Effective interactions between star polymers

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We study numerically the effective pair potential between two star polymers with equal arm lengths and equal number f of arms. The simulations were done for the soft core Domb-Joyce model on the simple cubic lattice, to minimize corrections to scaling and to allow for an unlimited number of arms. For the sampling, we used the pruned-enriched Rosenbluth method (PERM). We find that the potential is much less soft than claimed in previous papers, in particular for $f \gg 1$. While we verify the logarithmic divergence of $V(r)$, with r being the distance between the two cores, predicted by Witten and Pincus, we find that the Mayer function for $f > 20$ is hardly distinguishable from that for a Gaussian potential.

Interactions between polymers in diluted solutions are of interest for several reasons, not the least because they influence both the equilibrium and the rheological properties of complex fluids. In early work by Flory *et al.* [1] it was suggested that polymer coils can be approximated by hard spheres, but this was shown to be wrong in [2]. Since then it is well understood that both linear and branched polymers are *soft* in the sense that they can penetrate each other, and that the effective potential is a rather smooth function of their distance. As shown in [3, 4], this can have dramatic effects on the phase diagram for semi-dilute solutions of star polymers, and can – with the effective potentials assumed by these authors – lead to a multitude of novel phases.

When discussing effective potentials between polymers – be they linear or star-shaped – one has to distinguish between $U(r)$ where r is the distance between the two centers of mass, and $V(r)$ where r is the distance between the two central monomers. In both cases, the potential is defined by

$$\exp(-\beta U(r)), \ \exp(-\beta V(r)) = Z^{(2)}(r)/[Z^{(1)}]^2 \quad (1)$$

where $Z^{(1)}$ is the partition function of a single polymer, while $Z^{(2)}(r)$ is the partition function of two polymers with fixed distance r. Finally, $\beta = 1/k_B T$ is used to give $V(r)$ the usual dimension of a potential, although any temperature is of course dummy for an a-thermal system as in the present case. For ease of writing, we shall set $\beta = 1$ in the following. Finally, all data shown in the following refer to lattice simulations with $\mathbf{r} = (r, 0, 0)$, but we checked in a few cases that distances not parallel to one of the coordinate axes gave basically the same results.

In the following we shall only discuss the case where the number f of arms is the same for both polymers (and might include the case $f = 2$ describing linear chains), and each arm has the same length N. Even if not spelled out explicitly, the main point of [3, 4, 5] is that, for large f, the potential $V(r)$ is more relevant than $U(r)$ for equations of state of semi-dilute or dense solutions, and that $V(r)$ is very different from $U(r)$: While the latter is essentially Gaussian, the former has a more complex structure with a Yukawa tail at large r. We will show in the following that at least the second claim is not correct, and
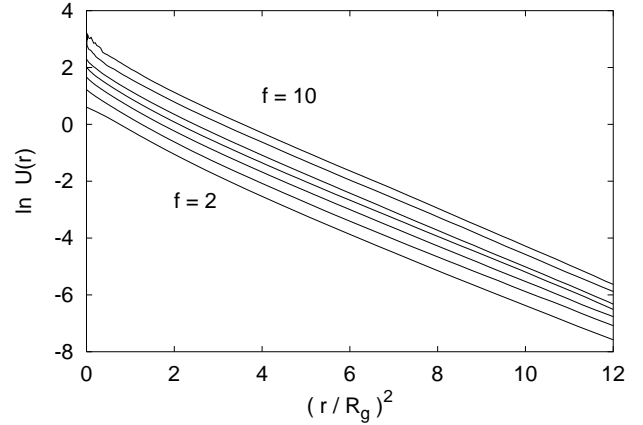

FIG. 1: Logarithms of the effective potential $U(r)$ with r being the center-of-mass distance, for star polymers with $f = 2, 3, 4, 5, 6, 8$, and 10 arms (bottom to top), plotted against $(r/R_g)^2$ where R_g is the gyration radius of a single star. Arm lengths are $N = 400$ monomers. Linear curves would correspond to Gaussian $U(r)$.

that $V(r)$ can also be approximated by a Gaussian for most practical purposes.

The center-of-mass potential $U(r)$ is well known to be approximately Gaussian for linear [2, 6, 7, 8] polymers. For star polymers there are much fewer computations [9], so we present in Fig. 1 our own results which clearly indicate that $U(r)$ is roughly Gaussian, too. Notice that the deviation from a Gaussian at small r (i.e. the upward bending in Fig. 1) is practically irrelevant for > 8 arms per star, since it occurs only when $e^{-U(r)} \leq 10^{-3}$.

The data in Fig. 1 as all data in this paper were obtained for the soft repulsion Domb-Joyce model [10] at the 'magic' value $v^* = 0.6$ of the repulsion parameter, on the simple cubic lattice. This model was chosen because it leads to minimal corrections to scaling and it allows an arbitrary number f of arms to be attached to a single central site [11, 12] The simulations were made with the PERM algorithm [13], adapted for star polymers as described in [11]. The partition sum $Z^{(2)}(r)$ was estimated as usual (e.g. [7]) by simulating two *independent* stars simultaneously, and computing their overlaps at different

TABLE I: Main results. The numbers in brackets are single standard deviations in the last digit. A_f is defined by $R_g^2 \approx A_f N^{2\nu}$, b_f is obtained through Eq. (5) from the data of [11], $U(0)$ is the effective potential when the two centers of mass coincide, and a_f is defined in Eq. (4), c_f and d_f are defined in Eq. (8), and τ_f is defined in Eq. (10). We do not quote errors for the latter four, since they are strongly correlated and individual error estimates would not make sense.

f	A_f	b_f	$U(0)$	a_f	c_f	d_f	τ_f
2	0.2902(2)	0.815(2)	1.791(2)	1.869	0.372	0.405	4.5
3	0.3587(2)	1.540(3)	3.357(6)	1.759	0.74	0.473	2.2
4	0.4017(2)	2.415(5)	5.11(2)	1.720	1.17	0.506	1.35
5	0.4337(3)	3.42(1)	7.27(4)	1.707	1.76	0.527	1.00
6	0.4596(4)	4.52(2)	9.60(11)	1.682	2.90	0.548	0.98
8	0.5008(5)	7.05(2)	15.9(4)	1.690	4.62	0.582	0.62
10	0.5343(6)	9.90(3)	23.2(11)	1.691	7.0	0.600	0.50
12	0.5629(8)	13.15(6)	34.(4)	1.70	10.6	0.610	0.53
14	0.588(1)	16.71(8)	-	1.71	14.1	0.62	≈ 0.6
16	0.612(2)	20.54(10)	-	1.67	19.0	0.65	≈ 0.6
18	0.632(2)	24.73(14)	-	1.69	22.5	0.65	≈ 0.5
20	0.652(2)	29.3(2)	-	1.73	26.	0.64	≈ 0.5
24	0.689(3)	39.7(3)	-	1.76	39.	0.65	≈ 0.7
30	0.735(3)	57.3(6)	-	1.75	54.	0.67	≈ 0.7
35	0.764(4)	76.3(11)	-	1.78	76.	0.68	≈ 0.5
40	0.790(4)	94.6(20)	-	-	-	-	-
50	0.846(5)	-	-	-	-	-	-
60	0.870(7)	-	-	-	-	-	-

distances.

From general scaling arguments we expect $U(r)$ and $V(r)$ to depend on the arm length N, for $N \gg 1$, only via the scaling variable $x = r/R_g$, where R_g is the gyration radius of the star (for large N, R_g scales as $R_g \approx \sqrt{A_f} N^\nu$, with values of A_f given in Table 1). We checked this by making plots similar to Fig. 1 also for other values of N (not shown here) and by estimating $U(0)$ for different N. As argued in [6, 8] for linear polymers ($f = 2$), the convergence for $N \to \infty$ is from above, $U_{N,f}(0) \approx U_{\infty,f}(0) + a/N^{0.7}$, for small f ($f \leq 6$); for larger f the data were ambiguous. For $f = 2$ and 4, which are the only cases where precise comparisons to previous work are possible, the data shown in Fig. 1 are in perfect agreement with [8, 9]. Values of $U(0)$, extrapolated to $N \to \infty$, are also given in Table 1. They seem to scale as $U(0) \approx 0.6 f^{1.58}$.

Much more attention had been given in the literature previously to the potential $V(r)$ with r being the central monomer distance, and we shall also concentrate on $V(r)$ in the following. The first result on it was obtained by Witten and Pincus [14]. They pointed out that the scaling [15]

$$Z_{N,f}^{(1)} \sim \mu^{-fN} N^{\gamma_f - 1} , \qquad (2)$$

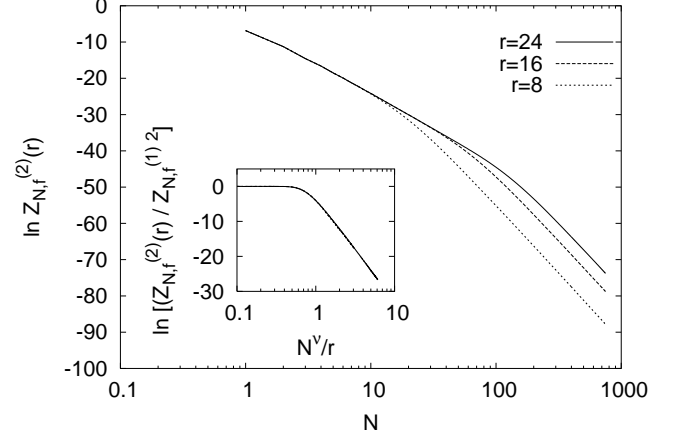of the partition sum of a star with f arms and arm length

FIG. 2: Logarithms of partition functions $Z_{N,f}^{(2)}(r)$ against N for $f = 12$. The data collapse expected from the cross-over ansatz Eq. (3) is shown in the insert.

N, together with the assumption that $Z_{N,f}^{(2)}(r)/[Z_{N,f}^{(1)}]^2$ is for any fixed f a function of $x \equiv r/R_g$ only,

$$Z_{N,f}^{(2)}(r)/[Z_{N,f}^{(1)}]^2 = \psi_f(r/R_g) , \qquad (3)$$

implies that

$$V(r) \approx V_{\text{WP}}(r) \equiv b_f \ln(a_f R_g/r) \qquad (4)$$

for $1 \ll r \ll R_g$ with

$$b_f = (2\gamma_f - \gamma_{2f} - 1)/\nu . \qquad (5)$$

Precise estimates of γ_f can be found in [11]. They show that the scaling $b_f \sim f^{3/2}$ obtained in [14] by assuming the phenomenological Daoud-Cotton model [16] is not exact, a power law fit gives instead $b_f \approx 0.27 f^{1.58}$. Both a_f and b_f should be universal and should not depend on the specific microscopic realization.

This is illustrated in Fig. 2 where we show $\ln Z_{N,f}^{(2)}(r)$ as a function of N, for $f = 12$ and for three different values of r. In contrast to the data shown in Fig. 1, these data were obtained by growing the two stars at distance r and *with the mutual interactions taken into account* during the growth [17]. This allows to measure $Z_{N,f}^{(2)}(r)$ down to very small distances and large N, where it is so small that the ratio $Z_{N,f}^{(2)}(r)/[Z_{N,f}^{(1)}]^2$ measured from independently grown stars would be indistinguishable from zero. On the other hand, at large distances this second method would give very bad estimates of $V(r)$, since it is obtained by subtracting the (nearly equal) free energies obtained in two independent runs. Therefore, in the following, all plots will show data obtained either by the first or by the second method, or will contain combinations of both types of data.

Eq. (4) cannot hold for large distances, and it is there where previous results were most uncertain. An analytic ansatz which is supposed to cover all values of r was made by Likos et al. [5]. Using a 'corona' radius σ [14] which is
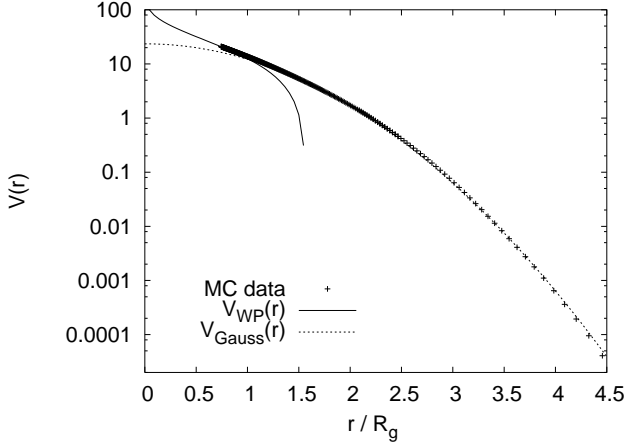
FIG. 3: $V(r)$ for $f = 18$, plotted on a logarithmic scale against r/R_g. The short continuous curve on the left corresponds to Eq. (4), the dashed curve is a Gaussian.

FIG. 4: Rescaled radial Mayer functions against r/R_g for $f = 18$. The dashed curve is the prediction from Eq. (6) with $\sigma = 1.3R_g$ [21].

roughly comparable in size to the gyration radius, they assumed that

$$V(r) = \frac{5 f^{3/2}}{18} \begin{cases} -\ln(r/\sigma) + \frac{1}{1+\sqrt{f/2}} & \text{for } r \leq \sigma \\ \frac{\sigma/r}{1+\sqrt{f/2}} \exp\left(-\sqrt{f}(r-\sigma)/2\sigma\right) & \text{for } r > \sigma \end{cases} \quad (6)$$

This was supported by molecular dynamics simulations and was also shown to be compatible with experimental results. It was used in extensive simulations of semi-dilute and concentrated solutions, and gave rise to a number of very interesting predictions [3, 4]. But for linear polymers it disagrees with the analytic results of [6] and seems hard to be reconciled with the simulations of [6, 8, 9]. In particular, it was shown in [18] that Eq. (6) is in gross violation with simulations of off-lattice stars with up to 18 arms. But these arms were very short, whence one might doubt the relevance of the results of [18].

Anyhow, in a later paper Jusufi *et al.* [19] proposed to use Eq. (6) only for $f > 10$, and to replace it for $f < 10$ by an ansatz with Gaussian decay for $r > \sigma$,

$$V(r) = \frac{5}{18} f^{3/2} \begin{cases} -\ln(r/\sigma) + \frac{1}{2\tau^2\sigma^2} & \text{for } r \leq \sigma \\ \frac{1}{2\tau^2\sigma^2} \exp(-\tau^2(r^2-\sigma^2)) & \text{for } r > \sigma \end{cases} \quad (7)$$

Notice that this does not alleviate the serious conflict with [18]. Also, we would expect that the center of mass gets closer to the central monomer as f increases. Thus, if $U(r)$ is roughly Gaussian for large r, we should expect that also $V(r)$ is Gaussian there for $f \gg 1$.

Let us for the moment concentrate on $f = 18$ arms, the case studied in [5]. In order to get a first overall impression of $V(r)$, we show in Fig. 3 its logarithm, obtained for fixed $r = 20$ and for all $N \leq 400$, against r/R_g. The short continuous curve at small r is the Witten-Pincus
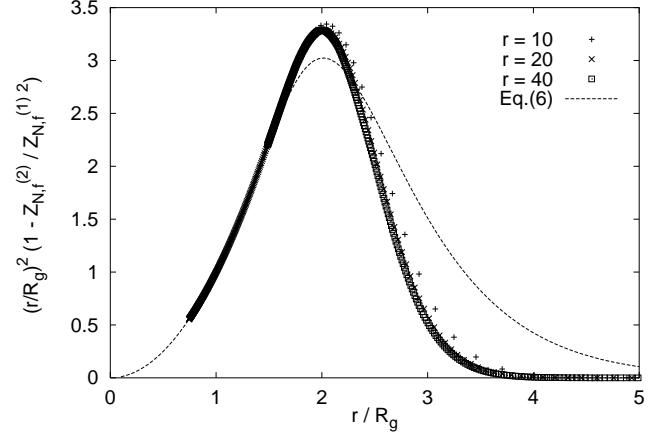
prediction, modified by taking the measured values of γ_f and γ_{2f}. It is relevant only for $r \ll R_g$. For $r \gg R_g$ the MC data can be approximated by a parabola, i.e. $V(r)$ is roughly Gaussian,

$$V(r) \approx V_{\text{Gauss}}(r) \equiv c_f e^{-d_f r^2/R_g^2} . \quad (8)$$

We conjecture that c_f and d_f are universal. A Yukawa tail as in Eq. (6) would essentially correspond to a straight line in Fig. 3 and is definitely ruled out [23].

Since $r = 20$ is not very large, one might be worried about finite size corrections. When plotted as in Fig. 3, finite size corrections would be visible only in the r.h.s. tail where V is so small that they are irrelevant. Thus we plotted in Fig. 4 the rescaled radial Mayer function,

$$(r/R_g)^2 f_M(r) = (r/R_g)^2(1 - \exp(-V(r)) \quad (9)$$

which is the most interesting quantity, for three values of r. This plot agrees very well with the simulations of [18], although those authors used a continuum model with much shorter arms. On the other hand, our data disagree strongly with Eq. (6) which is indicated by the dashed curve.

Linking the small- and large-r behaviours seen in Fig. 3 into a piecewise analytic form as in Eqs. (6) or (7) would obviously give a discontinuous slope and a bad fit. Rather we found that the following ansatz describes all our data quantitatively, for all $2 \leq f < 35$ and for all values of r:

$$V(r) = \frac{1}{\tau_f} \ln \left[e^{\tau_f V_{\text{WP}}(r) - d_f r^2/R_g^2} + e^{\tau_f V_{\text{Gauss}}(r)} \right] . \quad (10)$$

with $V_{\text{WP}}(r)$ and $V_{\text{Gauss}}(r)$ defined in Eqs. (4) and (8), and with τ_f being an additional parameter for every f. It is easy to see that $V(r) > 0$ for all r and that $V(r) = V_{\text{Gauss}}(r) [1 + O(r^{-b_f})]$ for $r \to \infty$, while $V(r) = V_{\text{WP}}(r) [1 + O(r^2)]$ for $r \to 0$. Like the previous parameters, also τ_f should be universal. Values for $a_f, c_f, d_f,$ and τ_f obtained by fitting our MC simulations
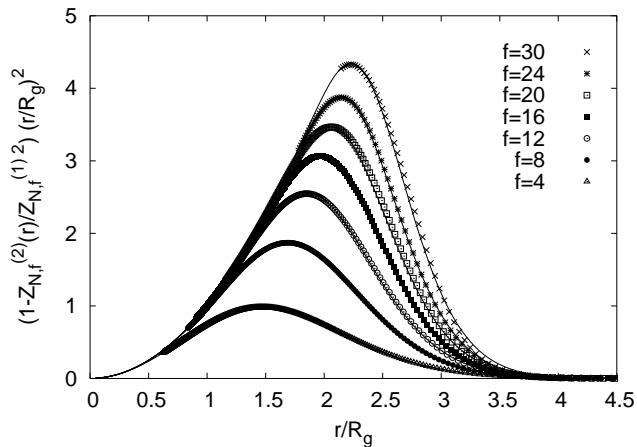
FIG. 5: Rescaled radial Mayer functions against r/R_g for several values of f. Curves are obtained from Eq. (10), with fitted parameters a_f, c_f, d_f and τ_f given in Table 1.

are given in Table 1. One sees that τ_f is between $1/2$ and 1, except for the smallest values of f. The strength of $V_{\text{Gauss}}(r)$ increases roughly as $c_f \approx 0.1 f^{1.88}$. Its range increases faster than R_g and the peak of the radial Mayer function increases even faster, roughly as $R_g \ln f$. For several values of f, radial Mayer functions are shown in Fig. 5 together with the fits obtained with Eq. (10). For $f \gg 1$, their peaks are at $r/R_g > a_f$, i.e. at distances where $V_{\text{WP}}(r)$ would be negative.

For $f > 20$ our ansatz for $V(r)$ can be simplified. For such stars the potential is so big for small r that the Witten-Pincus term can be neglected for dilute so-

lutions: Whenever it would be relevant in comparison to the Gaussian term, the pair distribution function $\exp(-V(r))$ is already zero for all practical purposes [22]. The Witten-Pincus part becomes important only for very dense systems. But there the description in terms of effective two-body forces is questionable. For the same reason, also the parameter τ_f is less precisely determined than a_f, c_f and d_f.

In summary, we have obtained very precise Monte Carlo estimates of the effective potentials between two star polymers with equal number of arms and equal arm lengths. Using a soft core polymer model (the Domb-Joyce model) we have reduced corrections to scaling to a minimum, and we have been able to simulate many arms without having to use a large central particle. We thus believe that our results present essentially the scaling limit of long arms. Our most important finding is that effective potentials are much harder than previously believed. This refers to the case where the central monomers are used to define the distance. For the alternative case of the center-of-mass distance, it had already been assumed by previous authors that the potential is relatively hard at large r and approximately Gaussian. We found that basically the same is true also for the central mass definition. Which of these two alternatives is a better starting point for effective potentials in systems with finite concentration is another question, but our results suggest that it does not make much difference.

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ters were singly occupied (else, the center would have too large a weight). But we computed Boltzmann weights as if the centers were f-fold occupied. The latter has little effect on the outcome, except that it makes the simulations more efficient.
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[22] This might not be true if there are chemically reactive radicals at the star centers. In that case even a very small probability for the star centers to meet might be impor-

tant, and the difference between Eqs. (10) and the purely Gaussian approximation might be relevant.

[23] Actually, $V(r)$ decays for $r \to \infty$ *faster* than Gaussian, as $V(r) \sim e^{-r^{\delta} \cdot const}$ with $\delta = (1 - \nu)^{-1} > 2$ [20]. This follows from the fact that arms are very far from each other for $r \gg R_g$, and thus the potential is proportional to the product of the densities in a single unbranched chain [20]. But we expect this to hold only for very large r, far beyond the distances we could study in this paper.