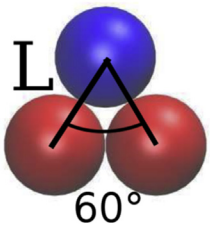

Fig. 1. The trimer model investigated in this work is illustrated using the Visual Molecular Dynamics program [43]. The blue site is attracted to other blue sites. All other pair interactions are purely repulsive. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Methods

The system of 500 trimers was placed in a rigid cubic cell with cell edge of 23.2 units so that the number density of the system was 0.04, or 6% packing fraction (see Fig. 2 for a visualization of this density). Periodic boundary conditions were applied in all three dimensions. The equations of motion were integrated using a Velocity-Verlet algorithm [44] modified [45] so that the orientation of the trimers was described using quaternions [46]. The time step for integration of the equations of motion was $\delta t = 0.01\tau$ for all cases unless otherwise indicated. This time step is sufficiently small, because it is expected to lead to a root-mean-squared fluctuation in energy approximately on the order of magnitude of 10^{-3} [47]. Simulations were performed in the canonical ensemble. The

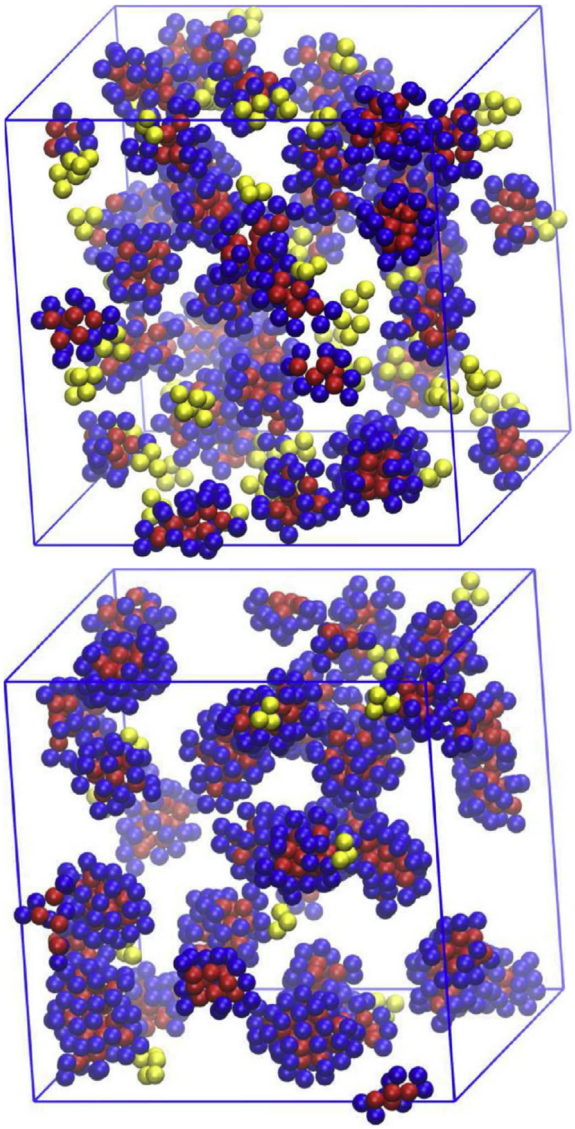

Fig. 2. The system of trimers as described in Section 3 with $T = 0.25$ and the periodic cell shown by the blue square for (top) no shear and (bottom) the highest exchange rate investigated (*i.e.*, high shear). Particles shown in yellow are in clusters of three or less other particles (see Appendix A for cluster definition). Otherwise, particles in clusters of size four or greater are colored red and blue. There are noticeably less yellow particles in the shear case than in the no shear case. Although shear was applied in the horizontal direction, the clusters have no apparent visual correlation with this shear direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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