Polymer-Grafted Nanoparticles as Patchy Colloids

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Spherical nanoparticles uniformly grafted with linear polymer chains behave as "nanoparticle amphiphiles" when the nanoparticle cores thermally interact differently with one another than with their polymer coronas [1]. In the sparse grafting limit, the corona cannot shield its core isotropically, suggesting an interesting analogy to patchy colloids [2]. The fluid phase behavior of patchy colloids, such as laponite clay [3], is known to exhibit a unique feature whereby the density difference between the high and low density phases collapses as the patchiness becomes more anisotropic, producing so-called "empty liquids" with arbitrarily low densities. We explore this analogy using grand canonical Monte Carlo simulations on a high-coordination number lattice, to reveal how the phase behavior of sparsely grafted, high-curvature particles can, in fact, be alternated between traditional and patchy behavior purely by tuning the corona's anisotropy. We observe self assembly in the high-density phase of the patchy systems into ordered structures reminiscent of the assembly observed with grafted nanoparticles in polymer matrices [1], while for all other cases, the high-density phase was disordered. In such cases, the fluid-phase behavior was found to behave in a qualitatively different fashion as the corona transitioned between the "mushroom" and the semi-dilute polymer brush regimes, consistent with a recent experimental study [4]. We found that simple scaling laws were sufficient to describe this behavior and clearly indicate the coincidence of a change in thermodynamic behavior and corona structure.

[1] P. Akcora, et al., Nature Materials, 8, 354—359 (2009).
[2] E. Bianchi, et al., Physical Review Letters, 97, 168301 (2006).
[3] B. Ruzicka, et al., Nature Materials, 10, 56—60 (2011).
[4] H. Koerner, et al., Macro Letters, 2, 607—676 (2013).