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Effective interactions between grafted nanoparticles in polymer melts: challenging high scale simulations, effect of entanglements and morphology of clusters

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The organization of grafted nanoparticles within a polymer matrix plays a crucial role in achieving mechanical reinforcement in nanocomposites. This process is complex due to various parameters including grafting density, the length of free and grafted chains, and the surface affinity between nanoparticles (NPs) and polymers. In this work, we systematically address how these parameters influence the effective potential of mean force (PMF) between two NPs embedded in an entangled polymer matrix. The PMF is calculated using an extended slip-spring model treating explicitly polymer grafted NPs in free polymer chains. While the PMFs converge in entangled and non-entangled cases at iso chain length averaging over all many configurations, we show that a significant potential dispersion emerges in entangled systems, likely related to the long relaxation time scale of entanglements between grafted chains. We propose to model this entanglement effect with potential ensembles. The obtained PMF ensemble allows to enhance the level of coarse-graining, enabling the simulation of larger systems and extended timescales through this implicit entangled polymer representation between NPs. First, we assess the quality of the effective PMF ensemble representation by comparing full-scale slip-spring simulations with explicit polymer matrix to that at the coarse-grained implicit polymer level with a 2-body PMF at a high filler volume fraction. We find that the structure of well-dispersed NP states, developing in the case of strong surface affinity and/or high grafting density, can be matched quite well by an effective 2-body PMF ensemble, whereas more discrepancies appear for the clustered NP systems, suggesting the necessity of incorporating many-body interactions. The NP phase diagram is then explored systematically at low filler volume fractions, reproducing the transition between percolated and well-dispersed states upon increasing grafting density. The resulting NP morphologies are discussed with respect to experimental observations reported in the literature.