

Star Polymers Viewed as Ultrasoft Colloidal Particles

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Combining statistical-mechanical theories and neutron-scattering techniques, we show that the effective pair potential between star polymers is exponentially decaying for large distances and crosses over, at a density-dependent corona diameter, to an ultrasoft logarithmic repulsion for small distances. We also make the theoretical prediction that in concentrated star polymer solutions, this ultrasoft interaction induces an anomalous fluid structure factor which exhibits an unusually pronounced second peak. [S0031-9007(98)06148-1]

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Star polymers consist of a well-defined number f of flexible polymer chains tethered to a central microscopic core. By enhancing this functionality (or arm number) f which governs the interpenetrability of two stars, one can continuously switch from unbranched polymer chains ($f = 1, 2$) to a colloidal sphere ($f \gg 1$). Hence, star polymers can actually be viewed as hybrids between polymerlike entities and colloidal particles establishing an important link between these different domains of physics. Moreover, star polymer solutions reveal quite a number of novel structural and dynamical properties which occur neither in single-chain polymers nor in suspensions of colloidal spheres; for recent reviews see Refs. [1,2].

While the polymer conformations around a *single* star are well understood by computer simulation [3], scaling theory [4], and small-angle neutron scattering experiments [5], *concentrated* star polymer solutions are much more difficult to access due to the additional effective interactions between the stars. In particular, these interactions become relevant when the distance r between two star polymer centers is of the order of the so-called corona diameter σ , which describes the spatial extension of the monomer density around a single star (see the inset of Fig. 1). This translates immediately into an overlap density $\rho^* \equiv 1/\sigma^3$ of the core number density ρ . Close to this overlap density ρ^* , there is an effective repulsion between stars resulting from the osmotic pressure arising between polymers from different cores. The repulsion is purely entropic; i.e., it simply scales with the thermal energy $k_B T$. Witten and Pincus [6] were the first to derive the functional form of this repulsion. The effective potential between two stars, $V(r)$, was found to depend logarithmically on r and to scale asymptotically as $f^{3/2}$ with the arm number, i.e., $V(r) = -k_B T \gamma f^{3/2} \ln(r/\sigma)$, where k_B is Boltzmann's constant, T is the temperature, and γ is an unknown numerical prefactor. Note that this result was obtained only for large f and for small distances $r \leq \sigma$. Since this potential depends only weakly on r , the stars can be viewed as "ultrasoft" colloidal particles whose interaction

is very different from common soft spheres described, e.g., by an inverse-power potential [7,8].

The aim of this Letter is twofold: First, we describe the star polymer interaction *quantitatively*, proposing an explicit analytical expression for the effective pair potential $V(r)$, similar to that in Ref. [6] which is designed, however, for arbitrary r and f . Using fluid-state theory and Monte Carlo computer simulations, we have calculated the structural correlations. At the same time, we have performed small-angle neutron scattering measurements on 18-arm polyisoprene stars over a broad density regime, ranging from $\rho = 0.07\rho^*$ to $\rho = 0.6\rho^*$. The experimental data for the pair correlations compare favorably well with our theoretical results.

Second, more *qualitatively*, we predict theoretically an anomalous fluid structure factor $S(q)$ with a first peak that decreases and a pronounced second peak that increases with growing density slightly above the overlap concentration. This is unknown for common simple fluids [7] whose repulsive interaction potential is governed by a single length scale.

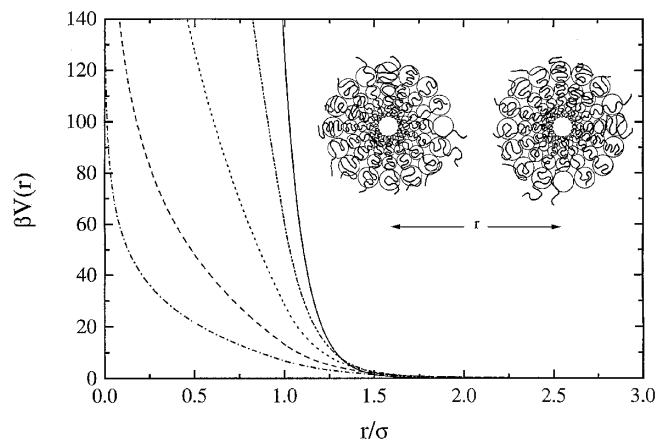


FIG. 1. The pair potential given by Eq. (1) for $f = 18, 32, 64, 128,$ and 256 (from left to right) as a function of the center-to-center separation r . Inset: two stars in the "blob" picture [4], at distance r from each other.

Let us start by stating and discussing the form of our pair potential [9] $V(r)$ which reads as follows:

$$\frac{V(r)}{k_B T} = \begin{cases} (5/18)f^{3/2}[-\ln(r/\sigma) + (1 + \sqrt{f}/2)^{-1}] & (r \leq \sigma); \\ (5/18)f^{3/2}(1 + \sqrt{f}/2)^{-1}(\sigma/r) \exp[-\sqrt{f}(r - \sigma)/2\sigma] & (r > \sigma). \end{cases} \quad (1)$$

The potential $V(r)$ is an interpolation between a Yukawa form, suitable for $r > \sigma$, and a logarithmic behavior, appropriate for $r < \sigma$, shifted by a constant which is chosen in such a way that the potential is smooth at $r = \sigma$. The logarithmic form of the interaction sets in when two stars are separated by such a distance that the outermost blobs of the stars in the Daoud-Cotton model [1,4] fully overlap; i.e., $\sigma/2$ is the distance from the center of the star to the center of the outermost blob. By geometry, the latter has a radius $R_b = \sigma/\sqrt{f}$. Let us discuss these two regimes in more detail.

(i) $r \leq \sigma$: Here our potential coincides with the expression given by Witten and Pincus [6]. The numerical prefactor γ is known to be equal to $5/18 = 0.277\dots$ for $f = 1$ and 0.28 for $f = 2$ [6]. Hence, even for the smallest values of the functionality the $f^{3/2}$ scaling holds almost perfectly, which gives us reason to assume that $\gamma = 5/18$ holds for arbitrary f .

(ii) $r > \sigma$: For the unbranched case ($f = 1, 2$), it is known that the long-distance behavior of $V(r)$ is exponentially decaying in r [10] which we assume to be of the special Yukawa form for arbitrary f . We fix the decay length in the exponential to be twice the largest blob radius. The amplitude of the Yukawa potential is finally determined by the requirement of continuity of the potential and its derivative with respect to r at $r = \sigma$.

The behavior of $V(r)$ is shown in Fig. 1 for different values of f . While for low f there is no dramatic change in its behavior as r crosses σ , a spectacular change between $r > \sigma$ and $r < \sigma$ is seen for $f = 128$ and 256 . In fact, in the ‘‘colloidal limit’’ $f \rightarrow \infty$, $V(r)$ diverges for $r < \sigma$ and vanishes for $r > \sigma$, and we recover the well-known hard-sphere potential [8].

We now take the pair potential given by Eq. (1) and apply the Rogers-Young (RY) closure [11] to obtain information about the pair structure of the liquid, in particular the center-to-center structure factor $S(q)$ of the stars. In addition, we have performed Monte Carlo simulations [12], finding that for all densities considered ($0 < \rho < 3\rho^*$) the Rogers-Young closure gives $S(q)$'s which are practically indistinguishable from the simulation data.

The labeled 18-arm polyisoprene (PI) star that we used for our small-angle neutron scattering (SANS) experiments was prepared by anionic polymerization. The synthesis of the arms started with deuterated PI and secondary butyl lithium as initiator and proceeded with protonated PI. The still living polymer chains were coupled to the 18-functional chlorosilane linking agent $[\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{SiCl}_3)_3]_2$. The result of the synthesis is a labeled 18-arm star with a near-monodisperse molecular weight distribution, where each arm commences with

27 protonated monomers in the core and continues with 81 monomers to the deuterated shell. The molecular weight of the arm is 8000 g/mol. The solvent and the deuterated shell have the same scattering length density and in the experiment only the protonated core is visible.

The SANS experiments were performed at the FRJ-2 reactor of the Forschungszentrum Jülich. Using fully deuterated methylcyclohexane as solvent, samples covering polymer volume fractions ϕ in the range $5 \times 10^{-4} \leq \phi \leq 0.3$ were investigated. The solutions were studied in 1 mm quartz cells, resulting in sample transmission between 55% and 85%. The SANS experiments were carried out at a neutron wavelength $\lambda = 7 \text{ \AA}$, employing sample-detector distances of 1.25, 2, 4, and 8 m. In this way a range of momentum transfer $0.005 \leq q \leq 0.25 \text{ \AA}^{-1}$, where $q = (4\pi/\lambda) \sin(\theta/2)$ and θ is the scattering angle, was covered. The scattering due to the empty cell and the solvent, as well as the incoherent scattering of the deuterated part of the star and the calculated incoherent background caused by the protonated part of the polymer were subtracted. The resulting q dependence of the scattered intensity $I(q)$ after scaling by the volume fraction ϕ is shown in Fig. 2. Assuming that the form factor $P(q)$ of the labeled inner part of the star is not affected by the polymer volume fraction ϕ , the influence of the structure factor $S(q)$ relating to interstar correlations enters the expression for the intensity $I(q)$ as a product [1]

$$I(q)/\phi = V_W P(q) S(q) = \frac{1}{\phi} \frac{N_A}{\Delta\rho^2} \frac{d\Sigma^{\text{coh}}(q)}{d\Omega}, \quad (2)$$

where V_W denotes the weight-average molar polymer volume of the labeled part of the star, $\Delta\rho^2$ is the contrast factor between the solvent and the protonated core of the star, N_A is the Avogadro constant, and $d\Sigma^{\text{coh}}(q)/d\Omega$ is the coherent macroscopic differential scattering cross section. The form factor $P(q)$ was determined by extrapolating $I(q)$ to zero volume fraction ϕ . In order to obtain an analytical expression for the quantity $V_W P(q)$, we fitted the data extrapolated to $\phi = 0$ with an empirical form factor given by Dozier [13,14]. Finally, in order to compare directly with the theoretical predictions, the quantity $V_W P(q) S(q)$ must be convoluted with the resolution function $R(q, q_0)$ of the experimental apparatus, where q_0 is the considered wave vector, given by

$$R(q, q_0) = \frac{1}{\sqrt{2\pi} \Delta q} \exp\left\{-\frac{1}{2} \frac{(q - q_0)^2}{(\Delta q)^2}\right\}, \quad (3)$$

where $(\Delta q)^2 = (2\pi\Delta\theta/\lambda)^2 + (q_0\Delta\lambda/\lambda)^2$, with $\Delta\theta = 3.6 \times 10^{-3}$ being the uncertainty in the angle and $\Delta\lambda/\lambda = 0.085$ the relative uncertainty in the wavelength.

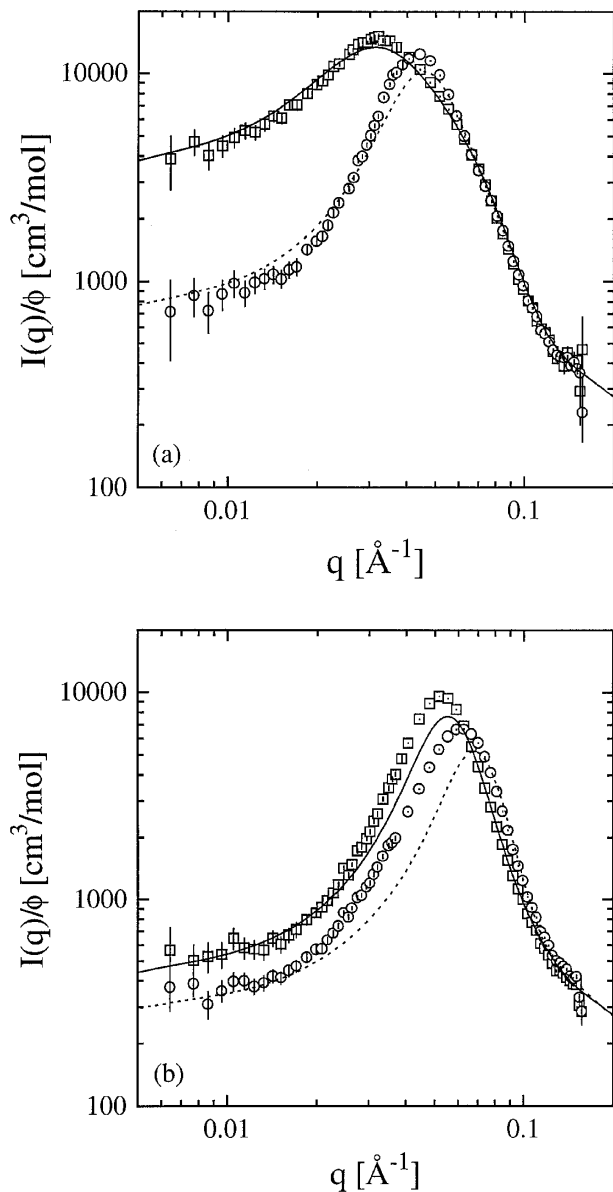


FIG. 2. Experimental (points) vs theoretical results (lines) for the total scattering intensity $I(q)/\phi$ of 18-arm stars at various volume fractions ϕ . From top to bottom: (a) $\phi = 2\%, 8\%$; (b) $\phi = 15\%, 30\%$.

In attempting to fit the experimental data for the total scattering intensity $I(q)$ with the theoretical predictions based on an analytic pair potential, we must take into consideration the fact that the star size itself has a dependence on the concentration ϕ , as was earlier found experimentally [5,15]. Indeed, the radius of gyration R_G of the star was found to be almost constant up to the overlap concentration $\phi^* \approx 10\%$, whereas a shrinkage of the star was observed at higher ϕ [5,16]. Accordingly, the length σ must also have a ϕ dependence, $\sigma = \sigma(\phi)$, to account for the influence of the deformation of the star on the pair interaction. We fixed this dependence as follows: for the lowest concentration considered, $\phi = 2\%$,

we obtain σ by optimizing the agreement between the theoretical prediction and the experimental results. For the potential given by Eq. (1), we obtain in this way $\sigma(\phi = 2\%) = 96 \text{ \AA}$. At the same concentration, the experimentally measured radius of gyration is $R_G(\phi = 2\%) = 76.1 \text{ \AA}$ [5,15]. This fixes once and for all the ratio $\sigma/R_G \equiv \tau = 1.26$. For all other concentrations ϕ we set $\sigma(\phi) = \tau R_G(\phi)$, where $R_G(\phi)$ is read from the experimental results [5,15]. In this way we can say that our fit contains *no adjustable parameters* since σ does not vary arbitrarily with ϕ , but rather in a way dictated by the measured values of the size of the star. Moreover, let us also remark that the value $\sigma = 96 \text{ \AA}$ gives a theoretical value for the total size of the star which is again consistent with the experimental results. Indeed, the theoretical radius of the star is $\sigma/2 + R_b = \sigma/2 + \sigma/\sqrt{f}$. For $\phi = 2\%$ and taking $\sigma = 96 \text{ \AA}$, this yields the value 70.63 \AA which is within two error bars from the experimental result [5,15].

In Fig. 2 we show representative results for $\phi = 2\%, 8\%, 15\%$, and 30% . It can be seen that the fit is quite satisfactory for the whole range of concentrations. In particular, the compressibility of the solution, being proportional to $I(q \rightarrow 0)$ is given correctly for all concentrations, as well as the general shape and wave number q_{\max} at which the scattering intensity displays a maximum. The height of the peak is underestimated by the theory and the agreement worsens somewhat as the concentration grows. However, at high values of ϕ the decoupling between form and structure factors implied in writing down $I(q) = V_w P(q) S(q)$ becomes questionable, and this is a possible source of discrepancies between theory and experiment. We emphasize that our logarithmic-Yukawa potential is the first that gives semiquantitative agreement between theory and experiment for such a wide range of concentrations. Earlier attempts to fit the experimental results with a hard sphere-Yukawa interaction, for example, failed at and beyond the overlap concentration ϕ^* [17]. Indeed, the existence of a “soft core,” such as the logarithmic term in our potential is crucial at high concentrations where the stars start interpenetrating.

In order to put the proposed pair potential into further tests, we have also made the following changes: first, we kept the logarithmic-Yukawa form, but changed the definition of σ . The new $\sigma/2$ is now the distance from the center of the star to the boundary between the two outermost blob shells. This choice gives $\sigma(\phi = 2\%) = 50 \text{ \AA}$; the quality of the fits, however, is systematically worse than that with the original definition of σ at all concentrations. Second, keeping the original definition of σ , we used a different functional form for the pair potential outside the length σ (but always maintaining the logarithmic form for $r < \sigma$). Earlier calculations of the effective repulsion between two *free* polymer coils show that it has a Gaussian form [10]. We thus matched the potential outside σ by a Gaussian having again a decay

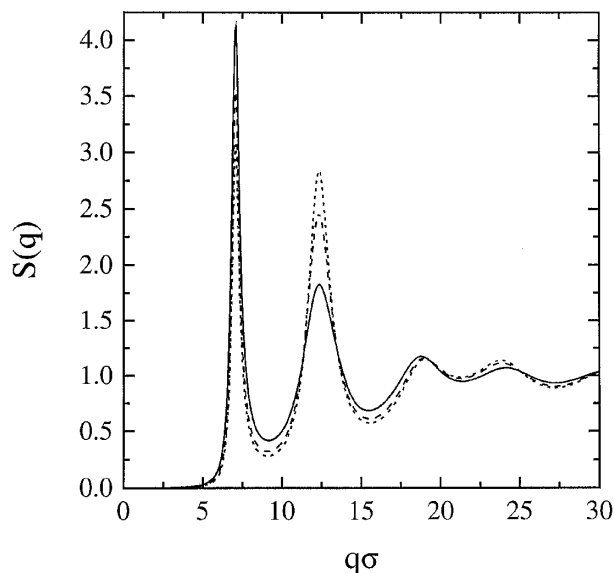


FIG. 3. Static structure factors for a system interacting by means of the pair potential given by Eq. (1) with $f = 64$. Solid line: $\rho = 1.91\rho^*$; dashed line: $\rho = 2.67\rho^*$; dotted line: $\rho = 3.05\rho^*$.

length proportional to R_b . This way we obtain a fit of the $\phi = 2\%$ data by fixing $\sigma(\phi = 2\%) = 150 \text{ \AA}$. However, the fit fails at the next value of concentration, $\phi = 5\%$, when σ is varied consistently with the measured values of R_G . Thus, we conclude that the combination of the logarithmic and the Yukawa forms is essential in bringing about reasonable agreement between theory and experiment.

Finally, we discuss some *theoretical predictions* for the structure factor of a system characterized by the pair potential of Eq. (1), as obtained from the RY closure and simulations. For $f = 18$, the height of the first peak of $S(q)$ grows with increasing density up to $\rho \approx 0.60\rho^*$, but upon further increase of the density it becomes lower. At very high concentrations, $\rho > 2\rho^*$, more unusual effects are seen. To demonstrate these, we now take the case $f = 64$, where the unusual features are more pronounced than for $f = 18$. As can be seen from Fig. 3, $S(q)$ has a first sharp peak whose height *decreases* with density, whereas the height of the secondary peak *increases* with density. Moreover, the position of the peaks is very insensitive to the density. For usual dense liquids (hard spheres, one-component plasma), whose interaction involves a single length scale, the structure factor displays peaks whose positions depend only on the length scale set by the density, $a = \rho^{-1/3}$. Moreover, in those cases, the height of all the peaks grows uniformly as the density is raised. Here, on the contrary, the ultrasoft character of the logarithmic potential and the crossover to a Yukawa form at $r = \sigma$ bring about unusual features in

$S(q)$. The relation of these features to the underlying pair distribution function $g(r)$ and the overall phase behavior of the system will be the subject of a future publication.

In conclusion, we have demonstrated by direct comparison with experimental data that the effective repulsion between two star polymers of functionality f has a logarithmic form at small center-to-center distances and crosses over to an exponential at larger distances. The ultrasoft character of the logarithmic potential brings about quite a few novel features in the fluid structure. We expect that unusual characteristics will also show up in the phase diagram of the system as well, e.g., in the variety of possible solid phases and in its topology.

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