Colloids with polymer stars: The interaction

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

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

[b] Institute for Condensed Matter Physics, Ukrainian Acad. Sci.,
1 Svientsitskii Str., UA-290011, Lviv, Ukraine

We derive the short distance interaction of star polymers in a colloidal solution. We calculate the corresponding force between two stars with arbitrary numbers of legs f_1 and f_2. We show that a simple scaling theory originally derived for high f_1, f_2 nicely matches with the results of elaborated renormalization group analysis for $f_1 + f_2 \leq 6$ generalizing and confirming a previous conjecture based only on scaling results for $f_1 = f_2 = 1, 2$.

Star polymers, i.e. structures of polymer chains that are chemically linked with one end to a common core, have found recent interest as very soft colloidal particles [1, 2]. Increasing the number of chains f they interpolate between the properties of linear polymers and polymeric micelles [3]. For large f the effective interaction between the cores of different polymer stars becomes strong enough to allow for crystal ordering of a dense solution of stars. While such a behavior was already predicted by early scaling arguments [4] only recently corresponding experiments have become feasible with sufficiently dense stars. In addition theory and computer simulation have refined the original estimate for the number of chains f necessary for a freezing transition from $f \sim 100$ to $f \sim 34$ and predicted a rich phase diagram [1]. These results were derived using an effective pair potential between stars [1] with a short distance behavior derived from scaling theory as explained below.

The scaling theory of polymers was significantly advanced by de Gennes observation that the n-component spin model of magnetic systems applies to polymers in the formal $n = 0$ limit [5]. This opens 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 [6]. Many details of the behavior of polymer solutions may be derived using the RG analysis [7]. Here, we use only the more basic results of power law scaling: The radius of gyration $R_g(N)$ of a polymer chain and the partition sum $\mathcal{Z}(N)$ are found to obey the power laws

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

with some fugacity z that shows the number of possibilities to locally add one more monomer to the chain, while the two exponents ν and $\gamma - 1$ represent the nontrivial corrections that are due to the self-avoiding interaction that is non-local along the chain.

These exponents are the $n = 0$ limits of the correlation length exponent $\nu(n)$ and the susceptibility exponent $\gamma(n)$ of the n-component model. 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 $n = 0$-component spin model can be extended to describe polymer networks and in particular star polymers [8]. A family of additional exponents γ_f governs the scaling of the partition sums $\mathcal{Z}_f(N)$ of polymer stars of f chains each with N monomers:

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

Again the exponents of any other power law for more general polymer networks is given by scaling relations in terms of γ_f and ν. For details of a proof and necessary restrictions on the chain length distributions see [8]. For large f each chain of the star is restricted approximately to a cone of space angle $\Omega_f = 4\pi/f$. In this cone approximation one finds for large f [9]

$$\gamma_f - 1 \sim -f^{3/2}. \tag{3}$$

Let us now turn to the effective interaction between the cores of two star polymers at small distance (small on the scale of the size R_g of the star). In the formalism of the $n = 0$ component model, the core of a star polymer corresponds to a local product of f spin fields $\phi_1(\mathbf{x}) \cdots \phi_f(\mathbf{x})$, each representing the endpoint of one polymer chain. The probability of approach of the cores of two star polymers at small distance r results in these terms from a short distance expansion for the composite fields. Let us consider the general case of two stars of different functionalities f_1 and f_2. The power law for the partition sum $\mathcal{Z}_{f_1 f_2}^{(2)}$ of two such star polymers at distance r [10]

$$\mathcal{Z}_{f_1 f_2}^{(2)}(r) \sim r^{\Theta_{f_1 f_2}^{(2)}} \tag{4}$$

is governed by the contact exponent $\Theta_{f_1 f_2}^{(2)}$. Then the short distance expansion provides the scaling relations

$$\begin{aligned}
\nu \Theta_{f_1 f_2} &= (\gamma_{f_1} - 1) + (\gamma_{f_2} - 1) - (\gamma_{f_1 + f_2} - 1), \\
\Theta_{f_1 f_2} &= \eta_{f_1} + \eta_{f_2} - \eta_{f_1 + f_2}.
\end{aligned} \tag{5}$$

Here, we have substituted an equivalent family of exponents η_f to replace $\gamma_f - 1 = \nu(\eta_f - \eta_2)$. The mean force $F_{f_1 f_2}^{(2)}(r)$ between two star polymers at short distance r is easily derived from the effective potential $V_{f_1 f_2}^{\text{eff}}(r) = \log \mathcal{Z}_{f_1 f_2}^{(2)}(r)$ as

$$F_{f_1 f_2}^{(2)}(r) = \frac{\Theta_{f_1 f_2}^{(2)}}{r}, \quad \text{with} \quad \Theta_{ff}^{(2)} \approx \frac{5}{18} f^{3/2}. \tag{6}$$

The factor $5/18$ is found by matching the cone approximation for $\Theta_{ff}^{(2)}$ to the known values of the contact exponents for $f = 1, 2$ [1]. This matching in turn proposes an approximate value for the η_f exponents,

$$\eta_f \approx -\frac{5}{18}(2^{3/2} - 2)f^{3/2}. \tag{7}$$

Table 1: The prefactor $\Theta_{f_1 f_2}$ of the force between two star polymers at short distance calculated in non-resummed 1-loop and resummed 3-loop RG analysis in comparison to the result of the cone approximation.

$\Theta_{f_1 f_2}$	$f_2 = 1$	$f_2 = 2$	$f_2 = 3$	$f_2 = 4$	$f_2 = 5$	app.
$f_1 = 1$	-.21	-.42	-.63	-.85	-1.06	1-loop
$f_1 = 1$	-.28	-.48	-.62	-.76	-.87	3-loop
$f_1 = 1$	-.27	-.45	-.60	-.73	-.84	cone
$f_1 = 2$		-.85	-1.27	-1.70		1-loop
$f_1 = 2$		-.82	-1.10	-1.35		3-loop
$f_1 = 2$		-.78	-1.05	-1.29		cone
$f_1 = 3$			-1.91			1-loop
$f_1 = 3$			-1.49			3-loop
$f_1 = 3$			-1.44			cone

Note that this is inconsistent with the exact result $\eta_1 = 0$. However, this assumption nicely reproduces the contact exponents as derived from 3-loop perturbation theory [11] as is displayed in table 1.

In table 1 we have used the approximate values of η_f to calculate the cone estimation of the contact exponents and compare these with corresponding values of a renormalization group calculation. We use here a perturbation series in terms of an expansion in the parameter $\varepsilon = 4 - d$ where d is the space dimension. In $d = 4$ the theory becomes trivial as is intuitively understood, because in $d = 4$ dimensions a random walk (polymer) never meets itself and thus the nontrivial self-avoiding interaction vanishes. The expansion in ε is thus an expansion starting from the theory that describes the polymer as a non-interacting random walk. The result labeled '1-loop' corresponds to optimal truncation of the series simply inserting $\varepsilon = 1$ or $d = 3$ in the first order term of the expansion. The 3-loop result includes a resummation procedure that takes into account the asymptotic nature of the series [11]. The large f result corresponds to the cone approximation.

To summarize, we have shown that the large f approximation for the short distance force between two star polymers can be consistently fitted to the results of perturbation theory for low values of the functionality f of the stars. We have at the same time generalized the approach to the interaction between two stars of different functionalities f_1 and f_2. This is essential in extending the theory of colloidal solutions of star polymers to general polydispersity in f as it appears naturally in any real experiment.

Acknowledgements

References

[1] C.N. Likos, H. Löwen, M. Watzlawek, B. Abbas, O. Jucknischke, J. Allgaier, and D. Richter, Phys. Rev. Lett. 80 (1998), 4450; M. Watzlawek, C.N. Likos, and H. Löwen, Phys. Rev. Lett. 82 (1999), 5289; A. Jusufi, M. Watzlawek, and H. Löwen, Macromol. 32 (1999), 4470.

[2] R. Seghrouchni, G. Petekidis, G. Fytas, A.N. Semenov, J. Roovers, and G. Fleischer Europhys. Lett., 42 (1998) 271.

[3] A.P. Gast, Langmuir, 12 (1996) 4060; G.S. Grest, L.J. Fetters, J.S. Huang, and D. Richter, Adv. Chem. Phys., XCIV (1996) 67.

[4] T.A. Witten and P.A. Pincus, Macromol., 19 (1986) 2509; T.A. Witten, P.A. Pincus, M.E. Cates, Europhys. Lett., 2 (1986) 137.

[5] P.G. de Gennes, Phys. Lett., A38 (1972) 339.

[6] H. Staudinger, Die Hochmolekularen Organischen Verbindungen. Springer, Berlin 1932, P.J. Flory, Principles of Polymer Chemistry. Cornell Univ. Pr., Ithaca, NY (1978)

[7] L. Schäfer, Excluded Volume Effects in Polymer Solutions, Springer, Berlin (1999)

[8] L. Schäfer, C. von Ferber, U. Lehr and B. Duplantier, Nuc.Phys. 374 (1992) 473

[9] K. Ohno and K. Binder, J. Phys. France 49 1329 (1988).

[10] B. Duplantier, J.Stat.Phys. 54 (1988) 581

[11] C. von Ferber and Yu. Holovatch, Europhys. Lett., 39 (1997) 31; Phys. Rev. E, 56 (1997) 6370; Physica A, 249 (1998) 327; Phys. Rev. E, 59 (1999) 6914.