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Block copolymer micelle coronas as quasi-two-dimensional dilute or semidilute polymer solutions

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Chain-chain interactions in a corona of polymers tethered to a spherical core under good solvent conditions are studied using Monte Carlo simulations. The total scattering function of the corona as well as different partial contributions are sampled. By combining the different contributions in a self-consistent approach, it is demonstrated that the corona can be regarded as a quasi-two-dimensional polymer solution, with a concentration dependence analogous to that of an ordinary polymer solution. Scattering due to the corona profile and density fluctuation correlations are separated in this approach. The osmotic compressibility is extracted from the latter, and it is shown to be a universal function of surface coverage, with some deviations at high coverage due to surface curvature effects.

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Polymers can be tethered to a surface, thus forming a diffuse layer on the surface [1,2]. The equilibrium properties of such a layer follow from the balance between entropic forces and excluded volume interactions. The latter favor a state with a minimum of monomer-monomer contacts, which can be achieved by increasing the available volume per chain by increasing the layer thickness. Entropic forces will tend to maximize the number of available chain configurations by opposing the chain stretching and by shifting the corona away from the surface to some extent. At low surface coverage the surface interaction will dominate, and the polymers will have a mushroomlike shape. At very high surface coverage, excluded volume interactions and chain-chain interactions dominate and chains will be strongly stretched forming a polymeric brush [3,4]. Between the mushroom and brush regime there is a broad region of intermediate surface coverages [5], which is the typical regime accessible by experiments, see, e.g., [6,7].

In the present work we study the scattering from the polymeric layer of a spherical particle such as the polymer corona of a diblock copolymer micelle. We use Monte Carlo (MC) simulation-generated data to show that a model in which the corona is regarded as a two-dimensional solution is applicable. The total corona scattering can be decomposed in two ways. In the analytical model of Pedersen and Gerstenberg [8], the intrachain and interchain scattering contributions are combined to give the corona scattering, however, the same result can be obtained by combining the scattering contribution due to the *average* corona profile and density fluctuation correlations [9]. The latter decomposition can be interpreted as being the scattering expected from a thin layer of dilute or semidilute solution confined to a thin layer around the core [10]. The approach presented in the present paper is based on self-consistent analysis of the MC results using the expressions provided by these two decompositions. The total corona scattering as well as the intrachain, interchain, and corona profile scattering contributions were sampled during the simulations. The effects of excluded volume interactions, core expulsion, and chain semiflexibility on the scattering was simulated and a series of simulations varying the number of chains, chain length, and core radius were performed. In the analysis of the two expressions, a random phase approximation (RPA) was used for the fluctuation scattering contribution, and excellent agreement was obtained when inserting the partial scattering contributions as obtained from MC simulations. The excellent agreement of the two expressions enables us to extract the scattering contribution due to density fluctuation correlations within the corona. These carry thermodynamic information about the apparent second virial coefficient and the osmotic compressibility of the polymer layer. These quantities show a surface coverage dependence analogous to that expected from an ordinary polymer solution.

Numerous approaches such as self-consistent field theory [11,12], variational techniques [13], and numerical simulations [14,15] have all been applied for investigating the profiles of brushes on curved interfaces. Polymer layers at low and medium surface coverages are not amenable to analytically treatment, due to the presence of large density fluctuations. However, the small-angle scattering from a polymeric interface depends not only on the profile, but also on the correlations of density fluctuations [9]. The scattering from a dilute or semidilute solution of star polymers were treated by Marques *et al.* using an empirical ‘‘blob’’ approach [16]. Our approach offers a clear quantitative picture of the interaction effects in micellar coronas, which are based firmly on Monte Carlo simulation results.

We describe the density of chains in a polymer corona on the surface of a spherical particle using a reduced surface coverage. Due to the chain entropy, the center of mass of a chain will be located at approximately a distance R_g from the core surface, where R_g is the unperturbed chain radius of gyration. The effective core surface area is thus $4\pi(R_{co}+R_g)^2$, where R_{co} is the core radius, whereas the cross-sectional area of N chains is $\pi R_g^2 N$. The reduced surface coverage is given by the ratio of cross-sectional chain area to available surface area as $\sigma = N\pi R_g^2/[4\pi(R_{co}+R_g)^2]$. The reduced surface coverage is a two-dimensional analogy of the c/c^* concentration [17,18] for ordinary polymer solutions. A surface coverage of unity corresponds to critical

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overlap, where the area occupied by an unperturbed chain equals the available surface area per chain. For $\sigma < 1$ chains are few and far apart and weakly perturbed by the presence of other chains, and the scattering is well described by the model of Pedersen and Gerstenberg [8]. However, in the brush regime ($\sigma \gg 1$) the surface will induce chain ordering perpendicular to the surface as chains are stretched. The scattering in this regime is expected to be described by a core-shell model [19]. Experimentally $\sigma < 5$ is found for copolymer micelles [20–22].

The normalized corona scattering $[F_{cor}(q=0)=1]$ consists of two weighted contributions: an intrachain contribution F_c and an interchain contribution S_{cc} as

$$F_{cor}(q) = \frac{1}{N} F_c(q) + \left(1 - \frac{1}{N}\right) S_{cc}(q). \tag{1}$$

Here q is the magnitude of the scattering vector, and F_c is the Fourier transform of the pair-distance distribution between sites on the same chain. The intrachain scattering is mainly due to chain connectivity and self-avoidance, and single-chain properties such as the radius of gyration, the contour length L, and the Kuhn length b can be determined from it. For a long semiflexible chain, the Kuhn length is the step length of an equivalent random walk. The interchain scattering S_{cc} is the Fourier transform of the pair-distance distribution between sites on different chains. The interchain scattering contains information about the corona profile, and the radius of the core. However, it also includes correlations due to chain-chain interactions such as the ‘‘correlation hole,’’ which is known to be present in ordinary polymer solutions [17,18].

Core-shell models [19] describe the corona scattering in terms of the configurationally averaged profile, and as a result all density fluctuation correlations due to chain connectivity, self-avoidance, and chain-chain interactions are neglected. The core-shell approximation is $F_{cor} = A_{cor}^2$, where the profile scattering is given by $A_{cor}(q) = \int_0^\infty f(r)\sin(qr)/(qr)4\pi r^2 dr$, and where $f(r)$ is the corona profile. If chain-chain interactions are negligible, different chains will be uncorrelated, and the interchain scattering will be given by $S_{cc} = A_{cor}^2$. Chain-chain interactions will yield an additional contribution to the interchain scattering due to short-ranged density fluctuation correlations, which will dominate the interchain scattering at high q values. These fluctuations are caused by the repulsive excluded volume interactions between different chains. Based on this we define a fluctuation scattering contribution F_{fluc}, leaving only correlations due to the average profile (given by A_{cor}^2). Thus the corona scattering is rewritten as

$$F_{sol}(q) = \frac{1}{N} F_{fluc}(q) + \left(1 - \frac{F_{fluc}(q=0)}{N}\right) A_{cor}^2(q). \tag{2}$$

The weighting ensures that F_{sol} is normalized for $q=0$, since F_{fluc} is not normalized. Rewriting Eq. (1) as Eq. (2) has the effect of shifting the influence of the correlation hole from S_{cc} into F_{fluc}. Therefore, interchain correlations has to be included in an expression for the $F_{fluc}(q)$ term. We apply an expression based on the polymer reference interaction site model (PRISM) theory for polymer solutions and melts, see e.g., [23]:

$$F_{fluc}(q) = \frac{F_c(q)}{1 - \rho c(q) F_c(q)}. \tag{3}$$

Here $c(q)$ is the Fourier transform of the direct correlation function between sites on different chains in an equivalent site approximation, which depends on the site-site interaction potential, and ρ is the density of scattering sites. The F_{sol} expression has the interpretation as being the scattering of a dilute or semidilute solution with a profile $f(r)$, and will be called solution scattering.

We use Monte Carlo (MC) simulation results for comparing F_{cor} and F_{sol}. The micelle was modelled as a number of semiflexible chains tethered to a spherical core. Interactions were included by placing six hard spheres of radius $0.1b$ per Kuhn length b of the chains, as this reproduces the excluded volume effects found experimentally for polystyrene in a good solvent [24]. Chains were excluded from the core region. The MC moves consisted of pivoting the chain tails [25], and two moves, that moved and reorientated chains on the core surface. We note that chains are not free to move about on the surface of a micelle with a glassy or crystalline core. However, the observed scattering is an ensemble average of all allowed corona configurations, and this includes an average over the location of the chain tethering points, which requires a surface move. The configurational ensemble averages of the F_c, S_{cc}, and A_{cor} scattering contributions were simultaneously sampled during the MC simulations [26]. The unperturbed chain radius of gyration was obtained from a separate set of simulations of a single chain. We chose a reference micelle defined as having $N=44$ chains, chain length $L=8.33b$, and core radius $R_{co}=3.33b$, this choice mimics a Pluronic P85 micelle [8]. We performed three series of simulations, where one of the three parameters was varied in turn, while keeping the remaining two fixed at their reference values. The range of variation was chosen to correspond to a variation of surface coverage σ in the range from 0.01 to about five, thus covering the experimental regime ranging from isolated chains to a reasonable chain overlap. It should be noted that the equilibrium corona configuration does not only depend on the reduced surface coverage, but also on the surface curvature R_g/R_{co} and number of chains N.

Comparing (1), (2), and (3) for the sampled scattering contributions allows us to obtain the $-\rho c(q)$ term from the simulation results. We found that it has a weak dependence on q, and as a result we approximate it with an effective excluded volume parameter $\nu(\sigma) \equiv -\rho c(q)$. This converts the PRISM expression (3) into the form of a random phase approximation. The excluded volume parameter is related to a virial expansion of the reduced osmotic compressibility as $\nu(\sigma) = 2A_2\sigma + 3A_3\sigma^2 + \ldots = 2A_2(\sigma)\sigma$, where $A_2(\sigma)$ is the reduced apparent second virial coefficient [27]. A_{cor} oscillates around zero, and we have determined $\nu(\sigma)$ from the first zero point of A_{cor}.

The sampled corona scattering from simulations varying the number of chains is shown in Fig. 1, normalized such

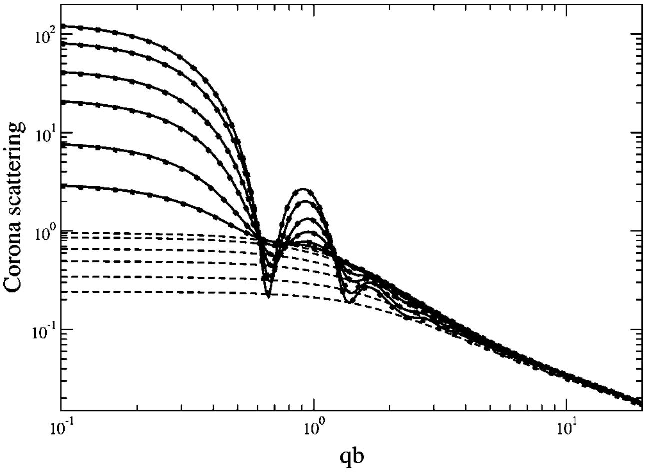

FIG. 1. Comparison between corona scattering F_{cor} and solution scattering F_{sol} for micelles with the number of chains: $N = 3,8,22,44,87,131$ (bottom to top). F_{cor} (thick line), F_{sol} (full boxes), and the fluctuation scattering F_{fluc} (thin dashed line) are shown. These are normalized such that the single chain scattering coincides in the large q limit.

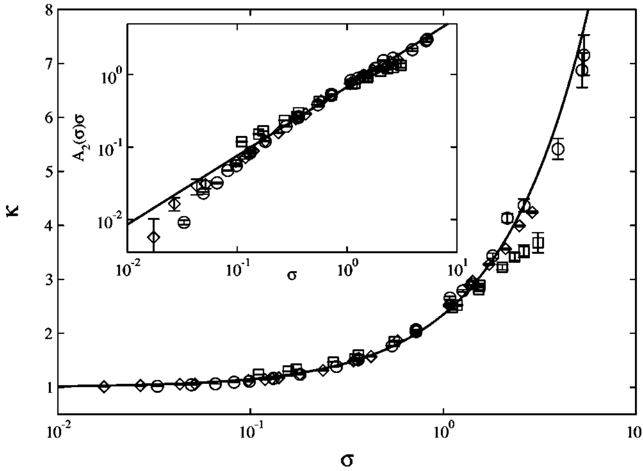

FIG. 2. The reduced osmotic compressibility κ plotted against surface coverage for simulations varying the number of chains (circle), the chain length (box), and the core radius (diamond). The insert shows the $A_2(\sigma)\sigma$ plotted against the surface coverage. The line in the inset is the power law $A_2(\sigma)\sigma = 0.675\sigma^{0.95}$ and the corresponding osmotic compressibility is shown as a line in the figure.

that they coincide for large q values. The huge increase in oscillations as the number of chains increases is caused by the change in weighting between the highly oscillatory interchain contribution and the nonoscillatory intrachain contribution. Also shown in Fig. 1 is the solution scattering. The two sets of curves show an excellent match, which demonstrates the self-consistency of our model of the corona scattering. Similar excellent agreement is obtained for simulations varying the length of chains and the core radius (not shown). Finally, the fluctuation scattering contribution F_{fluc} is shown. This contribution is seen to decrease with increasing surface coverage, analogous to the concentration dependence of the scattering from a polymer solution, see, e.g., [28]. The corona scattering is dominated by profile scattering at low q values, whereas the fluctuation scattering dominates at large q values.

A fluctuation-dissipation theorem relates the Fourier transform of the density fluctuation correlation function to the osmotic compressibility [17]. The reduced osmotic compressibility is given by $\kappa \equiv \partial\Pi^*/\partial\sigma = F_{fluc}(q=0)^{-1} = 1 + 2A_2(\sigma)\sigma$, where the reduced osmotic pressure is $\Pi^* = \pi R_g^2 \Pi/(k_b T)$. In this expression Π, k_b, and T are the osmotic compressibility, Boltzmann constant, and temperature, respectively. Figure 2 shows the reduced osmotic compressibility obtained from simulations varying number of chains, chain length, and core radius, and the points fall on a universal curve as function of surface coverage. Similar behavior has been predicted for polymers at flat interfaces by Carignano and Szleifer for Π^* [5] for $\sigma < 6$. The osmotic compressibility shows a weak dependence of surface coverage for $\sigma < 1$, as one would expect from the dilute polymer solution analogy, see, e.g., [18]. The inset of Fig. 2 shows the apparent second virial coefficient. The values from the three series of simulations approximately collapse onto a common power-law relation: $A_2(\sigma)\sigma = \alpha\sigma^{\beta}$ with $\alpha = 0.68 \pm 0.01$ and $\beta = 0.95 \pm 0.02$. The PRISM theory in the thread limit [23] predicts that $A_2(c/c^*)$ is a constant for low concentrations. We observe a weak dependence on surface coverage in the range of surface coverages we have simulated. At high surface coverages the deviations from power-law behavior observed in the inset of Fig. 2 is reflected in the compressibility. We attribute these deviations to the effects of chain stretching, which shows some dependence on the surface curvature.

In this paper we have demonstrated that the scattering from a corona of chains tethered to a spherical core for experimentally relevant surface coverages can be self-consistently re-expressed as the scattering one would expect from a quasi-two-dimensional dilute or semidilute polymer solution confined to a thin layer on the core surface. We note that the radius of gyration as well as the correlation length are comparable to the corona thickness, which is why the polymer layer can be regarded as being quasi-two-dimensional. In the brush limit the chains will be aligned perpendicular to the surface. This is clearly far from the case of a semidilute solution, and we expect the RPA expression to break down in this limit. It should be noted that we do not observe any deviations between the corona scattering and the solution scattering even for the largest surface coverages simulated. The expression we have proposed for the solution scattering bridges the gap between the model of Pedersen and Gerstenberg, valid at low surface coverage, and the core-shell models expected to be valid at very high surface coverage, while retaining formal similarities with both models.

We have also demonstrated that the scattering contributions due to the corona profile and fluctuations decouple, allowing us to deduce the osmotic compressibility of the corona from the density-fluctuation correlation function. The compressibility shows a universal dependence on surface coverage analogous to that observed for ordinary polymer solutions as function of concentration. We furthermore expect similar expressions to be valid for the scattering from micelles with elliptical and cylindrical cores, however, with some deviations due to the variation of the local surface curvature for such geometrical shapes. The model we have presented can be used for separating corona profile and chain-chain correlation information in real experiments, and thus allows more detailed information to be gained by analysis of experimental data.

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