EFFECT OF POLYMER-COLLOID INTERACTIONS ON POLYMER-MEDIATED FORCES, SELECTED STATIC AND DYNAMIC PROPERTIES OF POLYMER-NANOCOLLOID SYTEMS

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Effective interaction between colloids mediated by non-adsorbing and reversibly adsorbing polymers.

In order to study the effect of the polymer adsorption on the polymer-mediated (PM) interactions between nano-colloids, we have performed a comparative analysis of these interactions mediated by non-adsorbing and reversibly adsorbing excluded volume polymers by developing and making use of an analytic theory [1,2]. As a first application of this theory, we have calculated the potential of the depletion interactions acting between nano-colloids immersed in the bath of non-adsorbing polymers as a function of the separation H between colloids. Figure 1 shows the comparison of our theoretical findings with the results of Monte Carlo simulations of the depletion potential U in the protein limit where the colloid radius R is much smaller than the polymer gyration radius R_G. As is clearly seen from this Figure, the developed theory adequately describes the Monte Carlo simulation results [3] in the domain of polymer concentrations spanning across the dilute to dense regimes.
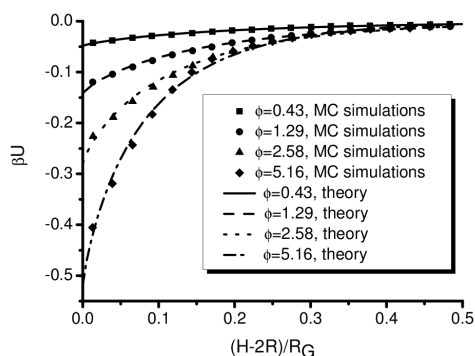

Figure 1. Comparison between theoretical results and Monte Carlo simulations [3] of the PM potential for several values of the polymer volume fraction ϕ and the colloid radius $R=0.1R_G$.

As a next step, we have calculated the potential of the polymer mediated interactions for the case of reversibly adsorbing polymers as a function of colloid radius R, separation H, polymer correlation length ξ, polymer volume fraction ϕ and the introduced absorbance α that quantifies the affinity of the colloid surface for polymers. The developed theory describes the limit of the weak adsorption where the correlation length ξ of the excluded volume polymer system is much smaller than the characteristic adsorption length (colloid absorbance) α. Similarly to the case of non-adsorbing polymers, the resulting expression for the PM potential U mediated by adsorbing polymers is shown to factorize into the product of the immersion free energies of the colloids and the correlation function of the uniform polymer system. A typical example of the calculation of U for several values of the reduced colloid radius R/ξ and $\xi/\alpha=0.1$ is shown in Figure 2.

Note that according to Figure 2, the dependence of the magnitude of the PM potential U on the colloid radius R for the case of adsorbing polymers shows just the opposite trend in comparison with the purely entropic depletion potential that increases with R. This difference stems from different dependencies of the colloids immersion energy W on its radius R for the above cases of non-adsorbing and adsorbing polymers. Specifically, in the case of non-adsorbing polymers W occurs to be proportional to the colloid surface $\sim R^2$. The dependence W(R) for the case of adsorbing polymers is much less pronounced, for that the main factor affecting the immersion energy in this case is the strength of the adsorption interactions. The above explained qualitative difference between the dependencies W(R) for adsorbing and non-adsorbing polymers results in the above mentioned quantitative difference in

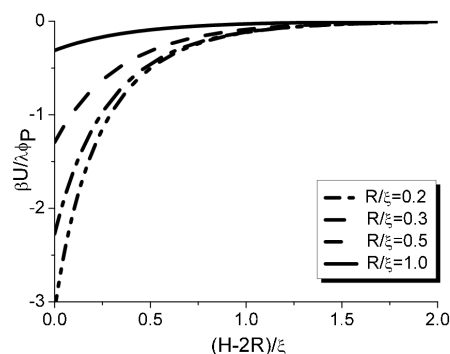the dependencies U(R) for the above two cases that can be elucidated from Figures 1 and 2.

Figure 2. Reduced PM potential for several values of the reduced colloid radius R/ξ and the selected value of the reciprocal adsorption length $\xi/\alpha=0.1$; $\lambda=\xi/R_G$.

Equation of state of the colloid-polymer-solvent system in the presence of adsorption interactions between polymers and colloids.

By making use of the obtained results for the potential of PM interactions mediated by adsorbing and non-adsorbing polymers, we have calculated the equation of state (EOS) of the nanocolloid-polymer-solvent system for the respective cases of polymer adsorption. For the case of non-adsorbing polymers, the equations of state shows non-trivial dependence on the polymer volume fraction that is overlooked by the previous theories. For the case of reversibly adsorbed polymers, the obtained EOS exhibits a complicated interplay between the purely entropic forces and the adsorption interactions that leads to different phase behavior of the colloid-polymer system in dependence on the colloid radius, affinity of the colloid surfaces for polymers, and the volume fractions of colloids and polymers in solution. As a main result of the described studies, we have identified the relative significance of the entropic interactions, physical adsorption and bridging of colloids by polymers for different domains of the above listed parameters.

Relaxation times of the colloid aggregation assisted by adsorbing and non-adsorbing polymers.

As a final stage of the reported work, we have calculated the relaxation time τ of the colloid aggregation for the case of dilute solution of colloids in polymer-solvent system. In line with the previous two stages, we have distinguished the cases of non-adsorbing and weakly adsorbing polymers. We have found that τ decreases with increasing the volume fraction of adsorbing polymers and increases with increasing the volume fraction of non-adsorbing polymers at fixed colloid radius R. The above difference in the behavior of τ as a function of the polymer volume fraction is attributed to different dependencies of the PM potential on the colloid radius and polymer volume fraction for the cases of adsorbing and non-adsorbing polymers.

Conclusions

In summary, we have comparatively investigated the effect of purely entropic and adsorption interactions between polymers and nano-colloids on the polymer mediated interaction among these colloids. We have used the obtained results in order to derive the equation of state of the colloid-polymer-solvent system for the respective cases of polymer adsorption. In addition, we have derived the characteristic times of the colloid aggregation in dependence of the strength of the polymer adsorption onto the nano-colloids. The obtained results are compared with the available Monte Carlo simulations.

References
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