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 dilute 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

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

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.

In the following refer to lattice simulations with \( r = (r, 0, 0) \), 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 [2, 3, 4] 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 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, 3, 4] polymers. For star polymers there are much fewer computations [5], 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 \( r^* = 0.6 \) 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. [1]) by simulating two independent stars simultaneously, and computing their overlaps at different

![Graph showing logarithms of the effective potential](image-url)

**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 \( U(r) \).
TABLE I: Main results. The numbers in brackets are single standard deviations in the last digit. \( A_f \) is defined by \( R^2 \approx A_f N^{2\nu} \), \( b_f \) is obtained through Eq. 9 from the data of 11, \( V(0) \) is the effective potential when the two centers of mass coincide, and \( \tau_f \) is defined in Eq. 4. \( c_f \) and \( d_f \) are defined in Eq. 8, and \( \tau_f \) 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.

| \( f \) | \( A_f \) (2) | \( b_f \) (2) | \( V(0) \) (4) | \( a_f \) (4) | \( c_f \) (4) | \( d_f \) (4) | \( \tau_f \) (4) |
|---|---|---|---|---|---|---|---|
| 2 | 0.2902(2) | 0.815(2) | 1.791(2) | 1.669 | 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 | 0.4564(5) | 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 | 0.606 | 0.50 |
| 12 | 0.5629(9) | 13.15(6) | 34.4(1) | 1.70 | 10.6 | 0.610 | 0.53 |
| 14 | 0.5881(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 | 0.662(2) | 29.3(2) | - | 1.73 | 26.0 | 0.64 | 0.5 |
| 24 | 0.689(3) | 39.7(3) | - | 1.76 | 39.0 | 0.65 | 0.7 |
| 30 | 0.753(6) | 53.7(3) | - | 1.75 | 54.0 | 0.67 | 0.7 |
| 35 | 0.764(4) | 76.3(11) | - | 1.78 | 76.0 | 0.68 | 0.5 |
| 40 | 0.790(4) | 94.6(20) | - | - | - | - | - |
| 50 | 0.846(5) | - | - | - | - | - | - |
| 60 | 0.870(7) | - | - | - | - | - | - |

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. 8 is shown in the insert.

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

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

implies that

\[
V(r) \approx V_{WP}(r) \equiv b_f \ln(a_f R_g/r)
\]

for \( 1 \ll r \ll R_g \) with

\[
b_f = (2\gamma_f - \gamma_2 f - 1)/\nu.
\]

Precise estimates of \( \gamma_f \) 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. 11 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. 15. Using a 'corona' radius \( \sigma \) which is

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short continuous curve at small \( r \) is the Witten-Pincus for fixed \( r \). 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 \( \gamma_f \) and \( \gamma_{2f} \cdot r > \sigma \). 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, 

\[
V(r) \approx V_{\text{Gauss}}(r) = c_f e^{-d_f r^2/R_g^2} .
\]

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. 4 and is definitely ruled out.

Since \( r = 20 \) is not very large, one might be worried about finite size corrections. When plotted as in Fig. 4 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, 

\[
(r/R_g)^2 f_M(r) = (r/R_g)^2(1 - \exp(-V(r)))
\]

which is the most interesting quantity, for three values of \( r \). This plot agrees very well with the simulations of [13], 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 \( r \):

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

with \( V_{\text{WP}}(r) \) and \( V_{\text{Gauss}}(r) \) defined in Eqs. (6) and (8), and with \( \tau_f \) 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 \( r \rightarrow \infty \), while \( V(r) = V_{\text{WP}}(r) [1 + O(r^2)] \) for \( r \rightarrow 0 \). Like the previous parameters, also \( \tau_f \) should be universal.
are given in Table 1. One sees that $\tau_f$ is between $1/2$ and 1, except for the smallest values of $f$. The strength of $V_{\text{Ga}}(r)$ 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 solutions: 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 $\tau_f$ 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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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 $V(r) \sim e^{-r^{\delta}} \text{const}$ with $\delta = (1 - \nu)^{-1} > 2$. 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.