Unusual Features of Depletion Interactions in Soft Polymer-Based Colloids Mixed with Linear Homopolymers

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We investigate the influence of the addition of polymer chains on the effective interaction between star polymers, as a model for the depletion potential in ultrasoft mixtures. The effects of size ratio and chain polymer concentration on the chain-modified star-star interactions at good (athermal) solvent conditions are investigated. For both hard sphere mixtures and colloid-nonadsorbing polymer mixtures the range of the depletion interaction increases with the size ratio. For the systems at hand, the range of the depletion potential is insensitive to the size of the depletant polymer. The physical origin of this and the associated effects, as well as a mapping of the mixtures onto a one-component system, are discusssed.

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The capability to tune the interactions between colloidal particles from short-range repulsions to short-range attractions has become a valuable tool for the study of fundamental and practical problems in soft matter physics. The question is of high relevance to recent and ongoing work on cluster formation and stability [1], dynamical arrest [2], and gelation [3]. In most cases, these interactions are effective in the sense that microscopic degrees of freedom have been averaged out through a coarse-graining procedure [4]. A typical example of that is the introduction of the depletion potential V_{dep}. In the scope of the coarse-grained approaches, the best known depletion model is that of Asakura and Oosawa (AO), in which both the range and strength of V_{dep} can be precisely tuned by varying the polymer-to-colloid size ratio and the polymer concentration [5,6]. By using this simplified, one-component description, many insights have been gained about the equilibrium phase behavior of colloid-polymer mixtures [7,8]. However, when interacting polymers are considered, the AO model breaks down as a result of the sensitivity of V_{dep} to variations in the direct interactions among the components of the system [9,10]. It is to be expected that a new range of possibilities emerges when the big hard colloids are replaced by soft ones; however, the AO model is still the paradigm serving as the guiding prototype in this context.

In recent years, the study of particles interacting via soft potentials, which are realized by, for example, micelles, star polymers, dendrimers, or microgel particles, has gained a lot of attention. In analogy with hard-core colloidal systems, the depletion mechanism has been also introduced to rationalize the effect of short-range attractions on suspensions of soft particles [11–13]. For example, in block copolymer micellar suspensions, depletion forces affect not only the intermicellar packing but also the intramicellar one, and they can also induce the disordering of ordered microstructures [14,15]. In multiarm star polymer solutions [16–18], osmotic forces due to the addition of small linear polymers lead to the formation of thermodynamically stable star clusters at the low star density regime, while at high star density they cause melting of the dense glassy state [19,20]. These findings provide physical mechanisms for tailoring the equilibrium and flow properties in a wide range of ultrasoft particle mixtures. From the theoretical point of view, they motivate us towards a better understanding of the depletion potential for such systems. In this Letter we consider the effective interaction between highly versatile models of soft colloids, i.e., star-polymers, resulting after the addition of small polymer chains by using coarse-grained representations of their mutual interactions [16,21–24].

In its simplest realization, the system of interest consists of $N_s = 2$ star polymers and N_c chains enclosed in a volume V, which define the partial number densities $\rho_s = N_s/V \to 0$ and $\rho_c = N_c/V$. The star-chain size ratio is given by $\xi = \sigma_c/\sigma_s$ where σ_i is the so-called corona diameter, which scales as $\sigma_i \simeq (4/3)R_g^{(i)}$ $(i = s, c)$, with $R_g^{(i)}$ the corresponding radius of gyration [21]. By choosing the center of the stars and the middle monomer of the chains as effective coordinates, the coarse-grained interactions between all components display a ultrasoft logarithmic dependence at short distances and crossover to exponentially decay at large ones. More explicitly, the effective interaction between two star-polymers whose centers are held at distance r apart reads as [16,17]:

$$\beta V_{ss}(r) = \frac{5}{18} f^{3/2} \times \begin{cases} -\ln\left(\frac{r}{\sigma_s}\right) + \frac{1}{1+\frac{\sqrt{f}}{2}} & r \leq \sigma_s \\ \frac{1}{1+\frac{\sqrt{f}}{2}}\left(\frac{\sigma_s}{r}\right)\exp\left[-\frac{\sqrt{f}}{2\sigma_s}(r-\sigma_s)\right] & r > \sigma_s \end{cases} \tag{1}$$

where f is the functionality (number of arms) of the stars and $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant and T the temperature. Similarly, the effective interaction between two chains is given by [25,26]

$$\beta V_{cc}(r) = \frac{5}{18} 2^{3/2} \begin{cases} -\ln(\frac{r}{\sigma_c}) + \frac{1}{2\tau^2\sigma_c^2} & r \leq \sigma_c \\ \frac{1}{2\tau^2\sigma_c^2} \exp[-\tau^2(r^2 - \sigma_c^2)] & r > \sigma_c \end{cases} \tag{2}$$

with $\tau\sigma_c = 1.03$, which guarantees the correct value of the second virial coefficient of a polymer solution. For the cross interaction between stars and chains we have [27]

$$\beta V_{sc}(r) = \begin{cases} -\Theta(f) \ln(\frac{r}{\sigma_{sc}}) + K & r \leq \sigma_{sc} \\ v_0 \int \varrho_s(\mathbf{r}') \varrho_c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' & r > \sigma_{sc} \end{cases} \tag{3}$$

where $\sigma_{sc} = \frac{1}{2}(\sigma_s + \sigma_c)$, $\Theta(f) = \frac{5}{36} \frac{1}{\sqrt{2}-1}[(f+2)^{3/2} - (f^{3/2} + 2^{3/2})]$ and v_0 is the excluded volume parameter. The latter one appears as a result of applying Flory-type arguments for the overlapping monomer density profiles $\varrho_i(r)$ $(i = s, c)$, which can be evaluated on the basis of the Daoud-Cotton blob model [25–28]. The constants K and v_0 are estimated by requiring continuity of both $V_{sc}(r)$ and its first derivative at $r = \sigma_{sc}$. The general scheme used to evaluate $V_{sc}(r)$ is consistent for arbitrary f and size ratio $\xi = \sigma_c/\sigma_s$, independently of the degrees of polymerization of the star and the chain; the only dependence on those comes implicitly through σ_s and σ_c.

We are interested in the effective interaction between star polymers immersed in a bath of smaller chains. From this perspective, the stars can be described by a renormalized, chain-modified effective potential $V_{ss}^{\mathrm{eff}}(r)$ in which the degrees of freedom of the chains have been traced out. The simplest way to achieve this mapping is to employ the inversion of the full, two-component solution for the star-star radial distribution function $g_{ss}(r)$ in the limit of low star density [29]. Once $g_{ss}(r)$ is known by solving the Ornstein-Zernike (OZ) equations with the Rogers-Young closure, the effective star-star potential can be calculated as $\beta V_{ss}^{\mathrm{eff}}(r) = -\ln[g_{ss}(r; f, \xi, \rho_s \to 0, \rho_c)]$. By construction, this chain-modified interaction potential leaves both the partial correlation function $g_{ss}(r)$ and the structure factor $S_{ss}(k)$ invariant.

In Fig. 1 some results for the effective star-star potential from the inversion procedure are displayed for different values of ξ. As expected, the increase in ρ_c reduces the range of repulsion and eventually leads to the emergence of an attractive well in $V_{ss}^{\mathrm{eff}}(r)$. It can be seen that, contrary to the AO case, the depth of attractive well behaves non-monotonically with the size of the chains: at high enough but equal chain density the well becomes deepest at the intermediate size ratio, while, at the same time, its minimum appears to be located roughly at the same position independently of ξ. This feature is also noticeable when we focus our attention to the induced depletion potential $V_{\mathrm{dep}}(r) = V_{ss}^{\mathrm{eff}}(r) - V_{ss}(r)$: for all conditions considered in Fig. 1, $V_{\mathrm{dep}}(r)$ displays the same qualitative behavior irrespective of the size and concentration of the depletant polymers. The range of $V_{\mathrm{dep}}(r)$, Δ_{dep}, changes very little with ξ, which is counterintuitive, as it would be normally expected that Δ_{dep} grows with the size ratio (and, in the case of the AO model, in a linear fashion).

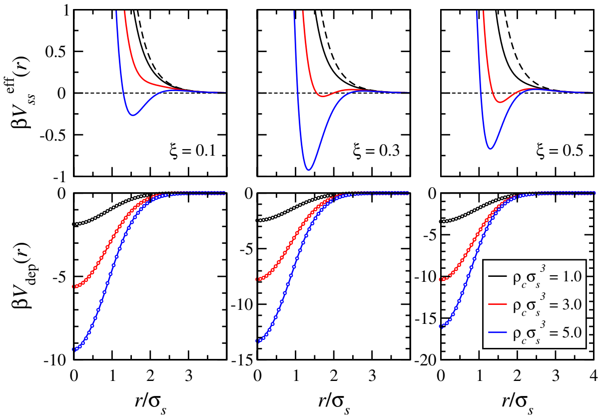

FIG. 1 (color online). Upper row: Chain-mediated effective star-star potential as obtained by inversion of the OZ equation with $f = 18$ for different size ratios and chain densities. The pure star-star potential $V_{ss}(r)$ is represented by the dashed lines. Bottom row: Corresponding depletion potentials are indicated by open symbols while the continuous lines result from fitting to Eq. (4).

To check the validity of these results we use as an alternative approach, the superposition approximation (SA) [30]. Here, the density profile of the chains induced by the presence of two stars at separation r is approximated by the product of the two chain-density profiles surrounding a single star polymer. The latter is proportional to the star-chain radial distribution function, $g_{sc}(r; f, \xi, \rho_s \to 0, \rho_c)$, also readily available from the solution of the OZ equations. In addition, standard NVT Monte Carlo (MC) simulations were performed on the coarse-grained two-component system, see Eqs. (1)–(3), by placing two stars in a reservoir of chains, and measuring the depletion force $F_{\mathrm{dep}}(r) = -\nabla V_{\mathrm{dep}}(r)$. A comparison of results from these three different approximations is shown in Fig. 2. The three methods yield quite good agreement and, as ρ_c and ξ increase, the SA leads to better agreement with the simulation data than the OZ inversion. This implies that the cross correlation between chains arising from their interaction $V_{cc}(r)$ is weak enough, so that we can still assume that the presence of a second star leads to an overall chain-density profile that is well approximated by the product of those originated from two isolated stars. Application of more sophisticated techniques based on a second-order expansion of a two-component density functional yields essentially identical results with those reported above.

To understand the physical origin of these unusual features, we look in detail at the chain-density profile, $\rho_c(r)$ around a single, fixed star, see Fig. 3. The depletion range can be estimated from there as $\Delta_{\mathrm{dep}} \cong 2\Lambda$, where Λ is the

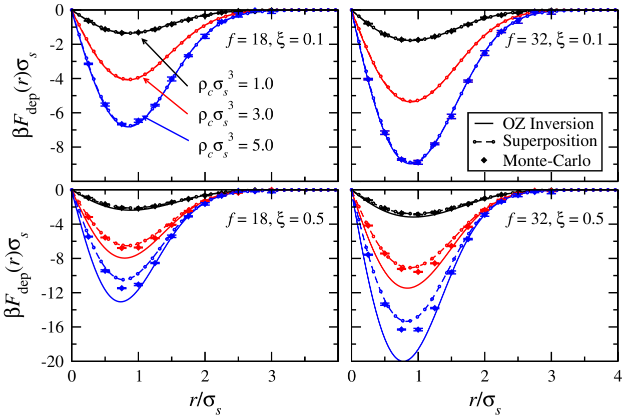

FIG. 2 (color online). Depletion force between two stars immersed in a bath of smaller chains at different functionalities, size ratios, and chain densities.

length scale at which $\rho_c(r)$ reaches its asymptotic, bulk value. To begin with, we consider $\rho_c(r)$ at the limit of very low chain density, which is proportional to the Boltzmann factor of the star-chain cross interaction, $\rho_c(r) \cong \rho_c \exp[-\beta V_{sc}(r)]$. At this limit, as ξ increases, the thickness of the depletion layer becomes only slightly larger and clearly *not* in proportionality to ξ. Thus, for the system at hand, Δ_{dep} is just slightly influenced by the size of the depletant polymer chain, even at the limit $\rho_c \to 0$. For the case $\xi = 0.1$ there is no significant change in $\rho_c(r)$, and therefore neither in the size of the depletion zone, as the chain number density ρ_c increases. Concomitantly, only the strength of $V_{\mathrm{dep}}(r)$ grows, as a consequence of the increase in the osmotic pressure $\Pi(\rho_c)$ of the chains. For larger ξ the size of the depletion zone decreases as ρ_c increases, as a consequence of the softness of the star: the chains access a region closer to the center of the star, due to the repulsive interactions with other chains. This penetrability of the star causes the shrinkage of the depletion layer around it and together with the stronger osmotic effects have as consequence a deeper and shorter-ranged depletion potential. Finally, since $V_{\mathrm{dep}}(r)$ itself depends on $V_{sc}(r)$ and $V_{cc}(r)$, but not directly on $V_{ss}(r)$, an increase of the functionality f at fixed size ratio ξ renders $V_{sc}(r)$ more repulsive and therefore the depletion zone around each star widens. This effect results in a larger Δ_{dep} and a deeper attraction, for higher functionality stars, see Fig. 2. Contrary to colloid-polymer mixtures, the range of the depletion potential is primarily determined by the nature of the *depleted* particles themselves and *not* by the depletants.

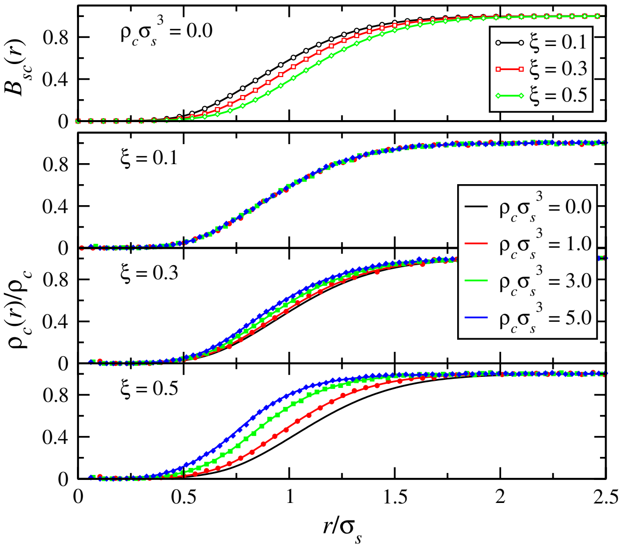

FIG. 3 (color online). Upper panel: the Boltzmann factors $B_{sc}(r) = \exp[-\beta V_{sc}(r)]$ of the star-chain effective interaction potential. Lower panels: the normalized density profile of chains around one isolated star with $f = 32$. Continuous curves were calculated by solving the OZ equation while filled symbols correspond to results from MC simulations. The curves for $\rho_c = 0$ are the Boltzmann factors $B_{sc}(r)$.

The interaction potentials given by Eqs. (1)–(3) have been recently used to study the phase behavior in a two-component description of star-linear mixtures [31]. For low and intermediate functionalities, $f \lesssim 32$, evidence was found showing star-cluster formation as a precursor stage for a fluid-fluid demixing transition. This behavior resembles the one predicted via a one-component model of the star suspension, for which one attractive contribution $V_{\mathrm{att}}(r)$ was added to $V_{ss}(r)$, and which had the form of a Fermi distribution [32–35]:

$$V_{\mathrm{att}}(r) = -\frac{C}{\exp[(r-A)/B] + 1}. \tag{4}$$

The above form and the describing parameters were, however, introduced *ad hoc*, arguing on general grounds that depletion would be a mechanism to induce such attractions. Although another model could be used, this Fermi-like model (FLM) has been shown to provide a rather convenient parametrization of generic attractive contributions, which allows for changing the characteristics (range and depth) of the latter; the parameters A and B control the position and width of the well potential and C its amplitude [32,33]. It is thus tempting to see whether star-linear mixtures can be described by this model.

For the system at hand, the FLM indeed describes remarkably well the depletion interactions, as can be seen in the lower panels of Fig. 1. Representative results for the dependence of the parameters A, B, and C on the chain density ρ_c are shown in Fig. 4 for different size ratios ξ and functionalities f. It is immediately seen that the length scales show a weak dependence on the size ratio ξ: by increasing ξ by as much as a factor five (from 0.1 to 0.5), we obtain very weak changes in the parameters A and B, of order 10% at any given chain density. As the chain density increases, the parameters A and B decrease and the trend becomes *opposite* to what conventional wisdom asserts:

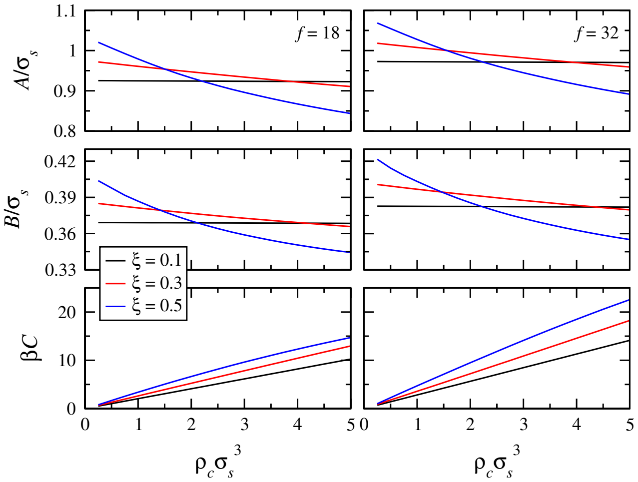

FIG. 4 (color online). Fitting parameters of $V_{\mathrm{dep}}(r)$ from SA to the Fermi-like model, Eq. (4), as a function of the chain concentration.

long polymers induce *shorter-ranged* depletion potentials than short ones, in strong contrast with the AO case. On the other hand, the strength of $V_{\mathrm{dep}}(r)$ grows, as expected, with ρ_c, due to the increase in $\Pi(\rho_c)$.

In summary, in this Letter we describe some remarkable characteristics of the depletion potential in a model soft mixture. We found its range to show a very weak dependence not only on the chain density ρ_c but also on the size ratio ξ. This is counterintuitive, since one would have expected the range to increase as the size of the depletant increases, and it is the result of the softness and penetrability characterizing the components and the ensuing effective interaction potentials of the system at hand. These two characteristics are not peculiar for star polymers but they are present in many other polymer-based colloidal systems. Microgels, micelles, polymer-grafted nanoparticles, dendrimers and, in general, hyperbranched polymers, are highly deformable systems whose topology can be well described through a core and shell structure. The size and softness of the latter one can be easily tuned by changing, for example, the cross-linking or the charge (microgels), the aggregation number (micelles), the grafted density (nanoparticles), and the generation number or the spacer between generations (dendrimers). We expect our results, which are based on the penetrability of the soft shell, to hold as long as the latter is thick enough to accommodate the chains in their full extent. As the range of the depletion potential exceeds that needed for phase separation and cannot be reduced by employing smaller depletants, we anticipate macroscopic, demixing (“liquid-gas”) transitions to take place for this family of systems. Therefore, at sufficiently high soft-colloid concentrations, they are expected to undergo the recently reported “arrested spinodal decomposition” [3,36], which constitutes a novel route to gelation. The mapping of the original full ultrasoft-colloidal mixture on the characteristic parameters of the FLM effective system turns this into a more tractable problem.

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[1] A. Stradner *et al.*, Nature (London) **432**, 492 (2004).
[2] K. N. Pham *et al.*, Science **296**, 104 (2002).
[3] P. J. Lu *et al.*, Nature (London) **453**, 499 (2008).
[4] C. N. Likos, Phys. Rep. **348**, 267 (2001).
[5] S. Asakura and F. Oosawa, J. Polym. Sci. **33**, 183 (1958).
[6] A. Vrij, Pure Appl. Chem. **48**, 471 (1976).
[7] W. C. K. Poon, J. Phys. Condens. Matter **14**, R859 (2002).
[8] R. Tuinier, J. Rieger, and C. G. de Kruif, Adv. Colloid Interface Sci. **103**, 1 (2003).
[9] A. A. Louis *et al.*, J. Chem. Phys. **117**, 1893 (2002).
[10] P. G. Bolhuis, A. A. Louis, and J. P. Hansen, Phys. Rev. Lett. **89**, 128302 (2002).
[11] A. A. Louis *et al.*, Phys. Rev. E **65**, 061407 (2002).
[12] O. Guzmán and J. J. de Pablo, J. Chem. Phys. **118**, 2392 (2003).
[13] G. Cinacchi *et al.*, J. Chem. Phys. **127**, 214501 (2007).
[14] S. Abbas and T. P. Lodge, Phys. Rev. Lett. **99**, 137802 (2007).
[15] S. Abbas and T. Lodge, Macromolecules **41**, 8895 (2008).
[16] C. N. Likos *et al.*, Phys. Rev. Lett. **80**, 4450 (1998).
[17] M. Watzlawek, C. N. Likos, and H. Löwen, Phys. Rev. Lett. **82**, 5289 (1999).
[18] D. Vlassopoulos *et al.*, J. Phys. Condens. Matter **13**, R855 (2001).
[19] E. Stiakakis *et al.*, Phys. Rev. Lett. **89**, 208302 (2002).
[20] E. Stiakakis *et al.*, Europhys. Lett. **72**, 664 (2005).
[21] A. Jusufi, M. Watzlawek, and H. Löwen, Macromolecules **32**, 4470 (1999).
[22] A. A. Louis *et al.*, Phys. Rev. Lett. **85**, 2522 (2000).
[23] P. G. Bolhuis *et al.*, J. Chem. Phys. **114**, 4296 (2001).
[24] V. Krakoviack, J. P. Hansen, and A. A. Louis, Europhys. Lett. **58**, 53 (2002).
[25] A. Jusufi *et al.*, J. Phys. Condens. Matter **13**, 6177 (2001).
[26] R. L. C. Vink *et al.*, Phys. Rev. E **72**, 030401(R) (2005).
[27] C. Mayer and C. N. Likos, Macromolecules **40**, 1196 (2007).
[28] M. Daoud and J. P. Cotton, J. Phys. (Paris) **43**, 531 (1982).
[29] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 2006).
[30] P. Attard, J. Chem. Phys. **91**, 3083 (1989).
[31] M. Camargo and C. N. Likos, J. Chem. Phys. **130**, 204904 (2009).
[32] F. Lo Verso, M. Tau, and L. Reatto, J. Phys. Condens. Matter **15**, 1505 (2003).
[33] F. Lo Verso *et al.*, Phys. Rev. E **70**, 061409 (2004).
[34] F. Lo Verso, C. N. Likos, and L. Reatto, Prog. Colloid Polym. Sci. **133**, 78 (2006).
[35] F. Lo Verso *et al.*, Mol. Phys. **104**, 3523 (2006).
[36] E. Zaccarelli, J. Phys. Condens. Matter **19**, 323101 (2007).