Eur. Phys. J. E **2**, 311–318 (2000)

THE EUROPEAN PHYSICAL JOURNAL E

EDP Sciences

Triplet interactions in star polymer solutions

C. von Ferber, A. Jusufi, C.N. Likos, H. Löwen, and M. Watzlawek[a]

Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, D-40225 Düsseldorf, Germany

Received 1 September 1999 and Received in final form 18 January 2000

Abstract. We analyze the effective triplet interactions between the centers of star polymers in a good solvent. Using an analytical short-distance expansion inspired by scaling theory, we deduce that the triplet part of the three-star force is attractive but only 11% of the pairwise part even for a close approach of three star polymers. We have also performed extensive computer simulations for different arm numbers f to extract the effective triplet force. The simulation data show good correspondence with the theoretical predictions. Our results justify the effective pair potential picture even beyond the star polymer overlap concentration.

PACS. 82.70.Dd Colloids – 64.60.Fr Equilibrium properties near critical points, critical exponents – 61.20.Ja Computer simulation of liquid structure

1 Introduction

Star polymers [1], *i.e.*, structures of f linear polymer chains that are chemically linked with one end to a common core, have found recent interest as very soft colloidal particles [2–6]. As the number f of chains increases, they interpolate between linear polymers and polymeric micelles [1,2,7]. For large f, the effective repulsion between the cores of different polymer stars becomes strong enough to allow for crystalline ordering in a concentrated star polymer solution. While such a behavior was already predicted by early scaling arguments [8,9] only recently corresponding experiments have become feasible with sufficiently dense star solutions. The crystallization transition occurs roughly at the overlap concentration c^* which is the number density of stars where their coronae start to touch experiencing the mutual repulsion. It is defined as $c^* = 1/(2R_{\rm g})^3$, where $R_{\rm g}$, the radius of gyration, is the root mean square distance of the monomers from the center of mass of a single star. In addition, theory and computer simulation have refined the original estimate for the number of chains f necessary for a freezing transition from $f \sim 100$ [8,9] to $f \sim 34$ [5] and predicted a rich phase diagram including stable anisotropic and diamond solid structures at high densities and high arm numbers. These results were derived using an effective *pair potential* between stars with a logarithmic short-distance behavior derived from scaling theory.

In general, while the pair interactions are the central focus and the typical input of any many-body theory, much less is known about triplet and higher-order many-body interactions. For rare gases, the Axilrod-Teller triplet interaction [10] has been found to become relevant in order to describe high-precision measurements of the structure factor [11]. For charged colloids, the effective triplet forces are generated by nonlinear counterion screening. This was investigated recently by theory and simulations [12]. For star polymer solutions in a good solvent such studies are missing. In all three cases, the effective triplet forces originate from formally integrating out microscopic degrees of freedom. For rare gases, these are the fluctuations of the outer-shell electrons while for charged colloids the classical counterions play the role of additional microscopic degrees of freedom. For star polymers, on the other hand, one is interested in an effective interaction between the star centers by integrating out the monomer degrees of freedom [13]. Usually one starts from an effective pair potential which is valid for large particle separation. The range of this effective pair potential involves a certain length scale ℓ which is the decay length of the van-der-Waals attraction, the Debye-Hückel screening length or the diameter of gyration $2R_{\rm g}$, for rare gases, charged colloids, and star polymers, respectively. Triplet forces, *i.e.* three-star forces, not forces between monomers, become relevant with respect to the pairwise forces if the typical separations between the particles are smaller than this typical length scale ℓ. This implies a triple overlap of particle coronae drawn as spheres of diameter ℓ around the particle centers. The triple overlap volume is an estimate for the magnitude of the triplet forces. Hence a three-particle configuration on an equilateral triangle is the configuration where triplet effects should be most pronounced.

The aim of the present paper is to quantify the influence of triplet interactions for star polymer solutions in a

[a] *Present address*: Bayer AG, Central Research, Building E 14, D-51368 Leverkusen, Germany.
e-mail: ferber@thphy.uni-duesseldorf.de

good solvent using both analytical theory and computer simulation. In doing so, we consider a set-up of three-star polymers whose centers are on an equilateral triangle. We found that the triplet part is attractive but its relative contribution is small (11%) with respect to the repulsive pairwise part. This relative correction is universal, *i.e.*, it is independent of the particle separation and of the arm number. It even persists for a collinear configuration of three-star polymers where the absolute correction is smaller than in the triangular situation for the same star-star distance. Consequently, the validity of the effective pair potential model is justified even at densities above the overlap concentration. In particular, our result gives evidence that the anisotropic and diamond solids predicted by the pair theory are indeed realizable in actual samples of concentrated star polymer solutions.

Our paper is organized as follows: in Section 2 we apply scaling theory to extract the triplet forces both for small and for large arm numbers. In Section 3 we briefly describe our Molecular Dynamics (MD) simulation scheme and present results in Section 4. Comparing these to the theoretical predictions, we find good agreement. Section 5 is devoted to concluding remarks and to an outlook.

2 Scaling theory of triplet forces between star polymers

2.1 Scaling of single stars

The scaling theory of polymers was significantly advanced by de Gennes' observation that the n-component spin model of magnetic systems is applicable to polymers in the formal $n = 0$ limit [14]. This opened the way to apply renormalization group (RG) theory to explain the scaling properties of polymer solutions that have been the subject of experimental and theoretical investigations since the pioneering works in this field [15]. Many details of the behavior of polymer solutions may be derived using the RG analysis [16]. Here, we use only the more basic results of power law scaling: the radius of gyration $R_{\rm g}(N)$ of a polymer chain and the partition function $\mathcal{Z}(N)$ are found to obey the power laws

$$R_{\rm g}(N) \sim N^{\nu} \qquad \text{and} \qquad \mathcal{Z}(N) \sim z^N N^{\gamma-1}. \tag{1}$$

The fugacity z measures the mean number of possibilities to add one monomer to the chain. It is microscopic in nature and will depend on the details of the model or experimental system. The two exponents ν and γ on the contrary are the $n = 0$ limits of the correlation length exponent $\nu(n)$ and the susceptibility exponent $\gamma(n)$ of the n component model and are universal to all polymer systems in a good solvent, *i.e.*, excluding high concentration of polymers or systems in which the polymers are collapsed or are near the collapse transition. For any such system the exponents of any other power law for linear polymers may be expressed by these two exponents in terms of scaling relations.

It has been shown that the n component spin model may be extended by insertions of so-called composite spin operators that allow to describe polymer networks and in particular star polymers in the $n = 0$ limit [17–19]. A family of additional exponents γ_f governs the scaling of the partition function $\mathcal{Z}_f(N)$ of a polymer star of f chains each with N monomers:

$$\mathcal{Z}_f(N) \sim z^N N^{\gamma_f - 1}. \tag{2}$$

Again the exponents of any other power law for more general polymer networks are given by scaling relations in terms of γ_f and ν. Here, we substitute another family of exponents η_f to replace $\gamma_f - 1 = \nu(\eta_f - f\eta_2)$. The first two members $\eta_1 = 0$ and $\eta_2 = (1-\gamma)/\nu$ are defined by the requirement that the $f = 1$ star and the $f = 2$ star are just linear chains with scaling exponents $\gamma_1 = \gamma_2 = \gamma$. The values of these exponents are known from renormalization group analysis (RG) and Monte Carlo (MC) simulations [20]. Several equivalent approaches have been elaborated to evaluate the renormalized perturbation theory. Early first-order perturbative RG results were given in reference [21]. Here, we explicitly present the result of an expansion in the parameter $\varepsilon = 4 - d$ where d is the space dimension. The ε-expansion for the η_f reads [19]

$$\begin{aligned}\eta_f = &-\frac{\varepsilon}{8} f(f-1) \\ &\times \left\{1 - \frac{\varepsilon}{32}(8f-25) + \frac{\varepsilon^2}{64}\left[(28f-89)\zeta(3) + 8f^2 \right.\right. \\ &\left.\left. - 49f + \frac{577}{8}\right]\right\} + \mathcal{O}(\varepsilon^4)\end{aligned} \tag{3}$$

with the Riemann ζ-function. Note that this series is asymptotic in nature and to evaluate it for $\varepsilon = 1$ it is necessary to apply resummation. An alternative expansion for the star exponents makes use of an RG approach at fixed dimension $d = 3$ proposed by Parisi [22]. This expansion has been worked out in references [23–25]. The corresponding expressions are lengthy and not presented here. In Table 1, in the first two lines we have calculated the resummation for the series in equation (3) as well as for the expansion at fixed dimension. The resummation procedure that we apply combines a Borel transform with a conformal mapping using all information on the asymptotic behavior of the perturbation expansion of the corresponding spin model [26,27]. Results for $f \leq 9$ have been given before in references [19,23–25] whereas we have added here the calculation of values for $f = 10, 12, 15$. The deviation between the two approaches measures the error of the method. For large f the leading coefficient of the k-th order term ε^k in equation (3) is multiplied by f^{k+1}. This is due to combinatorial reasons and occurs also for the alternative approach. It limits the use of the series to low values of f.

Another possibility to estimate the values of the star polymer scaling exponents γ_f is to consider the limiting case of many arm star polymers. For large f each chain of the star is restricted approximately to a cone of solid angle $\Omega_f = 4\pi/f$. In this cone approximation one finds

Table 1. Calculation of the exponents that govern the pair and triplet interactions. The labels a and b stand for the two complementary renormalization group approaches (expansion in $\varepsilon = 4 - d$ and massive renormalization at $d = 3$) used to calculate the exponents η_f. The difference of the two results may be taken as an estimation of the error of the method. Label c stands for the cone approximation result with matching to $f = 1, 2$ as explained in the text.

f	1	2	3	4	5	6	8	9	10	12	15
a η_f	0	−0.28	−0.75	−1.36	−2.07	−2.88	−4.71	−5.72	−6.80	−9.12	−12.98
b	0	−0.28	−0.76	−1.38	−2.14	−3.01	−5.06	−6.22	−7.48	−10.23	−14.93
a $\Theta^{(2)}_{ff}$	0.28	0.80	1.38	1.99	2.66	3.36					
b	0.28	0.82	1.49	2.30	3.20	4.21					
c	0.28	0.79	1.44	2.22	3.11	4.08					
a $\Theta^{(3)}_{fff}$	0.75	2.04	3.47	5.04	6.77						
b	0.76	2.17	3.94	6.09	8.51						
c	0.74	2.08	3.83	5.89	10.82						
a $\Delta F/F$	−0.11	−0.15	−0.16	−0.16	−0.15						
b	−0.09	−0.12	−0.12	−0.12	−0.11						
c	−0.11	−0.11	−0.11	−0.11	−0.11						

for large f [28]

$$\gamma_f \sim -f^{3/2}. \tag{4}$$

2.2 Two-star polymers

Let us now turn to the effective interaction between the cores of two-star polymers at small distances r that are small on the scale of the size R_g of the stars. Let us for the moment consider a more general case of two-star polymers with f_1 and f_2 arms, respectively. The cores of the two stars are at a distance r from each other. We assume all chains involved to be of the same length. The power law for the partition sum $\mathcal{Z}^{(2)}_{f_1f_2}(r)$ of two-star polymers may then be derived from a short-distance expansion. This expansion is originally established in the field-theoretic formulation of the n component spin model. While we do not intend to give any details of these considerations here, applications to polymer theory may be found in references [29,30]. The relevant result on the other hand, is simple enough: the partition sum of the two stars $\mathcal{Z}^{(2)}_{f_1f_2}(N, r)$ at small distance r factorizes into a function $C_{f_1f_2}(r)$ of r alone and the partition function $\mathcal{Z}_{f_1+f_2}(N)$ of the star with $f_1 + f_2$ arms that is formed when the cores of the two stars coincide,

$$\mathcal{Z}^{(2)}_{f_1f_2}(N, r) \sim C_{f_1f_2}(r)\mathcal{Z}_{f_1+f_2}(N). \tag{5}$$

For the function $C_{f_1f_2}(r)$ one may show that power law scaling for small r holds in the form

$$C_{f_1f_2}(r) \sim r^{\Theta^{(2)}_{f_1f_2}}, \tag{6}$$

with the contact exponent $\Theta^{(2)}_{f_1f_2}$. To find the scaling relation for this power law we change the length scale in (5) in an invariant way by $r \to \lambda r$ and $N \to \lambda^{1/\nu}N$. The scaling of the partition function $\mathcal{Z}^{(2)}_{f_1f_2}$ may be shown to factorize into the contributions for the two stars. This transforms (5) to

$$\lambda^{-1/\nu(\gamma_{f_1}-1)}\lambda^{-1/\nu(\gamma_{f_2}-1)}\mathcal{Z}^{(2)}_{f_1f_2}\big(\lambda^{1/\nu}N, \lambda r\big) \sim \lambda^{-\Theta^{(2)}_{f_1f_2}}C_{f_1f_2}(\lambda r)\lambda^{-1/\nu(\gamma_{f_1+f_2}-1)}\mathcal{Z}_{f_1+f_2}\big(\lambda^{1/\nu}N\big). \tag{7}$$

Collecting powers of λ provides the scaling relation

$$\nu\Theta^{(2)}_{f_1f_2} = (\gamma_{f_1} - 1) + (\gamma_{f_2} - 1) - (\gamma_{f_1+f_2} - 1),$$
$$\Theta^{(2)}_{f_1f_2} = \eta_{f_1} + \eta_{f_2} - \eta_{f_1+f_2}. \tag{8}$$

We now specialize our consideration to the interaction between two stars of equal number of arms $f_1 = f_2 = f$. The mean force $F^{(2)}_{ff}(r)$ between the two-star polymers at short distance r is then easily derived from the effective potential $V^\mathrm{eff}(r) = -k_\mathrm{B}T\log[\mathcal{Z}^{(2)}_{ff}(r)/(\mathcal{Z}_f)^2]$ with $k_\mathrm{B}T$ denoting the thermal energy. For the force this results in

$$\frac{1}{k_\mathrm{B}T}F^{(2)}_{ff}(r) = \frac{\Theta^{(2)}_{ff}}{r}. \tag{9}$$

The cone approximation for the contact exponents [31] $\Theta^{(2)}_{ff}$ may be matched to the known values for $f = 1, 2$ (see Tab. 1), fixing the otherwise unknown prefactor. Assuming that the behavior of the $\Theta^{(2)}_{ff}$ may be described by the cone approximation for all f one finds

$$F^{(2)}_{ff}(r) \approx \frac{5}{18}\frac{f^{3/2}}{r}. \tag{10}$$

This matching in turn suggests an approximate value for the η_f exponents,

$$\eta_f \approx -\frac{5}{18}\big(2^{3/2} - 2\big)^{-1}f^{3/2}. \tag{11}$$

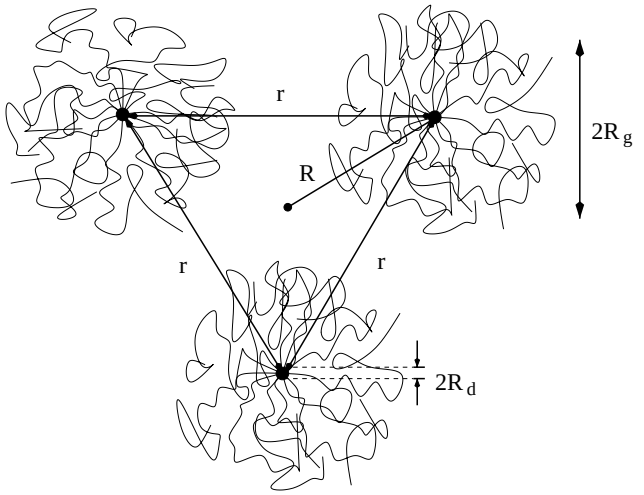

Fig. 1. Three-star polymers at mutual distance r. The cores of the stars (with radius $R_{\rm d}$) are located at the corners of an equilateral triangle. The distance from the center is R. The mean radius of gyration of a single star is $R_{\rm g}$.

Note on the other hand that this approximation is inconsistent with the exact result $\eta_1 = 0$. However, the approximation works well for $\Theta^{(2)}_{ff}$ in the range $f = 1, \ldots, 6$ were we have calculated the corresponding values from the perturbation theory results as well as according to the cone approximation. Our results, displayed in the second part of Table 1, show good correspondence of the cone approximation with the resummation values.

2.3 Three stars

We now use the idea of the short-distance expansion once more to derive the triplet interaction of three-star polymers at close distance. We consider a symmetric situation in which the three cores of the polymer stars are located on the corners of an equilateral triangle (see Fig. 1). The distance between the cores is r while their distance to the center of the triangle is R. We assume that the radius of gyration $R_{\rm g}$ of the star polymers is much larger than their mutual distance $R_{\rm g} \gg r$.

To make the argument more transparent we first consider the slightly more general case of three stars with f_1, f_2 and f_3 arms, respectively. Shrinking the outer radius R of the triangle on which the cores are located, the partition function of this configuration of three stars will scale with R according to

$$\mathcal{Z}_{f_1 f_2 f_3}(R) \sim R^{\Theta^{(3)}_{f_1 f_2 f_3}}, \tag{12}$$

$$\Theta^{(3)}_{f_1 f_2 f_3} = \eta_{f_1} + \eta_{f_2} + \eta_{f_3} - \eta_{f_1+f_2+f_3}. \tag{13}$$

Now, the scaling exponent $\eta_{f_1+f_2+f_3}$ of the star that results by collapsing the cores of the three stars at one point has to be taken into account as follows from an argument analogous to the above consideration for two stars.

Let us specify the result for the symmetric situation of three equivalent stars $f_1 = f_2 = f_3 = f$. Furthermore we assume that the large f approximation (11) is valid for the exponents η_f. Then the three-star contact exponent may be written as

$$\Theta^{(3)}_{fff} = \frac{3^{3/2} - 3}{2^{3/2} - 2} \times \frac{5}{18} f^{3/2}. \tag{14}$$

An effective potential of the system of the three stars at small distance R from the center may then be defined by

$$V^{(3)\rm eff}_{fff}(R) = -k_{\rm B}T\Theta^{(3)}_{fff} \ln\left(\frac{R}{R_{\rm g}}\right). \tag{15}$$

We now derive the corresponding three-body force underlying this effective potential. Note that the absolute value of the force is the same for all three stars. The relation of the potential to the force on the core of one star is then

$$V^{(3)\rm eff}_{fff}(R + {\rm d}R) - V^{(3)\rm eff}_{fff}(R) = \sum_{i=1}^{3} \mathbf{F_i} \cdot {\rm d}\mathbf{R}_i = 3F^{(3)}_{fff}(R){\rm d}R. \tag{16}$$

The final result for the total force on each of the stars that includes any three body forces is therefore

$$F^{(3)}_{fff}(R) = \frac{-k_{\rm B}T\Theta^{(3)}_{fff}}{(3R)}. \tag{17}$$

If one starts instead from a sum of two-body forces, then one star experiences the sum of the two forces calculated for the star-star interaction. With the given geometry of the equilateral triangle this is easily calculated to give

$$F^{(2)}_{fff}(R) = \left| \frac{\hat{r}_{12}\Theta^{(2)}_{ff}}{r_{12}} + \frac{\hat{r}_{13}\Theta^{(2)}_{ff}}{r_{13}} \right| = \frac{-k_{\rm B}T\Theta^{(2)}_{ff}}{R}. \tag{18}$$

Here, $r = r_{12} = r_{13} = R\sqrt{3}$ denote the distance between two of the stars, while the $\hat{r}_{ij}$ are the unit vectors along the edges of the triangle (see Fig. 1). The relative deviation from the pair potential picture is then given by

$$\frac{\Delta F}{F^{(2)}_{fff}} = \frac{F^{(3)}_{fff}(r) - F^{(2)}_{fff}(r)}{F^{(2)}_{fff}(r)} = \frac{\Theta^{(3)}_{fff} - 3\Theta^{(2)}_{ff}}{3\Theta^{(2)}_{ff}}. \tag{19}$$

Using the cone approximation for the contact exponent we finally obtain for the relative deviation caused by triplet forces alone

$$\frac{\Delta F}{F^{(2)}_{fff}} = \frac{3^{3/2} - 3}{2^{3/2} - 2} \approx -0.11. \tag{20}$$

This result is independent of the number of arms and valid in the full region that is described by the logarithmic potential. In Table 1 we have calculated the exponents as derived from the perturbation expansion of polymer field theory [23–25] checking the relation equation (20). Taking into account the error that may be estimated from the

difference of the results obtained by the two complementary approaches, the results are in good agreement with the cone approximation even for low f values. The fair coincidence is rather surprising as additional numerical errors might be introduced by the calculation of the contact exponents from the original star exponents. It confirms our estimate of the relative deviation caused by triplet forces to be of the order of not more than 11% for all analytic approaches we have followed here. Let us note that the analogous calculation for a symmetric linear configuration of three stars yields the same relative deviation equation (20). The absolute triplet forces for the linear configuration are smaller by a factor $\sqrt{3}/2$ than for the triangular configuration with the same star-star distance.

3 Computer simulation method

Molecular dynamics (MD) simulations were performed using exactly the model that three of the present authors devised to test the effective pair potential [6] and had been originally proposed to study single-star polymers [32,33]. In this model the configuration of star polymer $i = 1, 2, 3$ is given by the coordinates $\mathbf{r}_m^{(i,j)}$ of the N monomers $m = 1, \ldots, N$ of the f chains $j = 1, \ldots, f$ and the position of its core $r_0^{(i)}$. The main features of this model are the following: 1) A purely repulsive truncated Lennard-Jones–like potential acts between all monomers $m = 0, \ldots, N$ on all chains. 2) An attractive FENE-potential [32,33] that preserves the chain connectivity and acts only between consecutive monomers $m, m+1$ along each chain. 3) These potentials have to be slightly modified for the interaction between the first monomer $m = 1$ and the core $m = 0$ of the star to allow the core to have a radius R_d that is sufficiently large to place f monomers in its vicinity.

The three cores of the stars were placed at the corners of an equilateral triangle, see again Figure 1 where also the core radius R_d is shown. A typical snapshot of the three star simulation is displayed in Figure 2 for a functionality of $f = 5$ and $N = 100$ monomers per chain. The force on the star core was averaged during the MD simulation for a number of edge lengths r of the triangle varying in the range between the diameter of the two cores $2R_\mathrm{d}$ and the diameter of gyration $2R_\mathrm{g}$ of a single-star polymer. We have produced data for $f = 3, 5, 10, 18, 30$. For the smaller functionalities ($f = 3, 5, 10$) the number of monomers per chain was $N = 100$ while for $f = 10, 18, 30$ a number $N = 50$ was chosen. Note that the total system comprises between 900 and 4500 mutually interacting particles. As equilibration is slow and the statistical average converges slowly, the simulation becomes increasingly time-consuming beyond such system sizes. As for reference data, we have also produced data for a two stars situation according to the calculations in reference [6].

4 Results

Results of the computer simulation are compared to the theory in Figures 3a and 3b. The reduced averaged force

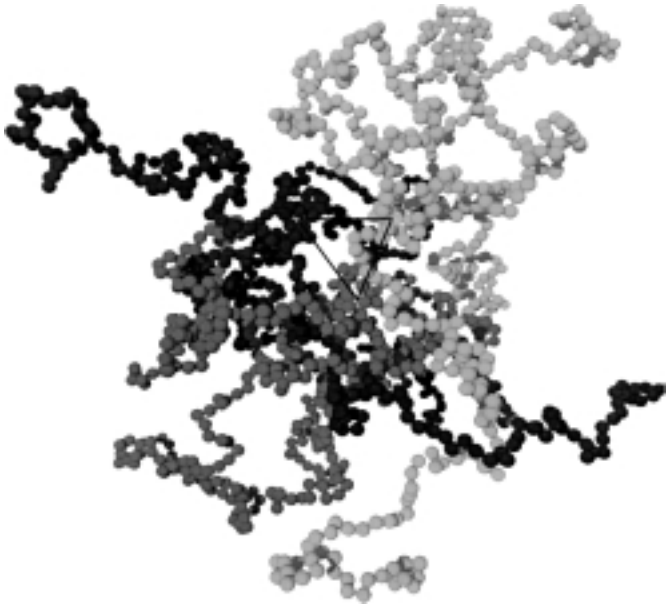

Fig. 2. Snapshot of the simulation of three stars with $f = 5$ arms each with $N = 100$ monomers. The cores are located at the corners of the equilateral triangle that is depicted in the center. The monomers that belong to the same star are represented by balls of the same color: either black, dark gray, or light gray.

on a single star is shown *versus* the reduced triangle length for different arm numbers. As a reference case, also the corresponding results in a pair potential picture are shown, both within theory and simulation. For technical reasons we kept a small core radius R_d in the simulation, which is roughly 10% of the radius of gyration of the whole star. In the theory, on the other hand, the core size was zero. Hence, to compare properly [6], a shift $r - 2R_\mathrm{d}$ has to be performed.

As expected, in both theory and simulation, the triplet forces become relevant only within the coronae. A comparison with pure pairwise forces leads to the first important observation that the triplet force is smaller, *i.e.* the pure triplet contribution is *attractive*. (Note that one has to multiply the pure two-star force by a factor of $\sqrt{3}$ for simple geometrical reasons.) The relative magnitude of the triplet term, however, is small. A quantitative comparison with theory and simulation leads to good overall agreement. The triplet contribution itself, however, is subjected to larger statistical errors of the simulation. Hence we resorted to a different strategy to check the theory by plotting the inverse force *versus* distance. If the theory is correct the simulation data should fall on a straight line both for the pure pairwise and the full triplet case. The slope should then give the theoretical prefactor of the logarithmic potential. The advantage of this consideration is that the slope bears a smaller statistical error as more data points are included. Such a comparison is shown in Figure 4 for $f = 10$. The first consequence is that the simulation data indeed fall on a straight line confirming the theory. In fact this is true for all other parameter

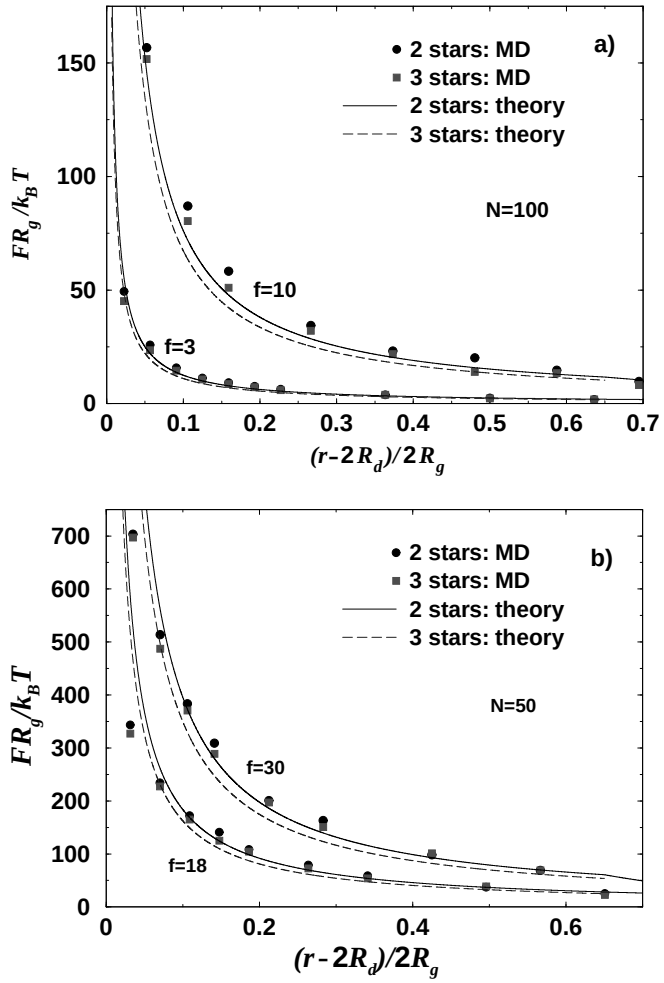

Fig. 3. a) Comparison of the force F measured in the three-star MD with that calculated from a corresponding two-star MD simulation for $f = 3$ and $f = 10$ with $N = 100$. Also the results predicted by the theory are plotted as a continuous line (only pair forces) and a broken line (including triplet forces). b) Same as a) but for $f = 18$ and $f = 30$ with $N = 50$.

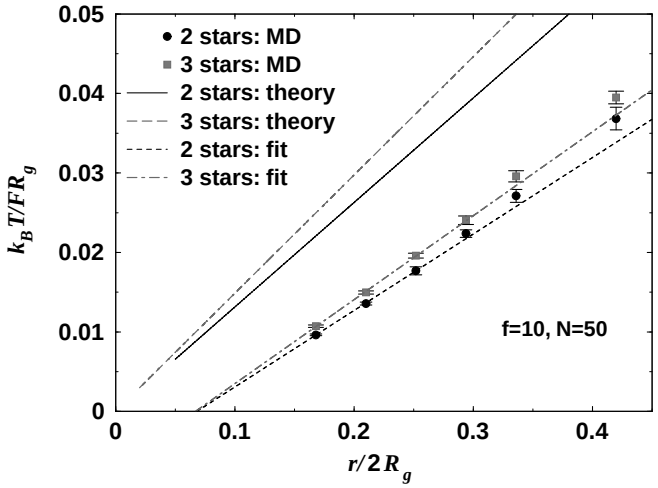

Fig. 4. Comparison of the inverse force $1/F$ measured in the three-star MD with that calculated from a corresponding two-star MD simulation for $f = 10$ with $N = 50$. The linear fits for the pair forces (short-dashed line) and the full three body force (dash-dotted line) are shown together with the respective results predicted by the theory which are depicted by a continuous line (only pair forces) and a broken line (including triplet forces).

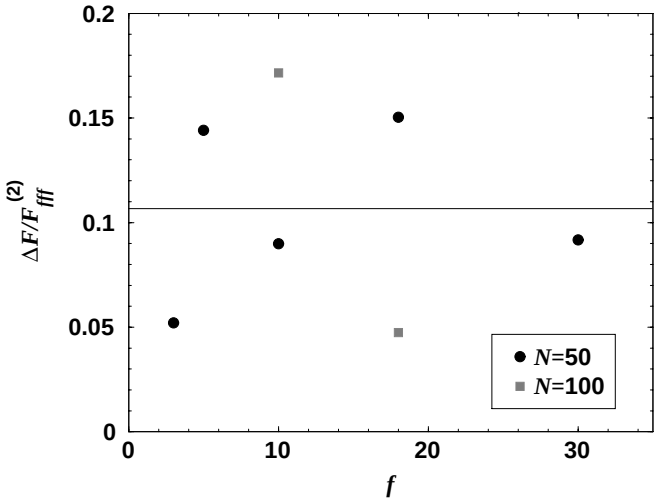

Fig. 5. The slopes of the linear fits to the data as shown in Figure 4 were extracted from the simulation data for $f = 3, 5, 10, 18, 30$ and $N = 50, 100$ to calculate the relative deviation $\Delta F/F^{(2)}_{fff}$ induced by the triplet forces. The line at 0.11 corresponds to the analytic result.

combinations considered in the simulations. The slope is higher for the triplet and lower for the pair case, both in theory and simulation. The actual values in Figure 4 are in the same order of magnitude but a bit different.

In order to check this in more detail, we have extracted the slope for all simulation data. The result is summarized in Figure 5 where the relative differences of the slopes between the pair and triplet cases are plotted *versus* the arm number f. The theory predicts a constant value of 0.11, see equation (20). The simulation data scatter a lot in the range between 0.05 and 0.15 due to the large statistical error but the theoretical value falls reasonably within the data. Consequently, the triplet contributions are found to be attractive and small even for nearly touching cores where the triplet overlap of the coronae is substantial.

5 Conclusions

In conclusion, we have calculated, by theory and computer simulations, the triplet interaction between star polymer centers in a good solvent positioned on the corners of an equilateral triangle. The triplet part was found to be attractive but only about 11% of the pairwise repulsion. Our calculations justify earlier investigations [5] where the pair potential framework was used even slightly above the star overlap concentration.

We finish with a couple of remarks: First, the scaling theory can also be performed for any triplet configurations beyond the equilateral triangle studied in this paper. Second, arbitrary higher-order many-body forces can be investigated assuming a cluster of M stars. Such a calculation is given in Appendix A. As a result, the deviations from the pair potential picture increase with the number M and even diverge for $M \to \infty$. This implies that the pair potential picture breaks down for very high concentrations. This is expected as for high concentration a star polymer solution is mainly a semi-dilute solution of linear chains where it is irrelevant at which center they are attached to [8]. As far as further simulational work is concerned, there are many open problems left. Apart from the investigation for arbitrary triplet configurations and their extensions to an arbitrary number of stars, the most challenging problem is a full *ab initio* simulation of many stars including many-body forces from the very beginning. This is in analogy to Car-Parrinello simulations [34] which were also applied to colloidal suspensions [35]. A first attempt has been done [36], but certainly more work is needed here. Another (a bit less demanding) task is to study stars on a periodic solid lattice with periodic boundary conditions and extract the many-body interactions from there.

It would be interesting to study the relevance of triplet forces for star polymers in a *poor* solvent near the Θ-point [37]. It can, however, be expected that the triplet forces here are even less important than for a good solvent as the effective interaction becomes stiffer in a poor solvent. Furthermore, the effect of polydispersity in the arm number which has been briefly touched in our scaling theory treatment should be extended since this is important to describe real experimental samples.

We are grateful to the DFG for financial support within the SFB 237.

Appendix A. Higher-order forces between star polymers

Here, we derive for the general case of M simultaneously interacting star polymers with f arms the effective M-th order force. Generalizing the equilateral triangle geometry, we study the situation where the M cores of the stars are evenly distributed on a sphere with radius R. In particular, the cores of the stars may be located at the corners of a regular polyhedron. Then the non-radial forces on each star polymer cancel. The latter condition may be fulfilled approximately also for large numbers M for which a regular polyhedron does not exist.

We first calculate the force on one star by the sum of $M-1$ pairwise forces effected by the other stars. For the pairwise force (9) that acts according to a $1/r$-law it is easy to verify that the radial component of the force between any two points on the sphere is $\Theta^{(2)}_{ff}/(2R)$ independent of their relative position. With this simplification the total (radial) force on one star is

$$\frac{1}{k_{\mathrm{B}}T} F^{(2)}_{M,f} = \frac{M-1}{2} \frac{\Theta^{(2)}_{ff}}{R}. \tag{A.1}$$

Here, $F^{(2)}_{M,f}$ denotes the sum of pairwise forces on one of the M stars each with f arms. In the case $M = 3$ this is the result of equation (18).

The total M-th order force $F^{(M)}_{M,f}$ between M star polymers with f arms brought close together may again be derived from a short-distance expansion resulting in the scaling relation

$$\Theta^{(M)}_{M,f} = M \cdot \eta_f - \eta_{M \cdot f}. \tag{A.2}$$

The force on one star is then found in the same way as for three stars as

$$\frac{1}{k_{\mathrm{B}}T} F^{(M)}_{M,f} = \frac{\Theta^{(M)}_{M,f}}{M \cdot R}. \tag{A.3}$$

The leading contributions for large numbers of stars M in the two cases differ even in the power of M. While the first is linear in M the latter grows only with the square root of M. In the large-f and large-M approximations this reads

$$\frac{1}{k_{\mathrm{B}}T} F^{(2)}_{M,f} \approx \frac{5}{18} \frac{f^{3/2}}{2R} M, \tag{A.4}$$

$$\frac{1}{k_{\mathrm{B}}T} F^{(M)}_{M,f} \approx \frac{5}{18} (2^{3/2} - 2) \frac{f^{3/2}}{R} M^{1/2}. \tag{A.5}$$

Note that for large M the factors M and $M^{1/2}$ in these two approaches are not a result of the large f approximation but are of combinatorial and geometrical origin. This shows that for large M the sum of pairwise forces largely overestimates the force on one star.

References

1. G.S. Grest, L.J. Fetters, J.S. Huang, D. Richter, Adv. Chem. Phys. **XCIV**, 67 (1996).
2. A.P. Gast, Langmuir **12**, 4060 (1996).
3. R. Seghrouchni, G. Petekidis, G. Fytas, A.N Semenov, J. Roovers, G. Fleischer, Europhys. Lett. **42**, 271 (1998).
4. C.N. Likos, H. Löwen, M. Watzlawek, B. Abbas, O. Jucknischke, J. Allgaier, D. Richter, Phys. Rev. Lett. **80**, 4450 (1998).
5. M. Watzlawek, C.N. Likos, H. Löwen, Phys. Rev. Lett. **82**, 5289 (1999).
6. A. Jusufi, M. Watzlawek, H. Löwen, Macromolecules. **32**, 4470 (1999).
7. G. Fleischer, F. Rittig, J. Kärger, C.M. Papadakis, K. Mortensen, K. Almdal, P. Stepanek, J. Chem. Phys. **111**, 2789 (1999).
8. T.A. Witten, P.A. Pincus, Macromolecules **19**, 2509 (1986).
9. T.A. Witten, P.A. Pincus, Europhys. Lett. **2**, 137 (1986).
10. B.M. Axilrod, E. Teller, J. Chem. Phys. **11**, 229 (1943).

11. M. Tau, L. Reatto, R. Magli, P.A. Egelstaff, F. Barrochi, J. Phys. Condens. Matter **1**, 7131 (1989).
12. H. Löwen, E. Allahyarov, J. Phys. Condens. Matter **10**, 4147 (1998).
13. H. Graf, H. Löwen, Phys. Rev. E **57**, 5744 (1998).
14. P.G. de Gennes, Phys. Lett. A **38**, 339 (1972).
15. P.J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley Interscience, New York, 1969).
16. L. Schäfer, *Excluded Volume Effects Polymer Solutions as Explained by the Renormalization Group* (Springer, Berlin, 1999).
17. B. Duplantier, Phys. Rev. Lett. **57**, 941 (1986).
18. K. Ohno, K. Binder, J. Phys. (Paris) **49**, 1329 (1988).
19. L. Schäfer, C. von Ferber, U. Lehr, B. Duplantier, Nucl. Phys. B **374**, 473 (1992).
20. J. Batoulis, K. Kremer, Macromolecules **22**, 4277 (1989).
21. A. Miyake, K.F. Freed, Macromolecules **16**, 1228 (1983).
22. G. Parisi, J. Stat. Phys. **23**, 49 (1980).
23. C. von Ferber, Y. Holovatch, Theor. Math. Phys. (Moscow) **109**, 3 (1996).
24. C. von Ferber, Y. Holovatch, Europhys. Lett. **39**, 31 (1997).
25. C. von Ferber, Y. Holovatch, Phys. Rev. E **56**, 6370 (1997).
26. E. Brézin, J.C. Le Guillou, J. Zinn-Justin, Phys. Rev. D **15**, 1544 (1977).
27. J.C. Le Guillou, J. Zinn-Justin, Phys. Rev. B **21**, 3976 (1980).
28. K. Ohno, Phys. Rev. A **40**, 1524 (1989).
29. B. Duplantier, J. Stat. Phys. **54**, 581 (1989).
30. C. von Ferber, Nucl. Phys. B **490**, 511 (1997).
31. J. des Cloizeaux, J. Phys. (Paris) **36**, 281 (1975).
32. G.S. Grest, K. Kremer, T.A. Witten, Macromolecules **20**, 1376 (1987).
33. G.S. Grest, Macromolecules **27**, 3493 (1994).
34. R. Car, M. Parinello, Phys. Rev. Lett. **55**, 2471 (1985).
35. H. Löwen, J.-P. Hansen, P.A. Madden, J. Chem. Phys. **98**, 3275 (1992).
36. T. Pakula, D. Vlassopoulos, G. Fytas, J. Roovers, Macromolecules **31**, 8931 (1998).
37. C.N. Likos, H. Löwen, A. Poppe, L. Willner, J. Roovers, B. Cubitt, D. Richter, Phys. Rev. E **58**, 6299 (1998).