Molecular simulations of organically modified clays. The cut-sphere model and electrostatics.

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Polymer-clay nano-composites include a wide range of materials with applications in, for example, the automotive, microelectronics and plastics industries. These compounds exhibit remarkable improvements in thermal and mechanical properties when compared to pure polymer based materials. A key issue for their synthesis concerns the dispersion of clay particles in monomer solvents. The monomer solvent is subsequently polymerised in-situ to create the desired solid composite material.

Here we present results of a preliminary simulation study aimed at modelling the phase behaviour of organically modified Laponite and Montmorillonite dispersed at high temperature in a monomer solvent. Taking hard cut-spheres as a primitive model for the clay particles and using Monte Carlo simulation methods, we studied the isotropic and nematic phases, including the isotropic-nematic transition (I-N), for aspect ratios $L/D<0.1$ (where L and D are the thickness and diameter respectively of the hard platelets). Our focus is on the nature of the transition and the structure of each phase, which can both be used to analyse experimental data of corresponding systems. We find that that the free energy barrier separating the isotropic and nematic phases increases exponentially with aspect ratio. For the thinnest particles ($L/D \leq 0.04$) the transition is very weak indeed, which could have consequences for experimental observation of each phase. Due to the weakness of the transition, and hence large fluctuations, the average nematic order parameter for the nematic phase at the transition decreases with the aspect ratio, being ~0.8 for $L/D=0.1$ and ~0.4 for $L/D=0.01$. The results for the nematic order parameter are in general agreement with other theoretical [Esztermann et al. Phys. Rev. E 73 (2006) 011409] and simulation [Piñeiro et al. Soft Matter 3 (2007) 768] studies although our work is the first to report the free energy barrier for the I-N transition. We also find that the structure of both phases depends strongly at close range on the aspect ratio.

The primitive model analysed above does not include any electrostatic contributions due to charged sites and counter-ions distributed over the clay platelet surface, whose effect is significant at ambient temperatures. We also present initial steps in the development of a model that does include these charge distributions, and some initial results that illustrate the importance of using detailed models.