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ORIGINAL CONTRIBUTION

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Determination of the amplitude of the repulsive-pair potential between particles clothed by end-grafted polymers

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Abstract We examine the problem of the determination of the repulsive potential between spherical particles clothed by long end-grafted flexible polymers. This potential varying with the distance according to a logarithmic law has a potential amplitude that depends on the number, L, of grafting chains per particle. The purpose of this work is to compute such a potential amplitude. The clothed particles are first regarded as star polymers with small enough diameter and the same number of arms. Then, the amplitude potential is identified to the critical exponent related to the contact probability between cores of these stars, which allows us to find a universal function for the expected potential amplitude depending on L and d-space dimension only. In two-dimensional space, conformal invariance is used to extract the potential amplitude as a function of L. For dimensions greater than 2, the potential amplitude is obtained within the framework of renormalization theory to third order in $\varepsilon = 4 - d$, where d is the critical dimension of the system. To determine the best three-dimensional expression for the potential amplitude, A_L, use is made of the Padé–Borel transformation, which provides a closer form valid for small, intermediate and high values of L. This form of potential amplitude, consistent with the exact scaling asymptotic value of Witten and Pincus [(1986) *Macromolecules* 19:2509], allows us to find the associated prefactor. The procedure is also extended to interacting stars of different numbers of arms.

Introduction

Most colloidal systems are made of grains having a tendency to flocculate owing to the existence of certain long-range van der Waals attractions. The introduction of soluble polar head polymers leads to a grafting phenomenon such that two adjacent clothed grains repel each other until the stabilization of the colloids is achieved owing to the excluded-volume forces between monomers. Grafted polymers on solid walls or fluid interfaces are of considerable interest and find many physicochemical applications [1]. We can quote, as typical examples, adhesion [2], wetting [3], chromatography [4] and colloidal stabilization [5]. A classic overview on steric stabilization can be found in the textbook of Napper [6] and in the review article of Halperin et al. [7]. From a theoretical point of view, grafted chains or simply polymer brushes on a plane surface were studied for the first time by Alexander [8] and by de Gennes [9], using essentially scaling arguments. In the same way, Milner and coworkers [10] elaborated a self-consistent-field (SCF) method for studying the end effects in polymer brushes.

Some years ago, Witten and Pincus (WP) [11] were interested in the determination of the repulsive potential between spherical particles clothed by long end-grafted flexible chains. According to these authors, the potential varies with the distance, r, between a pair of particles as a logarithmic law. In addition, using a blob argument, the authors stated that the potential amplitude, A_L, increases with the number, L, of branches per particle as $A_L \sim L^{3/2}$.

The present work deals with the same problem. More precisely, the purpose is to carry out a calculation of the potential amplitude A_L, for any value of the number, L, of arms per clothed particle of small enough diameter. The key to the problem consists of regarding the small-clothed particles as star polymers and to take advantage of the results already established within the framework of the star polymer field. The physics of star polymers in good solvents is the subject of a great deal of attention in both experimental [12] and theoretical studies. A useful reference concerning star polymers is the review of Grest et al. [13]. Theoretical work was pioneered by Daoud and Cotton [14] (DC) and Birnstein and Zhulina [15] and was followed by several others using renormalization techniques [16–19], Monte Carlo [20, 21] and molecular dynamics simulations [22, 23]. All these works agree with the DC picture, at least in the dilute regime, for which each chain of the star can be viewed as a sequence of growing spherical blobs. We note that the conformational study of a star polymer is quite different from that relative to a polymer brush having the same number of arms. For star polymers, the dense region is a small domain barely greater than the core of the polymer, while beyond the core the system becomes diluted because of the excluded-volume forces. This is not the case for polymer brushes, where the system remains dense over a length of the same order as the maximal extension of an isolated chain, which scales as the degree of polymerization [8–10]. This explains why the DC picture is more adequate to study star polymers than the SCF method, which is useful for studying polymer brushes.

In this article, we consider a low-density assembly of very small particles clothed by end-grafted chains that we regard as star polymers. These particles are assumed to be immersed in a good solvent and to interact via an effective-repulsive-pair potential due to the excluded-volume forces between monomers. The aim of this work is to determine the associated potential amplitude, A_L, at two and three dimensions. Our findings are the following. We first show that the expected potential amplitude can be identified with the contact critical exponent [24, 25], which is related to the contact probability between cores of two star polymers [19]. In two-dimensional space, where particles are small discs, conformal invariance [26] enables us to find an exact expression for A_L as a function of L. For dimensions greater than 2, the renormalization theory [27, 28] is used to deduce the potential amplitude to third order in $\varepsilon = 4 - d$, where $d = 4$ stands for the critical dimension of the system. In order to get a better three-dimensional form for A_L, use is made of the Padé–Borel transformation techniques [29, 30]. In particular, we find a closer form for the potential amplitude valid for any value of L and consistent with the asymptotic law obtained by WP [11]. An exact expression is also proposed for the proportionality constant, and the results are extended to interacting star polymers with different numbers of arms (polydisperse system).

This article is organized as follows. We give a brief presentation of the static study of single end-grafted polymers and of the repulsive potential that is related to the contact probability. Then, our results concerning calculations of the potential amplitude and related discussions are presented.

End-grafted polymer problem: conformation and interactions

In a set of identical spherical particles of small radius, r_0, embedded in a good solvent, each particle is supposed to be clothed by L end-grafted linear chains (Fig. 1), all grafted chains having the same degree of polymerization, N, so they can be regarded as L-arm star polymers.

To study the conformation of an isolated star polymer, use will be made of the DC model [14], which is briefly reviewed, whose spirit consists of regarding each chain as a sequence of growing spherical blobs. If it is assumed that L blobs of the same size are located at a given distance, r, from the center (one for each arm), the following expression is immediately obtained from geometrical considerations,

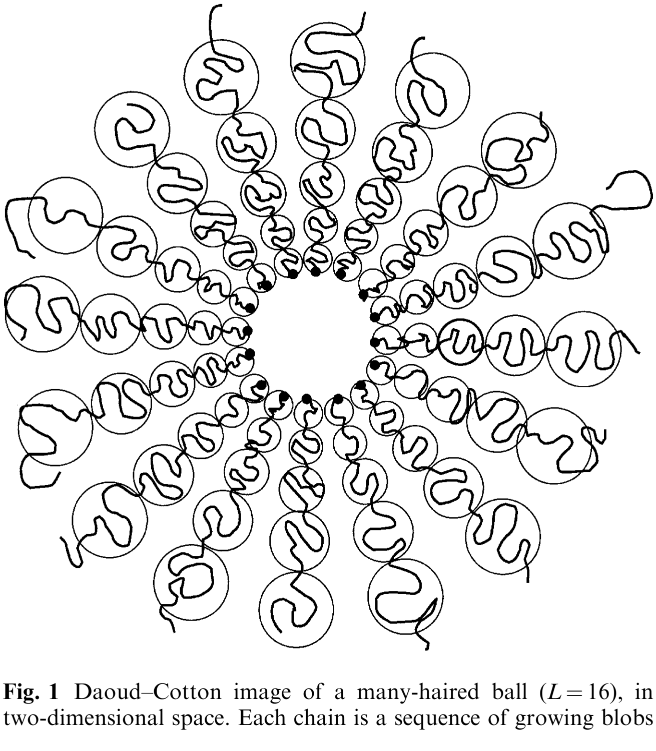

Fig. 1 Daoud–Cotton image of a many-haired ball ($L = 16$), in two-dimensional space. Each chain is a sequence of growing blobs

$$\xi(r) \sim L^{-1/2} r \ . \tag{1}$$

This leads to an L-dependent local density,

$$\phi(r) \sim L^{\frac{3\nu-1}{2\nu}} r^{\frac{1}{\nu}-3} \ , \tag{2}$$

as well as to an L dependence of the radius of gyration, R, of the star, after integrating the L-dependent local density, namely

$$R \sim aL^{(1-\nu)/2} N^{\nu} \ , \tag{3}$$

where a is the monomeric dimension. In the DC model the correlation length critical exponent, ν, is taken to be the same as for the linear chain ($\nu = 3/5$). It is found that Eq. (2) holds only in the outer-part regime of a star: $\phi(r)$ is first given by a constant value in the core of the star and then looks like a concentrated solution at an intermediate region up to $r < aL^{1/2}\nu^{-1}$, where ν is the excluded volume. It should be stressed that the existence of the two inner-part regimes could not be seen in a simulation of many-arm stars, while the prediction of the DC model is remarkable [21, 22] for large distances where the excluded-volume effects are considered.

In the following we restrict our study to dilute solutions for a particle volume fraction lower than the threshold value:

$$\rho^* \sim \left(\frac{r_0}{R}\right)^3 \ . \tag{4}$$

This important formula shows that the knowledge of the particle radius, as well as of the radius of gyration obtained by X-ray measurement, allows the characteristic particle volume fraction, ρ^*, to be estimated. So, it is possible to generalize the previous results to the case of a dilute solution of particles clothed by end-grafted chains in any arbitrary space dimension (balls if $d = 3$, discs if $d = 2$). Specifically, a comparison between the results for $d = 2$ and $d = 3$ clearly shows the importance of the excluded volume at two dimensions.

After these main outlines of the conformation study of star polymers in dilute solutions, we focus on the effective interaction between clothed particles and on its connection with the contact probability between particles. From a topological point of view, an L-star polymer is a connected trivial network made of L chains tied together at one core. If the system is assumed to be immersed in a good solvent, the chains interact through the excluded-volume interactions. The polymer chains can be regarded as Brownian chains with two-body contact interactions and can be treated with the so-called Edwards continuous model [25, 31], with two phenomenological parameters. One is the Brownian area proportional to the degree of polymerization, N, of chains, which has a dimensionality compatible with the fact that a Brownian chain is a fractal object whose Hausdorff [32] dimension is 2. The other parameter involving the two-body contact interaction is proportional to the excluded volume. Note that this coupling parameter becomes marginal [25, 33] at the critical dimension $d = 4$.

The effective-pair potential expresses the competition between two kinds of interactions. One is the long-range van der Waals attraction giving rise to the flocculation of small particles [34]. The other is the short-range repulsive interaction produced by polymers that can be sufficient, in certain cases, to stabilize a dispersion of small particles despite their inherent tendency to precipitate. As a matter of fact, the important question that arises is about the determination of the form of the short-range repulsive potential, $U(r)$. This problem, partially solved by WP [11], was based on the possibility to express the expected potential, $U(r)$, in terms of the contact probability, $P(r)$, owing to the standard relationship

$$P(r) = P(\infty)\exp[-U(r)/k_{\mathrm{B}}T] \ , \tag{5}$$

where $P(\infty)$ is just the concentration of small particles. The problem, solved by WP for two opposite cases (small-L limit and large-L limit), was to show how the $U(r)$ depends on the degree of polymerization, N, as well as on the number, L, of arms, for very large polymers compared to the size of the particles.

In the case where each particle has one chain polymer only ($L = 1$), the following form for $P(r)$ was assumed

$$P(r) = P(\infty)\Phi(r/R) \ , \tag{6}$$

where R is the chain dimension and $\Phi(r/R)$ a universal scaling function that vanishes at small distances according to the des Cloizeaux law [24]:

$$\Phi(r/R) \sim (r/R)^{(\gamma-1)/\nu} \ . \tag{7}$$

The critical exponents ν and γ characterize, respectively, the behavior of the radius of gyration and the total number of a self-avoiding walks of N steps describing the real chain on the lattice. The combination of Eqs. (5), (6) and (7) gives the expected result for the short-range repulsive interaction, namely

$$\frac{U(r)}{k_{\mathrm{B}}T} \sim \frac{(\gamma-1)}{\nu}\ln(R/r) \ . \tag{8}$$

In the realistic situation where L becomes larger than unity, each grafted chain can be viewed as a sequence of growing spherical blobs and can be described along the lines of the DC model. Taking account of the blob argument, if two particles are brought within a distance of the order r_0 of each other, it is found that the bulk of the system is similar to a single particle with $2L$ arms. As a consequence, the increase in the free energy per particle, in this process, is exactly the repulsive potential, and the probability, $P(r)$, that two particles are at a displacement r is again a power law

$$P(r) \sim P(\infty)(r/R)^{\theta(L)} \ , \tag{9}$$

where $\theta(L)$ varies as $L^{d/(d-1)}$, in contrast with the leading behavior for small values of L. Thus, the interparticle pair potential generated by the repulsion of many arms again follows a logarithmic law with a potential amplitude $\theta(L)$ depending on the number of arms.

Determination of the potential amplitude

Monodisperse system

The purpose of this section is to extend the WP power law to star polymers of any arbitrary number of arms and to examine the behavior of the potential amplitude for a given value of L. Owing to the high monomer density, a strong repulsive potential takes place at short distances as discussed previously, and the contact probability, $P(r)$, between the cores of two-star polymers made, respectively, of L_1 and L_2 arms (Fig. 2) can be assumed under the scaling form

$$P(r) \sim r^{\theta(L_i)} \quad (r \to 0) \ , \tag{10}$$

where $\theta(L_i)$ are universal exponents that depend on the numbers of arms, L_1 and L_2, as well as on the d-dimensional space. Mention has to be made that the contact exponents, $\theta(L_i)$, are directly related to configuration exponents, γ_{L_i}, by the scaling relation [19]

$$v\theta(L_i) = \sum_{i=1}^{2} (\gamma L_i - 1) - \left(\gamma_{L_i+L_2} - 1\right) \ . \tag{11}$$

This relationship, known as the fusion rule, means that the configuration exponents of the new star made of $(L_1 + L_2)$ arms must be subtracted from those of the stars before their contact.

When the two stars have the same number of arms (monodisperse system), the simple notation $\theta(L_i) = \theta_L$ is used. Thus, as far as a star polymer made of L arms with the same degree of polymerization, N, is concerned, it has been shown [19] that the number of configurations of an L-arm star is

$$Z_L \sim \mu^{LN} N^{\gamma_L - 1} \ , \tag{12}$$

where μ stands for the effective connectivity constant [35], which depends strongly on the nature of the lattice.

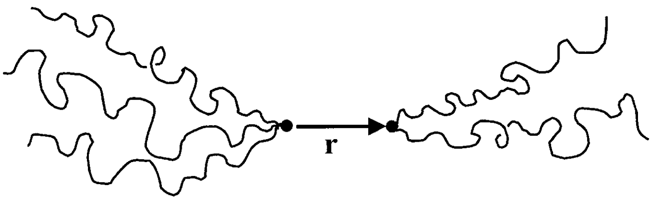

Fig. 2 Contact between two L_1 and L_2 star polymers ($L_1 = 3$, $L_2 = 2$) separated by a distance r

In contrast γ_L is a universal exponent crucially depending on the topology, i.e. the number of arms and d-dimensional space. In two-dimensional space, the exponent γ_L is calculable exactly using conformal invariance [36] by the expression

$$\gamma_L(d = 2) = \frac{68 + 9L(3 - L)}{64} \ . \tag{13}$$

Note that the equality between γ_1 and γ_2 is readily verified by Eq. (13). In three-dimensional space, γ_L is also calculable [37, 38] to third order in $\varepsilon = 4 - d$, indicating that a star polymer has a critical dimension ($d = 4$) irrespective of the number of arms.

By substituting Eq. (13) into the formally exact expression (Eq. 11), we are now in a position to obtain the potential amplitude $\theta_L = A_L$ for a two-dimensional monodisperse system, namely

$$A_L(d = 2) = \frac{2 + 9L^2}{24} \ . \tag{14}$$

The variation of the two-dimensional potential amplitude versus L is depicted in Fig. 3. Incidentally, we remark that $A_L(d = 2)$ is a rational number for all values of L.

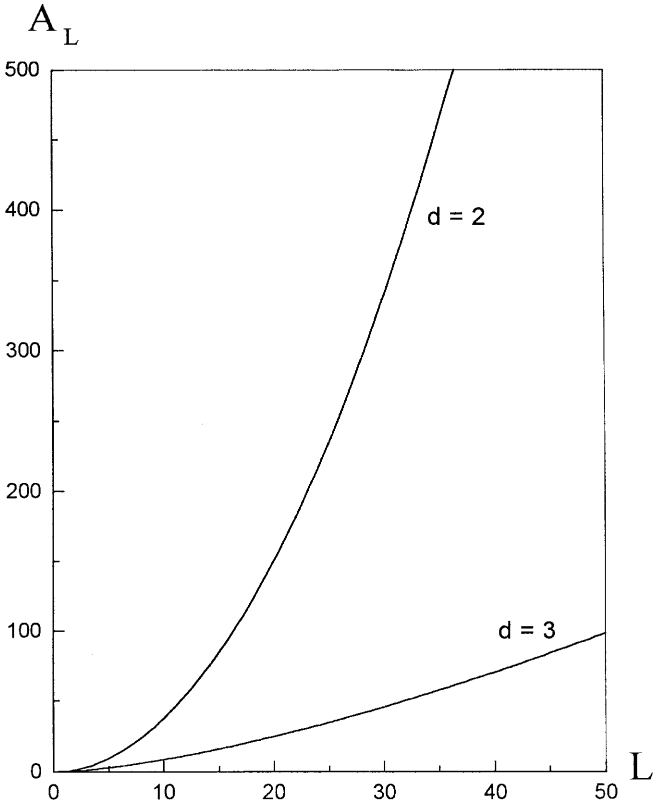

Fig. 3 Potential amplitude, A_L, in two- and three-dimensional spaces upon the number of arms by star

In order to apply the model to monodisperse systems for dimensions greater than 2, we use the expressions [37, 38] of the exponents v and γ_{L} expanded to the third order in $\varepsilon = 4 - d$. After making their substitution into Eq. (11), the following expression of the potential amplitude is obtained under the formal power series

$$A_L = \left\{2L^2\left(\frac{\varepsilon}{8}\right)\left\{1+\left(\frac{\varepsilon}{8}\right)\left(\frac{33}{4}-6L\right)\right.\right. \\ \left.\left. +\left(\frac{\varepsilon}{8}\right)^2\left(56L^2+\left[84\zeta(3)-171\right]L-117\zeta(3)+\frac{\varepsilon}{8}\right)\right\}\right\}, \tag{15}$$

where $\zeta(3) = 1.202$ is the Riemann function, ($\zeta(x) = \sum_{n=1}^{\infty} n^{-x}$), for the value $x = 3$.

It is worth noting that the series in Eq. (15) no longer has a sense since its representation fails to converge for any value of L; therefore, we estimate the asymptotic behavior of A_{L} from the knowledge of the first three coefficients of the series, by using the standard Padé approximant and the Borel–Leroy transform [29, 30]. To this end, we first set the infinite series

$$A_L = 2L^2 uF(u) \ , \tag{16}$$

where $u = \frac{\varepsilon}{8}$ and $F(u) = \sum_n F_n u^n$, in which the first three coefficients, F_{n}, are

$$F_0 = 1 \ , \tag{17}$$

$$F_1 = \frac{33}{4} - 6L \ , \tag{18}$$

$$F_2 = 56L^2 + [84\zeta(3) - 171]L - 117\zeta(3) + \frac{973}{8} \ . \tag{19}$$

Then we use the integral representation of the Borel–Leroy transform to express the initial series, $F(u)$, as

$$F(u) = \int_0^{\infty} \mathrm{d}t \cdot t^b \exp(-t) F_{\mathrm{B}}(ut) \ , \tag{20}$$

where

$$F_{\mathrm{B}}(ut) = \sum_n F'_n (ut)^n \ ,$$

with

$$F'_n = \frac{F_n}{\Gamma(n+b+1)} \ . \tag{21}$$

In Eq. (21), $\Gamma(x)$ is the gamma function and b a fit parameter that will be determined later.

The next step consists of replacing the function $F_{\mathrm{B}}(ut)$ in the right-hand side of Eq. (20) by its convenient $P(0,2)$ Padé approximant [39] written as

$$F_{\mathrm{B}}(ut) = \frac{F'_0}{1 + \alpha(ut) + \beta(ut)^2} \ , \tag{22}$$

where

$$\alpha = \tfrac{F'_1}{F'_0} \quad \text{and} \quad \beta = \tfrac{(F'_1)^2 - F'_2}{(F'_0)^2} \ . \tag{23}$$

Substituting Eq. (21) into Eq. (23) yields

$$\alpha = \frac{6L - 33/4}{b+1} \ , \tag{24}$$

$$\beta = \frac{(6L - 33/4)^2}{(b+1)^2} - \frac{56L^2 + [84\zeta(3) - 171]L - 117\zeta(3) + \frac{973}{8}}{(b+1)(b+2)} \ . \tag{25}$$

With these two quantities it is now possible to find an approximate expression for $F_{\mathrm{B}}(ut)$ and to perform the integration in Eq. (20). We anticipate that the rational part of the quantity inside the integral is an analytic function of the ut variable for large-integer L and the selected b value. Therefore, the integral, absolutely convergent for the desired values of L and b, is simply evaluated using mathematics tables [40]. Thus $F(u)$ can be written as

$$F(u) = \frac{1}{\beta u^2} \frac{(-x_1)^b \exp(-x_1)\Gamma(-b, -x_1) - (-x_2)^b \exp(-x_2)\Gamma(-b, -x_2)}{(x_1 - x_2)} \tag{26}$$

provided that $Re(b + 1) > 0$. Here, $\Gamma(b,x)$ is the incomplete gamma function and x_1 and x_2 are the two roots of the polynomial in the denominator of Eq. (22), namely

$$(x_1, x_2) = \frac{-\alpha \pm \sqrt{\alpha^2 - 4\beta}}{2\beta u} \ . \tag{27}$$

It is found that $F(u)$ is a real quantity as the real parts of both roots are negative and the positive t-axis does not exhibit any pole. Finally, the substitution of Eq. (26) into Eq. (16) allows us to determine a close expression for the potential amplitude,A_{L}, depending on b and L through the quantities x_1 and x_2. In doing this, the asymptotic limits of the relevant quantities are calculated for large values of L and the gamma functions are replaced by their dominant parts. Under these circumstances, it is found that the asymptotic relation of the potential amplitude scales as $A_{\mathrm{L}} \sim L^{1-\mathrm{b}}$. Then, in order to extract the unknown value of b, we assume that the potential amplitude behaves like that of the WP model for star polymers with a large number of arms ($A_L \sim L^{d/(d-1)}$).

For the three-dimensional space, this implies the special value for the unknown parameter b equals to $-1/2$, leading to the following asymptotic behavior for the potential amplitude consistent with that of WP

$$A_L(d=3) = 0.234L^{3/2} \ . \tag{28}$$

For the two-dimensional space, the asymptotic expression of the potential amplitude is found by the same reasoning to vary as

$$A_L(d=2) = 0.5L^2 \ , \tag{29}$$

with $b = -1$ and $F(u) \sim 1$. Indeed, this approximate expression for $A_L(d=2)$ can be directly compared to the exact relation (Eq. 14), which is $A_L(d=2) \sim (3/8)L^2$. The model gives a rough estimation of the potential amplitude for $d=2$ and is likely to be worse than for $d=3$ if we consider that the Padé approximant is better for small values of ε.

The variation of the three-dimensional potential amplitude obtained with Eq. (16), as well as the two-dimensional one, versus the number of arms, L, is shown in Fig. 3. In two-dimensional space the number of contacts between monomers is less important than that in three-dimensional space, making the excluded-volume forces stronger; therefore, the curve for $d=2$ remains above that of $d=3$ for all values of L. While Eq. (16) is only valid for values of $L>5$, for which x_1 and x_2 are complex roots, it should be stressed that the asymptotic form (Eq. 26) is a good approximation for the potential amplitude even for small L, as shown in Table 1. For instance, the first two values of the contact exponent are in good agreement with those in the literature [24, 25].

Table 1 Potential amplitude, A_L, in two- and three-dimensional spaces, for a few small values of the number of arms by star, obtained with Eqs. (14) and (28), respectively

L	A_L ($d=2$)	A_L ($d=3$)
1	11/24	0.234
2	19/12	0.662
3	83/24	1.216
4	146/24	1.873
5	227/24	2.618

Polydisperse system

The previous expression for the amplitude potential can be extended to two interacting star polymers of different numbers of arms, L_1 and L_2. In two-dimensional space, the exact expression of the potential amplitude is

$$A_{L_1,L_2}(d=2) = \frac{2+9L_1L_2}{24} \ , \tag{30}$$

while its expression for dimensions greater than 2 is obtained under the following series, after that the critical exponents are expanded to third order in ε,

$$\begin{aligned} A_{L_1,L_2} = 2L_1L_2\left(\frac{\varepsilon}{8}\right)\Bigg\{ & 1 + \left(\frac{\varepsilon}{8}\right)\left(\frac{33}{4} - 3(L_1+L_2)\right) \\ & + \left(\frac{\varepsilon}{8}\right)^2 \Bigg[\left(16L_1^2 + 16L_2^2 + 24L_1L_2\right) \\ & + \left(42\zeta(3) - \frac{171}{2}\right)(L_1+L_2) \\ & - 117\zeta(3) + \frac{973}{8} \Bigg] \Bigg\} \ . \end{aligned} \tag{31}$$

As earlier, we use the Padé–Borel transformation, with $b = -1/2$, to get the expression for $A_{L_1,L_2}(d=3)$, which is analogous to that of the monodisperse system, namely

$$A_{L_1,L_2}(d=3) = \frac{16L_1, L_2(-y_1)^{-1/2}\exp(-y_1)\Gamma(1/2,-y_1) - (-y_2)^{-1/2}\exp(-y_2)\Gamma(1/2,-y_2)}{(y_1 - y_2)} \ , \tag{32}$$

where

$$(y_1, y_2) = 4\frac{-\sigma \pm \sqrt{\sigma^2 - 4\tau}}{\tau} \ , \tag{33}$$

with the coefficients

$$\begin{aligned} \sigma &= \frac{33}{2} + 6(L_1+L_2) \ , \\ \tau &= \frac{1321}{12} + 156\zeta(3) - [56\zeta(3) + 84](L_1+L_2) \\ &\quad + \frac{44}{3}(L_1^2 + L_2^2) + 40L_1L_2 \ . \end{aligned}$$

Using the same procedure as for monodisperse systems, we deduce the asymptotic form for $A_{L_1,L_2}(d=3)$,

$$A_{L_1,L_2}(d=3) = A_0(\eta)\left[\frac{L_1+L_2}{2}\right]^{3/2} \ , \tag{34}$$

where

$$A_0(\eta) = \frac{1}{8}\Gamma\left(\frac{1}{2}\right)\left(\frac{48}{-32\eta^2+32\eta+44}\right)^{1/4}\frac{1}{\cos(\theta/2)} \qquad (35)$$

and

$$\theta = \arctan\left(\frac{\sqrt{-32\eta^2+32\eta+17}}{3\sqrt{3}}\right) , \qquad (36)$$

with the fraction $\eta = L_1/(L_1+L_2)$. Note that all the corresponding expressions of the monodisperse system are recovered when $L_1 = L_2 = L$ and $\eta = 1/2$. Finally, as in the monodisperse case, we derive an extrapolated asymptotic form of the two-dimensional potential amplitude for polydisperse systems that reads $A_{L_1 L_2}(d=2) \sim 0.5 L_1 L_2$.

Conclusion

We recall that the aim of this work is to determine the potential amplitude of the repulsive potential experienced by particles clothed by L end-grafted linear chains. This potential results from excluded-volume forces between monomers along these chains. Firstly, we have regarded the clothed particles as star polymers. This assumption is tractable only when the particles have a small enough diameter. Secondly, we have identified the potential amplitude with the critical exponent related to the contact probability between cores of stars. In this sense, the expected potential amplitude is a universal function depending on the number of arms, L, and d-dimensional space only.

The potential amplitude, A_{L}, is first written in terms of a series expanded to third order in ε. Then its asymptotic behavior is estimated within the framework of renormalization theory from the knowledge of the first three coefficients of the series in using the standard Padé–Borel transformation technique. A close form of A_{L} is thus established with associated prefactors consistent with the asymptotic law $A_{\mathrm{L}} \sim L^{\mathrm{d}/(\mathrm{d}-1)}$, which is valid for intermediate and high values of L. As mentioned, in two-dimensional space, conformal invariance leads to an exact expression for the potential amplitude as a function of L against which our result can be compared. The calculations have also been extended to interacting star polymers of different numbers of arms, showing a similar asymptotic law for polydisperse systems.

It should be noted that this work must be considered as a starting point of a program dealing with the study of the structural and thermodynamic properties of particles clothed by end-grafted polymers immersed in a good solvent. Extension of our results to particles of high diameter is not trivial and necessitates a more careful analysis.

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