Crystallization of star polymers under shear flow

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Controlling crystallization in soft colloidal systems represents a fundamental challenge for material design. Among soft colloids, star polymers are a favourite model system, showing a rich phase diagram, encompassing multiple crystal phases[1]. In this work, we numerically study the crystallization of star polymers induced by the presence of a shear flow. To this aim, star polymers are represented by a coarse-grained effective pair potential between their centers, introduced by Likos and coworkers[2]. The potential is athermal, but is controlled by the number of arms f, that is called the functionality of the stars, and by an effective diameter σ. To apply the shear deformation, we have used two Molecular Dynamics approaches: the first is based on SLLOD equations with Gaussian thermostat (MD-GAUSSIAN) and the second uses Dissipative Particle Dynamics thermostat (MD-DPD). The latter has the advantage to implicitly include the effect of the solvent, which is neglected in the former approach but that is important in order to compare with experimental results on colloidal systems. In both cases we employ Lees-Edwards periodic boundary conditions. We focus on star polymers with $f = 203$ in order to compare with experimental results obtained by oscillatory shear flow from Vlassopoulos and coworkers [3]. Our simulations show that a transition from fluid to solid occurs in both types of simulations. However, we find the occurrence of different crystal structures: while for MD-GAUSSIAN we observe a crystal characterized by a bcc-like structure, for MD-DPD the crystal is characterized by a fcc-like structure. Remarkably, also in the experiments a transition from fluid to fcc crystal is observed, suggesting that the use of MD-DPD is accurate to reproduce the experimental behavior. Most interestingly, we find that sometimes a two-step crystallization takes place from fluid to bcc and then to fcc, showing the occurrence of a crystal-crystal transition in the simulations, as shown in Fig. 1. Such crystal-crystal transition is also observed in the experiments. Upon shear cessation the crystals do not melt, suggesting that the use of shear can be usefully exploited in order to control the phase behavior of these systems. ACKNOWLEDGMENTS: JRF and EZ acknowledge support from ETN COLLDENSE (H2020-MCSA-ITN-2014, No. 642774)

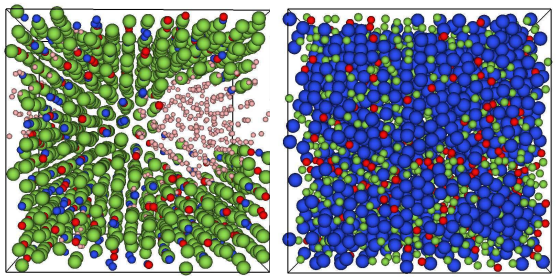

Figure 1: System state under shear by MD-DPD method to show as the structure changes in the solid-solid transition: liquid (pink), bcc(green), hcp(red) and fcc(blue) particles. A smaller radio is used to emphasize the predominant crystal structures *Left*: First step with bcc-like order; *Right*: Second step with fcc-like order.

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