Depletion interaction between colloids mediated by an athermal polymer blend

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(Received 26 October 2017; revised manuscript received 12 January 2018; published 29 March 2018)

We calculate the immersion energy of a colloid and the potential of the depletion interaction (DI) acting between colloids immersed in an athermal polymer blend. The developed theory has no limitations with respect to the polymer-to-colloid size ratios and polymer densities, covering, in particular, dense polymer blends. We demonstrate that in addition to the standard compressibility-induced mechanism of the DI there exists the mechanism relying on the correlations between compositional fluctuations specific to polymer blends. We quantitatively investigate this "compositional" mechanism of the DI and demonstrate that it causes significant contributions to the effective force acting between colloids. Further we show that relative significance of the contributions to the colloid immersion energy and the depletion potential caused by the above compositional mechanism strongly depends on the mass fractions of the polymer species and their size ratio. We find out that these contributions strongly affect the range of the DI, thus causing a significant increase in the absolute value of the second virial coefficient of the effective potential acting between colloids.

DOI: 10.1103/PhysRevE.97.032508

I. INTRODUCTION

The entropic mechanism of the polymer-induced interactions between colloids, termed "depletion interactions", is being investigated in great detail [1–4] for homopolymer systems composed of both noninteracting [5] and interacting [6–8] polymers. The depletion interactions in these systems are known [2–4] to arise from the loss of the conformational entropy of the polymer chains located in the vicinity of the colloids. The thus formed depletion layers, where the conformational entropy of the polymer chains is reduced, are therefore energetically unfavorable. The system tends to minimize the overall volume of these depletion layers by way of overlapping them with each other, thus causing an effective attraction mechanism pushing the colloids bearing these layers to each other.

The width of the depletion layers in the described homopolymer systems is known [9,10] to be primarily determined by the correlation length in these systems, which essentially depends on the interaction between the polymers. In the system of ideal polymers typically used as an idealized model to describe the polymers dissolved in the theta solvent [1], all interactions between the polymers are screened. The typical correlation length and, consequently, the width of the depletion layer in these ideal systems are of the order of the unperturbed gyration radius of the polymers. In realistic dense polymer systems, interactions between the polymers cause severe shortening [7,9] of the correlation length relative to its ideal counterpart. As a result, the range of the depletion interactions in these dense homopolymer systems amounts to several lengths of the polymer segments. As will be demonstrated in the present paper, the variations of a local composition in the vicinity of hard inclusions in a heterogeneous polymer system lead to an essentially different mechanism not directly relevant to the depletion of the polymer density in the vicinity of the colloids. This "compositional" correlation mechanism causes long-ranged effective interactions between colloids even at large polymer densities, where the standard depletion interaction is suppressed.

The described mechanism of the depletion attraction between hard inclusions immersed in a host system of flexible macromolecules is known to be of key importance for many technological and biological processes relevant to the polymer induced coagulation [11,12], flocculation, or agglomeration [4,13–15] of these fillers. In fact, the agglomeration of hard fillers is highly undesirable in such common industrial processes as reinforcement of rubbers widely used [14,15] in tire industry. The reversible formation of filler agglomerates in compressed or decompressed dense polymer-based nanocomposites can significantly affect electrical properties of these composites, which has been recently used [16,17] in nanocomposite-based mechanical sensors. A similar problem of controlling the size of red blood cell agglomerates (so called "rouleaux") formed as a result of the depletion interactions arises [18] in health science. The depletion force acting between fillers and physically rough surfaces mediated by polymers can be used as a driving force for self-healing of nanomaterials [19,20].

The practical need to govern the coagulation or flocculation of fillers through suppressing or promoting the attractive depletion interaction between them in a desirable way calls for a better theoretical understanding of the main factors affecting this depletion interaction. Note that in most of the practical settings a host polymer system contains macromolecules having different physical properties. In particular, polymers typically used in applications are polydisperse to a larger or smaller extent. Recall, the above described entropic effect underlying the depletion interactions is known [1] to increase with increasing the length of the polymer chains. One should

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therefore expect that having polymers of different lengths in a host polymer system must strongly affect the strength and range of the depletion interactions mediated by this system. Surprisingly, this important aspect of the depletion interactions has not yet received due theoretical attention.

In the present paper, we address a simplest case where the above effect of the presence of polymers of different lengths on the depletion force mediated by these polymers exhibits itself. Specifically, we consider an athermal blend of two polymer species having different mass fractions and polymerization degrees. The only interactions present in this system are the excluded volume interactions between the polymers of same and different species and those between the colloids and polymers. The enthalpic interactions are excluded from the consideration with the objective to highlight the entropic effects underlying the osmotic depletion interaction between the colloids. Despite the simplicity of the considered polymer system, the depletion interactions mediated by this system show several interesting features specific to polymer blends. By performing a detailed analytical analysis based on standard methods of the liquid state theory [21] described below we prove that the depletion interactions in an athermal polymer blend are caused by two different correlation mechanisms. The first mechanism described above relies on finite compressibility of the polymer system promoting the formation of the layers of depleted polymer density around the colloids. This "compressibility" mechanism is present in any compressible polymer system. The second mechanism, specific to polymer blends, is promoted by the correlations between the fluctuations of local composition in this polymer blend. The described compositional fluctuations give rise to long-ranged compositional correlations in the host polymer blend that in turn cause the long-ranged entropic interaction between colloids immersed in this blend. Quantifying the significance of the described compositional correlation-induced depletion interaction relative to that caused by finite compressibility of the polymer system is the main goal of the present paper.

This goal is achieved by making use of the standard polymer reference interaction site model (PRISM) [21]. The practical implementation of this model requires a specific closure relating the polymer pair-correlation functions to the direct correlation functions [22]. In the present paper we restrict ourselves to using the standard Percus-Yevick (PY) closure [22] that is equivalent [22] to the mean spherical approximation (MSA) [23] in the absence of the enthalpic interactions between the polymers and colloids. The used MSA approximation is chosen for its simplicity, mathematical transparency, and capacity to give qualitatively correct predictions demonstrated by previous work [2] on the depletion interactions in a polymer melt. Recently, Fuchs and Schweizer [24–26] gave an important contribution to the above described PY-PRISM approach by modifying the standard PY closure to include the direct entropic correlations between the polymers and the colloid surfaces. Although the modified m-PY closure is based on the plausible physical arguments and therefore provides deep physical insight, up to now there are no direct evidences that this closure provides a quantitatively accurate description of the simulation or experimental results for the polymer mediated potential. In addition, in contrast to the standard PY closure, the m-PY closure contains an adjustable phenomenological parameter λ (nonlocality length) that can be determined only by plausible arguments. In the case of a dilute colloidal suspension in a dense polymer melt that is the focus of the present paper, λ is evaluated to be of the order of the correlation length ξ of the excluded volume polymers [26]. The range of the compositional correlations investigated in the present paper is, in contrast, of the order of the polymer gyration radius that is much larger than $\lambda \sim \xi$ in the considered dense polymer system. Based on these arguments, we do not expect significant qualitative changes to the obtained results that may by caused by using the m-PY closure.

The paper is organized as follows. In Sec. II we derive the expression for the pair-correlation functions describing the correlations between the polymers of same and different polymer species. In Sec. III we study the polymer-colloid correlations and calculate the immersion free energy of a colloid immersed in an athermal polymer blend. In Sec. IV we calculate the potential of the depletion interaction acting between colloids immersed in an athermal polymer blend. In the same section we obtain the second virial coefficient of the total effective potential acting between colloids. In Sec. V we give the conclusions and discuss the obtained results.

II. LIQUID STATE THEORY OF AN ATHERMAL POLYMER BLEND

We consider spherical colloids of radius R immersed in a polymer blend composed of two homopolymer species 1 and 2, having polymerization degrees N_1 and N_2 and monomer number densities ρ_1 and ρ_2, respectively. For the sake of definiteness, we set $N_1 \geqslant N_2$. The segment length b is assumed to be the same for species 1 and 2. The relation between the gyration radii $R_G^i \equiv b\sqrt{N_i/6}$ and corresponding ideal correlation lengths [2] $\xi_i = R_G^i/\sqrt{2}$ of the species 1 and 2, therefore, depends only on the polymerization degrees N_i. It proves convenient to introduce the polymer size ratio $f = \xi_2/\xi_1 \equiv \sqrt{N_2/N_1} \leqslant 1$ and the mass fractions $\phi_i = \rho_i/(\rho_1 + \rho_2) \equiv \rho_i/\rho$ of the polymer species. For convenience, we denote $\phi_2 = \phi$, $\phi_1 = 1 - \phi$, ϕ being the mass fraction of the shorter polymer species that often enter the results presented below.

Density structure of a pure polymer blend is described by the structure factors S_{ij} (hereafter, $j = i$ or $\underline{i}$; $i = 1,2$; $\underline{i} = 3 - i$),

$$S_{ii} = \rho_i\omega_i(1 - \rho_{\underline{i}}\omega_{\underline{i}}\widehat{c}_{\underline{i}\underline{i}})/\Delta,$$
$$S_{i\underline{i}} = \rho_1\rho_2\omega_1\omega_2\widehat{c}_{12}/\Delta, \quad (1)$$

that can be obtained [21] directly from the standard Ornstein-Zernike (OZ) relations [22] without specifying an explicit form of the direct correlation functions c_{ij} defined below. Here,

$$\Delta = 1 - \rho_1\omega_2\widehat{c}_{11} - \rho_B\omega_B\widehat{c}_{22} + \rho_1\rho_2\omega_1\omega_2(\widehat{c}_{11}\widehat{c}_{22} - \widehat{c}_{12}^2), \quad (2)$$

$\widehat{\cdots} \equiv \int(\cdots)\exp(-i\vec{k}\vec{r})d^3r$ stands for the Fourier transform, c_{ij} are the direct correlation functions describing the interactions between the monomers of species i and j, and $\omega_{1,2}$ are the intramolecular structure factors [21] of polymer species 1 and 2, respectively, that describe the correlations within each polymer chain. For the sake of simplicity we employ the commonly used Lorentzian form [27]

$\omega_i = (N_i^{-1} + b^2k^2/12)^{-1}$ of the intramolecular structure factors, $k \equiv |\vec{k}|$ being the Fourier wave number. In addition to ω_i, specifying the structure factors given by Eqs. (1) for a given polymer system requires explicit expressions for the direct correlation functions that must be determined for any specific form of the interactions between the polymers in this system. In the present paper we consider a specific case of the athermal polymer blend [28] where the only interactions that occur between monomers are due to the steric repulsive forces. In this simplest case, the direct correlation functions $\widehat{c}_{ij}$ can be determined analytically by employing the thread polymer approximation [21]. This approximation amounts to assuming point interactions between the monomers that are described by the delta-functional form of the direct correlation functions. In the frameworks of the described thread approximation, the Fourier images of the direct correlation functions therefore reduce to constants that are to be determined from the excluded volume constraints. Mathematically, these constraints amount [22] to the requirement that the pair-correlation functions must tend to zero at the points corresponding to the positions of the monomers.

In order to use the above described constraints one should first determine the explicit expressions for the pair-correlation functions $1 + h_{ii}$, $1 + h_{i\underline{i}}$ describing the correlations between the monomers of same and different polymer species, respectively. The Fourier images $\widehat{h}_{ij}$ of the total correlation functions h_{ij} can be determined from the standard definitions [22] of the structure factors represented in the form

$$\rho_j \widehat{h}_{ij} = \rho_i^{-1} S_{ij} - \omega_i \delta_i^j, \quad i = 1,2, \tag{3}$$

where δ_i^j is the Kronecker delta symbol.

Inverting the expressions given by Eq. (3) back to real space parametrized by the position vector $\vec{r}$ and choosing the constants $\widehat{c}_{ij}$ such that the hard core constraints $h_{ij} \to -1$ are fulfilled at $|\vec{r}| \equiv r = 0$, one arrives at the explicit expressions for the total correlation functions of the form

$$h_{ii} = \eta_i \left[r\left(\lambda_i^{-1} - \lambda_{\underline{i}}^{-1}\right)\right]^{-1} \left[\left(\xi_i^{-1} + \eta_i^{-1} - \lambda_{\underline{i}}^{-1}\right) e^{-\frac{r}{\lambda_i}} - \left(\xi_i^{-1} + \eta_i^{-1} - \lambda_i^{-1}\right) e^{-\frac{r}{\lambda_{\underline{i}}}} - \left(\lambda_i^{-1} - \lambda_{\underline{i}}^{-1}\right) e^{-(\xi_i^{-1} + \eta_i^{-1})r}\right],$$

$$h_{12} = h_{21} = \left[r\left(\lambda_1^{-1} - \lambda_2^{-1}\right)\right]^{-1} \left(e^{-\frac{r}{\lambda_1}} - e^{-\frac{r}{\lambda_2}}\right), \tag{4}$$

where $\eta_i^{-1} = \pi \rho_i b^2/3$, and

$$\lambda_{1,2}^{-1} = \tfrac{1}{2}\left[\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1} \pm \sqrt{\left(\tilde{\xi}_1^{-1} - \tilde{\xi}_2^{-1}\right)^2 + 4(\eta_1\eta_2)^{-1}}\right] \tag{5}$$

are the roots of the equation $\Delta = 0$ describing the poles of the structure factors given by Eq. (1), where $\tilde{\xi}_i^{-1} = \xi_i^{-1} + \eta_i^{-1}$.

The obtained expressions for the polymer-polymer correlation functions can be directly used to obtain the equation of state of an athermal polymer blend. Integrating the negative of the reciprocal isothermal compressibility κ_T^{-1} defined [21] by $\beta\kappa_T^{-1} = \sum_{i=1}^2 \rho_i (N_i^{-1} - \sum_{j=1}^2 \rho_j \widehat{c}_{ij})$ over volume gives the pressure

$$P = P_1 + P_2 + \Delta P(\rho_1, \rho_2), \quad \beta \Delta P = -\rho_1 \rho_2 \widehat{c}_{12}, \tag{6}$$

where $\beta = (kT)^{-1}$, k and T being the Boltzmann constant and temperature, respectively; $\widehat{c}_{12} = -\pi b^4(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1})/36$ and $\widehat{c}_{ii} = (N_i\rho_i)^{-1}[1 - \xi_i^2(\tilde{\xi}_i^{-2} + \eta_1^{-1}\eta_2^{-1})]$ are the Fourier images of the polymer direct correlation functions that are k-independent in the employed thread approximation. The quantity

$$\beta P_i = \frac{\rho_i}{N_i} + \frac{\tilde{\xi}_i^{-1} + 2\xi_i^{-1}}{12\pi\eta_i^2}$$

that enters the right-hand side (rhs) of Eq. (6) is the partial pressure of the component i that coincides with the pressure of the homopolymer melt having density ρ_i, first derived in Ref. [2].

According to Eq. (6), the pressure of an athermal polymer blend does not reduce to the sum of the partial pressures of its components. This interesting feature is a consequence of the fact that the conformational entropy of the polymers of one species is affected by the presence of the polymers of the other species in the blend. This property of a blend of flexible polymers is in contrast to the properties of athermal mixtures of simple liquids where the total pressure reduces to the sum of partial pressures of each component. In Sec. IV we will demonstrate that the occurrence of the cross-species term in the expression for the pressure given by Eq. (6) causes essential contribution to the potential of the depletion interactions mediated by an athermal polymer blend.

III. COLLOID-POLYMER CORRELATIONS AND COLLOID IMMERSION ENERGY

The total correlation functions given by Eq. (4) describe the density structure of the polymer blend, serving as an input for determining the polymer-colloid correlations. At infinite dilution of colloids, the Fourier images of the polymer-colloid direct (c_{ci}) and total (h_{ci}) correlation functions are related by the OZ equation of the form

$$\rho_i \widehat{h}_{ci} = \widehat{c}_{ci} S_{ii} + \widehat{c}_{c\underline{i}} S_{i\underline{i}}, \quad i = 1,2, \tag{7}$$

where S_{ij} $(i,j = 1,2)$ are the partial structure factors of the pure polymer blend that can be straightforwardly obtained from Eqs. (3) and (4).

Note that solving the OZ equations given by Eqs. (7) requires an additional closure relation between the total and direct correlation functions that describes the physical nature of the interactions between the polymers and colloids. In the present paper, we restrict ourselves to taking into account only the entropic interactions between the polymers and colloid surfaces that cause purely depletion interaction between the colloids. This entropic repulsive interaction can be described [2] by setting the direct polymer-colloid correlation function equal to zero outside the hard core of the colloids. The second condition imposed on the solutions of Eqs. (7) is that the polymer-colloid pair-correlation functions $1 + h_{ci}$ must be equal to zero inside the hard core of the colloids, due to the standard [22] hard core constraint.

Using the expressions for the partial structure factors in Eqs. (3) with h_{ij} given by Eq. (4), Eqs. (7) can be inverted to real space to be conveniently represented in the form

$$\frac{b^2}{12}\left(\partial_r^2 - \lambda_1^{-2}\right)\left(\partial_r^2 - \lambda_2^{-2}\right) h_{ci} = \left(-\partial_r^2 + \tilde{\xi}_{\underline{i}}^{-2} + \eta_1^{-1}\eta_2^{-1}\right) c_{ci} - \eta_{\underline{i}}^{-1}\left(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1}\right) c_{c\underline{i}},$$

$$i = 1,2. \tag{8}$$

It is convenient to put the origin of the coordinate frame in the center of the colloid particle, so that $r \equiv |\vec{r}| > R$ describes the region outside of the colloid, available to the polymers. Finding a solution of Eq. (8) is greatly simplified by the fact that the rhs of this equation turns to zero in this outer region $r > R$ in the absence of the enthalpic ("direct") interactions between the colloids and polymers. In this region, the solution of Eq. (8) fulfilling the hard core constraint $h_{ci}(r = R) = -1$ describing the polymer-colloid excluded volume interactions [2] is given by

$$h_{ci} = -\frac{R}{r}\left(\frac{c_0^i - \lambda_2^{-2}}{\lambda_1^{-2} - \lambda_2^{-2}} \exp\left[-\lambda_1^{-1}(r - R)\right] + \frac{\lambda_1^{-2} - c_0^i}{\lambda_1^{-2} - \lambda_2^{-2}} \exp\left[-\lambda_2^{-1}(r - R)\right]\right), \tag{9}$$

where c_0^i are yet undetermined constants.

Since the total correlation functions h_{ci} are equal to -1 inside the hard core of the colloids, the expression for h_{ci} given by Eq. (9) solves the problem of determining the polymer-colloid pair-correlation function in the whole range of r, up to the two constants c_0^1 and c_0^2. These constants must be determined from the OZ relations given by Eq. (7), along with the direct correlation functions c_{ci}. Substituting the obtained expressions for h_{ci} into Eq. (8), one finds the expression for the direct correlation functions c_{ci} in the region $r \leqslant R$. These expressions read

$$c_{ci} = -\frac{b^2}{12}\left\{c_i^0 \Theta(r - R) + \delta(r - R)\left[R^{-1} + \left(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1}\right)^{-1}\left(c_i^0 + \lambda_1^{-1}\lambda_2^{-1}\right)\right]\right\}, \tag{10}$$

where $\Theta(r)$ and $\delta(r)$ are the Heaviside theta function and Dirac delta function, respectively, and the constants c_i^0 are given by

$$c_i^0 = \tilde{\xi}_i^{-2} + \eta_i^{-1}\left(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1} + \eta_i^{-1}\right). \tag{11}$$

The obtained expressions for the polymer-colloid total and direct correlation functions given by Eqs. (9) and (10), respectively, describe the density structure of an athermal polymer blend in the presence of a colloid in terms of the correlation lengths λ_i ($i = 1,2$) of a pure polymer blend given by Eq. (5). Recall, in the low density limit λ_i reduce to the ideal correlation lengths ξ_i describing the range of the correlations in the ideal blend where the polymers do not experience the excluded volume interactions. For finite densities of the polymer species the relation between the above correlation lengths is nonmonotonic. In order to investigate this relation, in Fig. 1 we plot the ratio λ_1/λ_2 as a function of the reduced total polymer density $\tilde{\rho} \equiv \pi b^2 \xi_2(\rho_1 + \rho_2)/3$ for the specific case $\rho_1 = \rho_2 = \rho/2$. As can be seen from this figure, the correlation length λ_1 is smaller than λ_2 in the whole range of the polymer densities and the polymer size ratios f. λ_1/λ_2 increases with increasing the size asymmetry of the polymer species quantified by f. At smaller densities, where it is mainly determined by the polymer size ratio f, λ_1/λ_2 increases with ρ to a f-dependent maximum value. At larger densities, λ_1/λ_2 steeply decays with increasing ρ, approaching zero in the limit

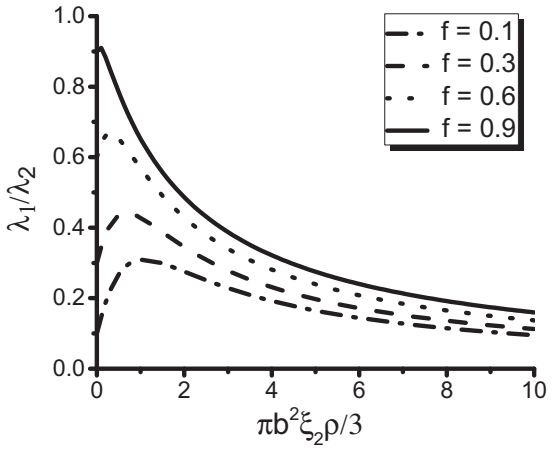

FIG. 1. Dependence of the ratio λ_1/λ_2 of the correlation lengths given by Eq. (5) on the reduced polymer density $\pi b^2 \xi_2(\rho_1 + \rho_2)/3$ for several selected values of the polymer size ratio parameter f and equal partial densities $\rho_1 = \rho_2 = \rho/2$.

$\rho \to \infty$. As will be shown in what follows, at $\tilde{\rho} \gg 1$ the correlation length λ_1 describes the compressibility induced correlations, while λ_2 describes the correlations due to the variations of the local composition of the polymer blend. The compressibility correlation length λ_1 is inversely proportional to the polymer density ρ, and the compositional correlation length λ_2 only weakly depends on ρ. This observation explains the above decaying trend of λ_1/λ_2 as a function of $\tilde{\rho}$ and justifies the approximation $\lambda_1 \ll \lambda_2$ used below for the case of a dense polymer blend.

In the present paper we concentrate on the case of moderate to large polymer densities that has immediate practical significance. In this case described by an inequality $N_i \rho_i b^3 \gg 1$, one can use approximate expressions for the correlation lengths λ_i in Eqs. (5) exact to next-to-leading order in the small parameter $(N_i \rho_i b^3)^{-1}$. These expressions read

$$\lambda_1^{-1} \approx \eta_1^{-1} + \eta_2^{-1} + (1 - \phi)\xi_1^{-1} + \phi\xi_2^{-1},$$
$$\lambda_2^{-1} \approx \phi\xi_1^{-1} + (1 - \phi)\xi_2^{-1}. \tag{12}$$

Note that the same limiting case covers the system of long polymers having moderate densities, as long as the above inequality is fulfilled.

According to Eqs. (12), in the considered large density limit the correlation length λ_1 is much larger than λ_2. In the limit $N_1 = N_2 = N$, λ_1 reduces to the correlation length of the polymer melt having density $\rho = \rho_1 + \rho_2$ and polymerization degree N. This observation can be rationalized by recognizing that the correlation length λ_1 mainly describes short-ranged density correlations caused by the excluded volume interactions. These correlations do not significantly depend on the composition of the polymer blend, so they have approximately the same range as those observed in a polymer melt having the same density. The long-range correlations described by the second correlation length λ_2 are specific to polymer blends and are strongly dependent on the local composition of the polymer species. These additional compositional correlations induced by local variations of the composition of polymer species can cause considerable contributions to thermodynamic properties

of filled polymer blends. In order to prove this statement, we calculate the immersion energy W of the colloid in a polymer blend.

The colloid immersion energy W is defined by $\beta\mu_{ex}$, where μ_{ex} is an excess chemical potential of the polymer blend caused by the presence of a single colloid in this blend. This excess chemical potential can be calculated using the compressibility equations $\partial_{\rho_i} W = -\int c_{ci} d^3r$ with the polymer-colloid correlation function c_{ci} given by Eq. (10). Integrating the above compressibility equations over the partial densities ρ_i of the polymer species, one arrives at the expression for the colloid immersion energy given by

$$W = \sum_{i=1}^{2}[W_0(\tilde{\xi}_i) - W_0(\xi_i)] + R^2\eta_1^{-1}\eta_2^{-1}\left(1 + \frac{R}{3}\left(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1}\right)\right), \qquad (13)$$

where

$$W_0(\xi) = \frac{R^3}{9\xi^3} + \frac{R^2}{2\xi^2} + \frac{R}{\xi}.$$

Note that the terms of the form $W_0(\tilde{\xi}_i) - W_0(\xi_i)$ in the rhs of Eq. (13) describe the partial energies of immersion of a colloid of radius R in a polymer system having density ρ_i and polymerization degree N_i obtained in Ref. [2]. The last cross-species term in the rhs of Eq. (13) is a nonadditive contribution arising from altering the conformational entropy of one species caused by the presence of polymers of other species in the system. This nonadditive contribution is proportional to the mean inverse correlation length $(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1})/2$ that quantifies the width of the depletion layer formed around the colloid. As has been alluded to above, the width of this layer therefore depends not only on the total density of the blend quantified by the correlation length λ_1 but also on the composition of polymer species in this layer quantified by λ_2. In the limit of large polymer densities or long polymer chains, mathematically described by the inequality $N_i\rho_i b^3 \gg 1$, W in Eq. (13) reduces to $W_0(\pi b^2\rho/3)$, the immersion energy of a colloid in a homopolymer melt of density $\rho = \rho_1 + \rho_2$. This observation corroborates the intuitive expectation that for the case of large polymer densities the contributions to the immersion energy due to changes in the polymer conformational entropy caused by the colloids are suppressed, along with the described compositional contributions.

It is instructive to investigate the dependence of the obtained immersion energy W on the density of the polymer blend for different polymer mass fractions ϕ and polymer size ratios f. This dependence is illustrated in Figs. 2 and 3 that show the reduced immersion energy $W/W_0[3/(\pi b^2\rho)]$ as a function of the reduced blend density $\pi b^2\xi_2\rho/3$ for the selected values of f (Fig. 2) and ϕ (Fig. 3). Note that the immersion energy $W_0[3/(\pi b^2\rho)]$ chosen for a convenient rescaling of the function W in Figs. 2 and 3 is the limiting value of the energy W of immersion of a colloid in an extremely dense polymer system having total density $\rho \gg N_1^{-1}b^{-3}$. Recall, in the large density limit $\tilde{\xi}_i^{-1}$ tends to $\pi b^2\rho_i/3$, so that $W_0(\tilde{\xi}_i)$ becomes independent on the polymerization degrees of the polymer species. As should be expected, the reduced immersion energy

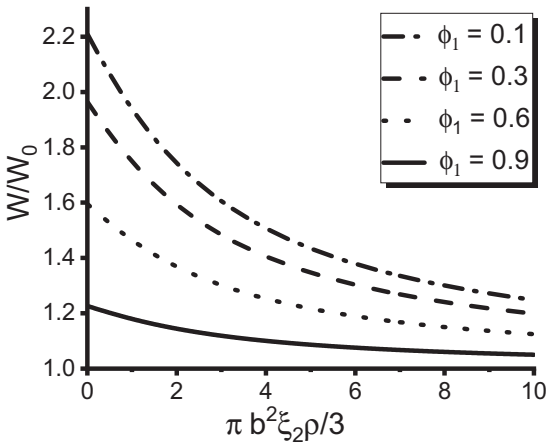

FIG. 2. Dependence of the reduced colloid immersion energy $W/W_0[3/(\pi b^2\rho)]$ on the reduced total blend density $\pi b^2\xi_2\rho/3$ for several selected values of the mass fraction ϕ_1 of longer polymers and the polymer size ratio parameter $f = 0.1$. The reduced colloid radius R/ξ_2 is set equal to unity.

W/W_0 decreases with increasing the total density ρ of the blends at all values of the mass fraction ϕ and size ratio parameter f. With increasing ρ, W/W_0 tends to unity. Since the reciprocal ideal correlation lengths ξ_i^{-1} tend to zero with increasing the degrees of polymerization N_i, in the limit $N_i \gg 1$ the correlation lengths of polymer species given by Eqs. (12) become mass fraction independent and blend composition independent. In this long-polymer limit, the colloid immersion energy W therefore tends to the same large density limit W_0. Accordingly, the larger the fraction of the shorter polymers in the blend, the larger the deviations of W/W_0 from unity. This tendency is illustrated in Fig. 2 that shows the function $W/W_0(\rho)$ for selected values of the mass fraction $\phi_1 = \rho_1/\rho$ of longer polymers for the size ratio $f = 0.1$ corresponding to a large degree of the polymer size asymmetry. As can be seen from this figure, one observes smaller absolute values of the

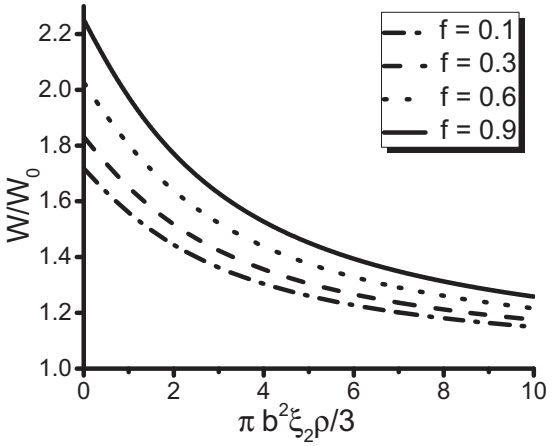

FIG. 3. Dependence of the reduced colloid immersion energy $W/W_0[3/(\pi b^2\rho)]$ on the reduced total blend density $\pi b^2\xi_2\rho/3$ for several selected values of the polymer size ratio parameter f and mass fraction $\phi = 0.5$. The reduced colloid radius R/ξ_2 is set equal to unity.

colloid immersion energy at smaller mass fractions of longer polymers.

Figure 3 shows $W/W_0(\rho)$ for several selected values of the polymer size ratio parameter f at equal mass fractions ($\phi = 0.5$) of the polymer species. According to Fig. 3, the larger degree of the size asymmetry always plays in favor of decreasing the immersion free energy. This finding can be rationalized by recognizing that the correction to the partial immersion free energies $W_0(\tilde{\xi}_i) - W_0(\xi_i)$ expressed by the second term in the rhs of Eq. (13) is proportional to the arithmetical mean of the inverse correlation lengths $\tilde{\xi}_i^{-1}$ that quantifies the average reciprocal width of the depletion layer surrounding the colloids. This width decreases with f (at a fixed polymerization degree N_1 of the longer polymer chains), which explains increasing the colloid immersion energy with f observed in Fig. 3.

IV. POTENTIAL OF THE DEPLETION INTERACTIONS

The obtained expressions for the polymer-colloid total and direct correlation functions given by Eqs. (9) and (10), respectively, can be directly used to calculate the colloid-colloid correlation function h_{cc}. In the infinite dilution limit with respect to the colloids, the corresponding OZ relation in Fourier space reads

$$\widehat{h}_{cc} = \widehat{c}_{cc} + \rho[(1-\phi)\widehat{c}_{c1}\widehat{h}_{c1} + \phi\widehat{c}_{c2}\widehat{h}_{c2}]. \tag{14}$$

Note that the real space counterpart of the first term in the rhs of Eq. (14) turns to zero at $r \geqslant 2R$ in the absence of direct interactions between the colloids. The Fourier inversion of the second term in the rhs of Eq. (14) can be performed directly, by making use of the explicit expressions for the correlation functions h_{ci} and c_{ci} given by Eqs. (9) and (10), respectively. The thus obtained expression for h_{cc} at $r \geqslant 2R$ can be directly used to obtain the depletion potential U acting between colloids by employing the standard formula [22] $\beta U = -\ln(1 + h_{cc})$. The resulting expression for the depletion potential reads

$$\begin{aligned}\beta U &\equiv -\ln(1+h_{cc}) \\ &= -\ln\left[1 + \frac{R}{2r}\sum_{i,j=1}^{2}\lambda_j\eta_i^{-1}\zeta_i^j\gamma_i^j\exp\left(-\frac{(r-2R)}{\lambda_j}\right)\right],\end{aligned} \tag{15}$$

where

$$\begin{aligned}\zeta_i^1 &= \frac{c_i^0 - \lambda_2^{-2}}{\lambda_1^{-2} - \lambda_2^{-2}}, \quad \zeta_i^2 = 1 - \zeta_i^1, \\ \gamma_i^j &= \left[1 - c_i^0\lambda_j^2 + R\left(\eta_1^{-1} + \eta_2^{-1} + \xi_i^{-1}\right)\right]\left(1 - e^{2R\lambda_j^{-1}}\right) \\ &\quad + Rc_i^0\lambda_j\left(1 + e^{2R\lambda_j^{-1}}\right).\end{aligned}$$

Interestingly, in the case of an athermal blend composed from the ideal (i.e., noninteracting) polymers, mathematically described by the limit $\tilde{\xi}_i \to \xi_i$, the argument of the logarithm in the rhs of Eq. (16) reduces to the density-weighted sum of the partial contributions corresponding to pure polymer species, which brings the expression for the depletion potential into a simple form:

$$\beta U_{\mathrm{id}} = -\ln\left[1 + \frac{R^2}{r}\sum_{i=1}^{2}\eta_i^{-1}\exp\left(-\frac{(r-2R)}{\xi_i}\right)\right]. \tag{16}$$

According to Eq. (16), the Mayer function $1 - \exp(-\beta U_{\mathrm{id}})$ of the depletion potential of an ideal polymer blend is additive, i.e., it can be represented as a mass fraction-weighted sum of the Mayer functions of the partial depletion potentials calculated for each component of the blend. The same conclusion holds for the second virial coefficient of the depletion potential of an ideal polymer blend defined by $B \equiv 1/2\int[1 - \exp(-\beta U_{\mathrm{id}})]d^3r$. In the dilute polymer limit $R\eta_i^{-1} \ll 1$, the potential U_{id} at contact (i.e., at $r = 2R$) reduces to $-\beta^{-1}\pi b^2 R\rho/6$. Interestingly, this expression depends only on the total density $\rho = \rho_1 + \rho_2$. In the considered ideal limit, the local composition of the blend, therefore, does not affect the maximal absolute value of the depletion potential. In contrast, the depletion force $f(r) \equiv -\partial_r U(r)$ at contact reduces to the composition-dependent expression $\beta f(2R) = -\pi R b^2[(2R)^{-1}\rho + \xi_1^{-1}\rho_1 + \xi_2^{-1}\rho_2]/6$. Note that in the special case of homopolymer melt $N_1 = N_2$ the above expression for $f(2R)$ agrees, up to a numerical prefactor of $\sqrt{2}$, with the classical Asakura-Oosawa result [29–31]. Note that this difference stems from the difference between the ideal polymer correlation length $\xi_i = R_G^i/\sqrt{2}$ obtained in the frameworks of the PRISM theory and its counterpart used in Asakura-Oosawa theory, where this length is associated with the polymer gyration radius R_G^i.

In contrast to the case of an ideal polymer blend, in the case of the excluded volume polymers the sum in the rhs of Eq. (15) does not decompose into partial contributions coming from pure polymer species. The presence of the excluded volume interactions leads to an occurrence of the cross-species contributions to the depletion potential that significantly complicate the mass fraction and size ratio dependencies of the depletion potential. It is therefore instructive to separately analyze the protein [32] and colloid [33] limits where the polymers are smaller and larger than the colloid particles, respectively. In the protein limit, the depletion potential reduces to

$$\beta U = \frac{R^2}{r}\sum_{i,j=1}^{2}\eta_i^{-1}\zeta_i^j\exp\left(-\frac{(r-2R)}{\lambda_j}\right). \tag{17}$$

The at-contact (maximal) value of the depletion potential in the protein limit therefore reduces to a simple expression $\beta U(2R) = -\rho\pi b^2 R/6$ that does not depend on the composition of the blend. This latter expression agrees with that previously obtained in Ref. [2].

In the opposite colloid limit $R \gg \xi_{1,2}$, it is instructive to analyze the depletion force $f(r) \equiv -\partial_r U(r)$ in order to compare that against well-known results for the homogeneous polymer melt. In this limit the previous theory [2] predicts a simple expression $\beta f(2R) = -\xi^{-1}$ for the at-contact depletion force, ξ being the correlation length of the excluded volume polymers defined by $\xi = 3/(\pi b^2\rho)$ [2]. Note that taking the same limit and setting the density of one of the blend species equal to zero in $f(r) \equiv -\partial_r U(r)$ with U given by Eq. (16) leads to the same result. Interestingly, the presence of the described compositional correlations completely changes the

leading term in the colloid limit of $f(r)$. Taking the limit $R \geqslant \xi_{1,2}$ at $\rho_{1,2} \neq 0$ leads to a quite cumbersome expression for $f(2R)$ that can be significantly simplified by recognizing that $\lambda_2 \sim R_G^1 \gg \lambda_1 \sim \xi$. These manipulations lead to a simple result $\beta f(2R) = -\lambda_2^{-1} \approx -\phi\xi_1^{-1} - (1-\phi)\xi_2^{-1}$ that provides an additional evidence that in the colloid limit the range of the depletion force is mainly determined by that of the compositional correlations in the polymer blend.

Recall that the obtained depletion potential given by Eq. (15) describes only an attractive part of the total effective potential acting between colloids. In order to estimate the significance of the attractive depletion interactions mediated by the excluded volume polymers relative to the steric repulsion between the hard cores of the colloids, it is instructive to calculate the second virial coefficient of the total effective potential. Substituting U given by Eq. (15) into the definition of the second virial coefficient, one obtains

$$\frac{B}{B_{\rm HS}} = 1 - \frac{\pi b^2}{4R}\sum_{i,j=1}^{2}\rho_i\lambda_j^2\xi_i^j\gamma_i^j\left(1+\frac{\lambda_j}{2R}\right), \qquad (18)$$

where $B_{\rm HS} = 16\pi R^3/3$ is the second virial coefficient of the hard sphere fluid [22].

In order to simplify the analysis of the obtained expression for the second virial coefficient given by Eq. (18) in the most relevant physical case of dense polymer blends, we resort to the limit $N_i b^3\rho_i \gg 1$ $(i = 1,2)$ used in the end of the preceding section to analyze the correlation lengths of an athermal polymer blend. Recall, this limit covers both the cases of dense polymer systems and systems of long polymers having moderate densities that fulfill the above inequality. Under this approximation, the expression in Eq. (18) reduces to

$$\frac{B}{B_{\rm HS}} = \frac{1}{4} - \frac{3\xi}{8R}[1+\kappa(\phi,f)],$$
$$\kappa \equiv \phi(1-\phi)\left(\frac{1-f}{1-\phi(1-f)}\right)^2 \qquad (19)$$

where $\xi = 3/(\pi b^2\rho)$ is the composition-independent correlation length that coincides with the large density or long polymer limit of the correlation length of the homopolymer system having the same total density $\rho = \rho_1 + \rho_2$.

As should be expected, in the cases $N_1 = N_2$ and $\phi = 0,1$, the expression for the reduced virial coefficient given by Eq. (19) reduces to its counterpart $B/B_{\rm HS}$ calculated [2] for the polymer melt having the same density ρ. The occurrence of the above described cross-species terms in the depletion potential results in the occurrence of the correction to $B/B_{\rm HS}$ described by the term κ in the brackets in the rhs of Eq. (19). Note that this additional term is always positive, which leads to the conclusion that the attractive depletion interactions generally have larger magnitude in a polymer blend relative to that in a homopolymer melt having the same density. In the limit where the partial densities ρ_i are larger than the polymer overlap densities [34] calculated for N_i, the virial coefficient is a simple increasing power function of the total density. This density dependence is imposed by the prefactor of the second term in the square brackets in the rhs of Eq. (19), which is proportional to the "melt" correlation length $\xi \sim \rho^{-1}$. Note that the factor in the square brackets in the rhs of Eq. (19) describes the correction to the melt value of the second virial coefficient, specific to the polymer blend characterized by the mass fraction ϕ of a shorter polymer species and the polymer size ratio parameter f. It is important to note that the described correction term depends only on ϕ and f, so it does not contribute to the dependence of the second virial coefficient on the total density of the blend. The described dependence of B on the quantities ϕ and f imposed by the described correction term κ shows several interesting features discussed below.

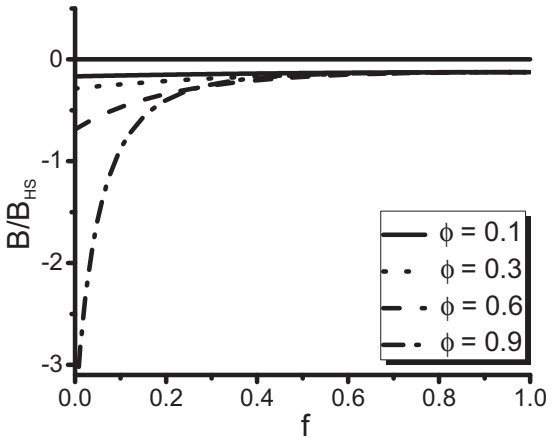

FIG. 4. Dependence of the reduced second virial coefficient $B/B_{\rm HS}$ on the polymer size ratio parameter f for several selected values of the mass fraction ϕ. The value of the reduced colloid radius R/ξ is set equal to unity.

Note that κ in the rhs of Eq. (19) can be represented in the form $\kappa = \phi(1-\phi)\lambda_2^2(\xi_1^{-1} - \xi_2^{-1})^2$ that clearly shows that the correction to the melt value of the virial coefficient is proportional to the square of the compositional correlation length λ_2. Recall, this length describes the compositional correlations caused by the local fluctuations of the composition of the polymer blend. According to the expression in Eq. (19), these long-range compositional correlations give the contribution to the depletion interactions of the same order as that caused by the compressibility of the polymer blend. The dependence of the compositional correlation length λ_2 on the mass fraction ϕ and size ratio f imposes a nontrivial behavior of the second virial coefficient as a function of ϕ and f illustrated in Figs. 4 and 5.

Figure 4 shows the dependence of the reduced second virial coefficient $B/B_{\rm HS}$ given by Eq. (19) on the size ratio parameter f for selected values of the mass fraction ϕ at $R = \xi$. As can be seen from this figure, the absolute value of $B/B_{\rm HS}$ monotonically increases with decreasing f. The larger difference between the polymerization degrees of the polymer species therefore plays in favor of increasing the depletion attraction between the colloids. This effect is stronger the larger the mass fraction of the shorter polymer species. This trend stems from the fact that the correlation length λ_2 quantifying the range of the compositional correlations increases with increasing the mass fraction of the shorter polymers in the blend. An increase in a relative amount of shorter polymers in the blend therefore leads to the observed increase in the absolute value of the second virial coefficient corresponding to increasing the attractive depletion interactions.

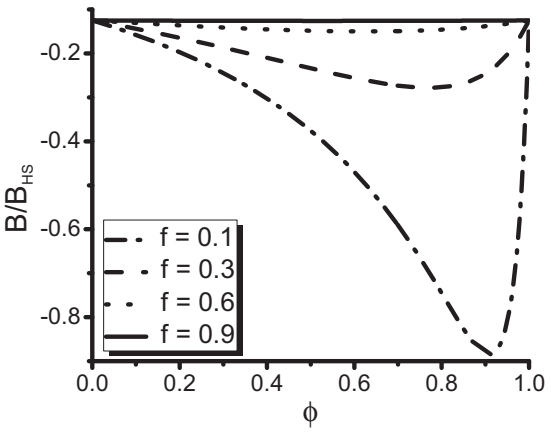

FIG. 5. Dependence of the reduced second virial coefficient $B/B_{\rm HS}$ on the mass fraction ϕ of shorter polymers for several selected values of the polymer size ratio parameter f. The value of the reduced colloid radius R/ξ is set equal to unity.

In contrast to the described simple monotonic dependence of the virial coefficient B on the size ratio parameter f, the dependence of B on the mass fraction ϕ is described by a nonmonotonic function featuring a minimum. This dependence is shown in Fig. 5 for several selected values of f and $R = \xi$. According to this figure, $B(\phi)$ is a decaying function of ϕ at small and moderate mass fractions of the shorter polymers in the blend. This behavior of $B(\phi)$ stems from the above described trend of increasing the correlation length λ_2 with increasing the relative amount of the shorter polymers. Interestingly, upon crossing the f-dependent threshold value of the mass fractions corresponding to the minima of the curves shown in Fig. 5, the virial coefficient becomes a monotonically increasing function of ϕ. The occurrence of the described minimum of the function $B(\phi)$ at $\phi = (1 + f)^{-1}$ is imposed by the factor $\phi(1 - \phi)$ that enters the correction term κ in the rhs of Eq. (19). Note that the same factor enters the nonadditive correction ΔP to the partial pressures caused by the cross-species contributions to the total pressure of a polymer blend given by the last term in the rhs of Eq. (6). This observation can be interpreted as that the described nonmonotonic behavior of the second virial coefficient as a function of the mass fraction ϕ stems from the similar nonmonotonic behavior of the pressure of a polymer blend as a function of ϕ. Recall that the pressure of a uniform polymer system is a counterpart of the grand canonical potential of a nonuniform polymer system that must be at minimum [5] under the full equilibrium conditions [8,34] with respect to the polymers. Recall, these conditions imply free exchange of the polymers between the depletion layers surrounding the colloids and the bulk polymer system. Under the described full equilibrium conditions, the local change of pressure (i.e., coordinate-dependent density of the grand potential) of a polymer blend is therefore a proper measure of the impact caused by the immersed colloids on the thermodynamic state of a polymer system. The depletion interaction between colloids is caused by a tendency to minimize this impact quantified by the described colloid-induced changes in local pressure. This argument explains the observed similarity of the nonmonotonic dependencies of the second virial coefficient of the depletion potential and the pressure of a pure polymer blend on the mass fraction ϕ.

V. CONCLUSIONS

In the present paper we investigate the depletion interactions acting between colloids immersed in an athermal polymer blend. The blend is composed of two species of polymers that differ in the polymerization degree and mass fraction. In order to describe the density structure of the polymer blend, we derive the expressions for the total correlation functions given by Eqs. (4). These expressions take into account the excluded volume interactions between monomers of same and different polymer species described in the frameworks of the thread polymer approximation [21]. The investigation of the structure of the obtained expressions for the total correlation functions shows that these functions contain two different correlation lengths λ_1 and λ_2, each describing different physical mechanisms of the correlations in a polymer blend. In the ideal polymer blend, where the excluded volume interactions between the polymers are totally absent, the above correlation lengths reduce to their ideal counterparts $R_G^i/\sqrt{2}$ proportional to the radii of gyration of the respective polymer species. This observation is explained by the fact that in the ideal polymer blend the correlations between density fluctuations of different polymer species are independent. In a blend of the excluded volume polymers, in contrast, the density correlations in different polymer species do not decouple, which causes cross-species correlations. These cross-species correlations are found to be especially pronounced in the case of a relatively dense polymer blend described by inequalities $b^3\rho_i N_i \gg 1$. Specifically, in this case one correlation length (λ_1) describes the density correlations imposed by a finite compressibility of the polymer blend. At large densities, this length is independent of the mass fractions ϕ_i of the polymer species and the blend composition quantified by the polymer size ratio $f = \sqrt{N_2/N_1}$. The second correlation length λ_2, in contrast, depends only on the above mentioned parameters ϕ_i and f, and therefore describes the compositional correlations caused by local fluctuations of the mass fractions of the polymer species. These compositional correlations are specific to a polymer blend, as they are caused by the local redistribution of polymer species without changing the local total density of the blend. In contrast to the density correlations observed in a polymer melt, the described compositional correlations are therefore not relevant to the compressibility of a polymer system.

In order to investigate the role of the described compositional correlations in the polymer-colloid correlations, we calculate the immersion energy W of the colloid defined as an excess chemical potential of the polymer blend caused by the presence of this colloid. The result of this calculation, given by Eq. (13), shows that W occurs to be a nonadditive quantity. Specifically, the obtained immersion energy does not reduce to the sum of the immersion energies caused by the presence of the polymer species taken separately. The correction nonadditive term in the immersion energy occurs to be proportional to the mean inverse correlation length $(\tilde{\xi}_1^{-1} + \tilde{\xi}_2^{-1})/2$ that quantifies the reciprocal width of the depletion layer formed around the colloid. Therefore, both the compressibility (λ_1) and

compositional (λ_2) correlation lengths equally contribute to the above nonadditive correction and the immersion energy W.

As a most important result of the present paper, we calculate the potential of the depletion interaction acting between colloids immersed in an athermal polymer blend. The obtained depletion potential is given by Eq. (15) as a function of the separation between colloids, colloid radius, correlation lengths $\tilde{\xi}_i$, and their ideal counterparts ξ_i. In order to take into account the steric interactions between colloids and their significance relative to the depletion interactions, we calculate the second virial coefficient B of the total effective potential acting between colloids given by Eq. (18). In the case of an ideal polymer blend, the second virial coefficient occurs to be additive, i.e., it reduces to the sum of the mass fraction weighted partial virial coefficients of the polymer species. This simple additive structure of the virial coefficient of the ideal polymer blend stems from the independence of the partial density correlations in different polymer species comprising this blend. In the case of a blend composed of the excluded volume polymers, the occurrence of the cross-species nonadditive terms significantly complicates the dependence of the virial coefficient on the density and composition of this polymer blend. The described nonadditive terms are caused by the correlations between the fluctuations of the partial densities of polymers of different species.

With the objective to understand the effect of different correlation mechanisms on the depletion interaction acting between colloids immersed in a dense polymer blend, we calculate the large density limit of the second virial coefficient B expressed by Eq. (19). In this limit, the above described compositional correlations cause a significant contribution to the second virial coefficient relative to its counterpart calculated for the homogeneous polymer system having the same density. This contribution is shown to promote increasing the attractive depletion interactions at all values of the mass fraction ϕ and the polymer size ratio f. The magnitude of the described contribution is proportional to the squared compositional correlation length λ_2, which corroborates an essential role of the compositional correlations, specific to a polymer blend, in shaping the mass fraction dependence of B. In addition, B has a minimum as a function of the mass fraction ϕ, which is shown to stem from the nonmonotonic dependence of the blend pressure on ϕ described by Eq. (6).

Note that the obtained expression for the depletion potential acting between colloids immersed in a polymer blend is obtained in the infinite dilution limit with respect to the colloids. Similarly to the previous work [2,3] on the depletion interactions, this approach does not cover the colloid many-body effects that can give essential [35] contributions to the thermodynamic properties of filled polymer systems in the protein limit of small colloids. Despite that fact, the obtained depletion potential can contribute a critical ingredient necessary to better understand the phase separation of the colloid-polymer blend systems [36]. Owing to the mentioned limitations, addressing the described phase separation requires an essential extension of the present approach that will be reported elsewhere.

The main qualitative conclusion that can be drawn from the above outlined results is that the described compositional correlations, specific to a polymer blend, are equally important for thermodynamic properties of colloid-polymer systems as the compressibility induced correlations. These correlations prove to give the same order contributions to the colloid immersion energy and the virial coefficient of the depletion potential, so they cannot be neglected in a quantitative analysis of statistical properties of polymer blends. The described contributions, calculated in the present paper, show a strong dependence on the composition and the polymer size ratio of a polymer blend. This fact can be effectively used, in particular, for governing the overall strength of the depletion interactions and associated phenomena of the colloid coagulation or flocculation by choosing the components of a host polymer blend having suitable physical properties.

ACKNOWLEDGMENT

Financial support from Deutsche Forschungsgemeinschaft through Grant No. CH 845/2-1 is gratefully acknowledged.

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