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Monte Carlo study of excluded volume effects in wormlike micelles and semiflexible polymers

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An off-lattice pseudocontinuous model for semiflexible polymerlike micelles with excluded volume interactions is presented. Expansion factors are determined for the radius of gyration squared and for three different characteristic point-point distances squared. They are found to scale with an exponent in agreement with renormalization-group results and with previous lattice simulations. A comparison with the Yamakawa-Stockmayer-Shimada theory gives a reduced binary cluster integral $B=0.30$ for the micelles which is similar to the value for polystyrene (PS) in a good solvent. We present an approach for simultaneously analyzing the point-point distance distribution functions and obtaining the characteristic parameters of these. Scattering functions are determined and used for analyzing small-angle neutron scattering data from PS in a good solvent. [S1063-651X(96)50812-3]

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Giant wormlike micelles have been found to behave essentially as semiflexible polymers in a good solvent [1–3]. This is most clearly reflected in the results of small-angle neutron (SANS) and static light scattering (SLS) experiments. The scattering function $S(q)$, where q is the modulus of the scattering vector, exhibits all the regions that are characteristic of the various length scales and properties of such polymers: overall size, flexibility, local stiffness, and finite cross-section size.

The scattering data in the literature have generally only been qualitatively analyzed using various asymptotic expressions. The exception is a recent light scattering study [3] in which the results were analyzed using the available theoretical expressions for semiflexible polymers in good solvents. One of the results of the scattering experiments is the root-mean-square radius of gyration, R_g. If R_g can be related to the contour length L of the chain, one has direct access to studying the growth law and the thermodynamics of the systems [3]. However, the dependence of R_g on L is not known, since the expansion factors of the chains due to excluded volume effects are not well known. Furthermore, the available semiempirical expansion factors of, e.g., R_g, from perturbation calculations [4] cannot be used, since the value of the binary cluster integral is not known for chains with the particular cross-section size and flexibility of the micelles. Moreover, there are currently no expressions available for the scattering function of semiflexible chains with excluded volume effects, which cover the entire q range and which could be used for analyzing SLS and SANS data from polymerlike micelles.

In this paper, we present a Monte Carlo model for self-avoiding semiflexible micelles based on the Kratky-Porod [5] (KP) model for semiflexible polymers. Polymerlike micelles are typically composed of thousands of amphiphilic molecules and are thus, for all practical considerations, continuous in nature. It can therefore be expected that the KP model can provide a good description of the micelles. Here we present a realization of the model with an approach for including the excluded volume interactions in a pseudocontinuous version of the model. An extremely efficient simulation algorithm [6] is used and this allows for the first time simulations to be performed on pseudocontinuous KP chains with excluded volume effects over five decades of contour length L/b, where b is the statistical (Kuhn) length. Determinations of R_g, the end-to-end distance D_{ee}, the end-to-middle distance D_{em}, and the distance between two inner points D_{ii}, situated at $L/4$ and $3L/4$ along the contour, as well as the distribution functions of the three latter parameters, have been performed. We present an approach, based on the empirical distribution functions suggested by Mazur [7] and the relation given by Fisher [8] for analyzing simultaneously the distributions in the large-L limit. This gives very accurate determinations of the characteristic parameters of the distribution functions, which can be compared with the predictions of renormalization-group calculations [9] and the results of simulations on lattice [10–12] and flexible polymer models [13–15].

The Monte Carlo model is based on the discrete representation [16] of the continuous KP model. The discrete model has N points separated by l_0, equal valence angles, and free rotation about the bonds. The contour length is $L=Nl_0$ and the Kuhn length, b, is related to the valence angle, θ, by $b=l_0(1+\cos\theta)/(1-\cos\theta)$. The two parameters that specify a certain micelle or chain are L/b and the dimensionless cross-section radius R/b of the micelle or chain. Typical values of b and R for micelles are 300 Å and 30 Å [2], which gives $R/b=0.1$. This value was used throughout the present work. In the model (and the simulations) the continuous limit is approached letting $N\rightarrow\infty$, $l_0\rightarrow 0$, and $\theta\rightarrow 0$ in such a way that L/b is constant.

The excluded volume effects are taken into account by placing hard spheres of radius R at each point along the chain. A hard-sphere potential has previously been found to give a correct description of intermicellar interactions in similar systems [17]. A test for volume overlap of a chain in the simulation can, in principle, be performed by checking the overlap between the spheres on the chain. However, for a large number of spheres per unit of b, i.e., for a large ratio of b/l_0, one encounters the problem that several consecutive spheres along the chain overlap irrespective of the chain conformation. Therefore, the search for overlap does not start in the immediate neighborhood (e.g., at the third nearest neighbor as in atomistic models [24]), but further along the chain depending on b/l_0. On a straight section of the chain, spheres separated by $2R$ along the contour do not overlap. However, the chain should be allowed to make a 180° bend. The spheres along the bend will have their centers on a semicircle of radius R, which means that the spheres separated by $\pi R = \pi b/10 \approx 0.314b$ along the contour should not overlap. Considering this, we have decided to look for overlap for spheres separated by more than $b/3$ along the contour (independent of the values of N, l_0, and L).

For fixed values of L/b the influence of the finite number of points on the chain, N, on $\overline{R_g}$, $\overline{D_{ee}}$, $\overline{D_{em}}$, and $\overline{D_{ii}}$, where $\overline{X}$ means ensemble root-mean-square value of X, was investigated by making extrapolations versus $1/N$. For the chains without excluded volume effects, comparisons were in addition made with the analytical results for $\overline{R_g}$ and $\overline{D_{ee}}$ [16,18]. For $N > 1000$ the error from finite-N effects was always smaller than 0.3%. For $L/b < 167$, $N = 1000$ was used. With this choice, the valence angle θ depends on L/b. For longer chains ($L/b > 167$) the number of spheres per unit b was six, which resulted in a sphere radius of $0.6l_0$. This gives a reasonable approximation to the local cylindrical structure for the long chains. For these chains $\theta = 44.42°$. For the longest chains with $L/b = 16384$ the number of points on the chain is 98305.

In the simulations for the short chains with $L/b < 100$, a simple rejection algorithm was used: chains were grown from scratch and those with overlap were simply discarded. This gives completely independent samples but the method is only efficient for short chains, since the number of rejections growths rapidly with L/b. For longer chains the pivot algorithm of Stellman and Gans [6,19] was used together with the ‘‘zippering method’’ for looking for overlap [20]. We have performed simulations for lengths ranging from $L/b = 0.25$ up to 16 384, both with and without excluded volume effects. For chain length $L/b < 100$, $10^4 - 10^5$ independent samples were generated by the rejection algorithm for each value of L/b. For $L/b > 100$ the typical ensemble size was 5×10^5. The errors on $\overline{R_g}$, $\overline{D_{ee}}$, $\overline{D_{em}}$, and $\overline{D_{ii}}$ were calculated by standard methods for the rejection algorithm, whereas a block analysis [22] was used for the pivot algorithm [21]. Typical standard errors are smaller than 0.3% and we note that the influence of finite N, mentioned in the previous paragraph is similar to or smaller than the standard errors. A comparison with methods involving more complicated schemes for the moves was performed for $L/b = 128$ [24]. The results agreed within the statistical errors.

The results for $\overline{R_g}$ [Fig. 1(a)] with and without excluded volume interactions start to differ around $L/b = 1$. The expansion factors α of $\overline{R_g}$, $\overline{D_{ee}}$, $\overline{D_{em}}$, and $\overline{D_{ii}}$ due to excluded volume effects have been calculated and are shown in Fig. 1(b). The expansion factor of, e.g., $\overline{R_g}$ is defined as $\alpha_{R_g}(L/b) = \overline{R_g}/(\overline{R_g})_0$, where $(\overline{R_g})_0$ is the value without excluded volume effects. The expansion factors exhibit a large crossover region between $L/b = 1$ and $L/b = 200$, and slowly approach the asymptotic behavior for $L/b > 200$. The exponents and the corrections to scaling were determined using [10,14]:

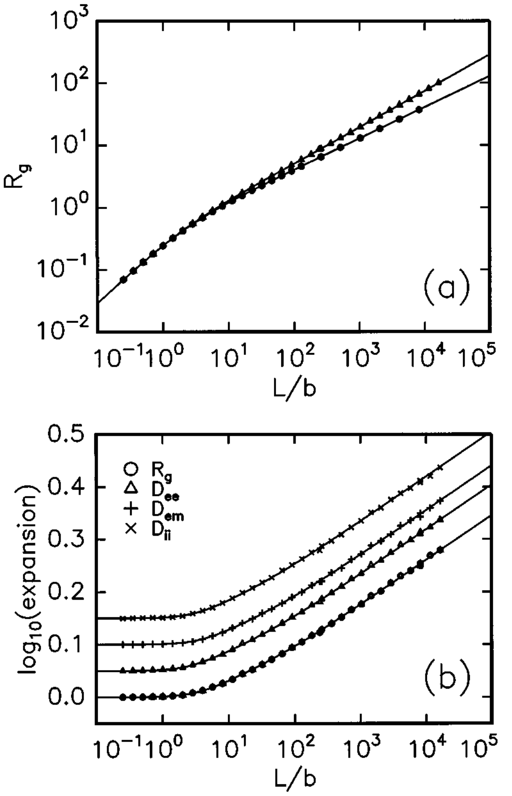

FIG. 1. (a) The dependence of $\overline{R_g}$ on L/b with (triangles) and without (circles) excluded volume interactions. (b) Expansion factors for $\overline{R_g}$, $\overline{D_{ee}}$, $\overline{D_{em}}$, and $\overline{D_{ii}}$ in a log-log representation. For clarity, the upper curves have been displaced by 0.05, 0.1, and 0.15, respectively. The curves are the fit obtained by the empirical expansion factors and the results for chains without excluded volume [18].

$$\alpha(x)^2 \approx A_1 x^{\epsilon}[1 + A_2/x^{\Delta}] \qquad (1)$$

with different values of A_1 and A_2 for the different parameters. A simultaneous least-squares fit for $L/b > 10$ to the expansion factors of the four parameters with the same value of ϵ gives $\epsilon = 0.1760 \pm 0.0035$ and $\Delta = 0.46 \pm 0.08$. The errors were estimated as described in [25]. The value of ϵ is in good agreement with the best renormalization-group calculation result of $\epsilon = 0.176$ [26], as well as with $\epsilon = 0.1754 \pm 0.0016$ found for lattice simulations [10].

In order to apply the simulation results in the analysis of experimental data, an expression for $\alpha(x)$ in the full range of the simulated data ($0.3 \leqslant L/b \leqslant 16384$) is required. The empirical expression $\alpha(x)^2 = [1 + (x/n_1)^2 + (x/n_2)^3]^{\tilde{\epsilon}/3}$ was found to give good fits in the full range. A simultaneous fit gave $\tilde{\epsilon} = 0.170$ and $n_1 = 3.12$, $n_2 = 8.67$ for R_g, $n_1 = 2.42$, $n_2 = 6.90$ for D_{ee}, $n_1 = 3.56$, $n_2 = 9.95$ for D_{em}, and $n_1 = 2.88$, $n_2 = 6.76$ for D_{ii}. $\tilde{\epsilon}$ deviates significantly from the value of ϵ found using Eq. (1) due to the different way the two expressions approach the asymptotic limit. The two expressions for α were found to have a root-mean-square de-

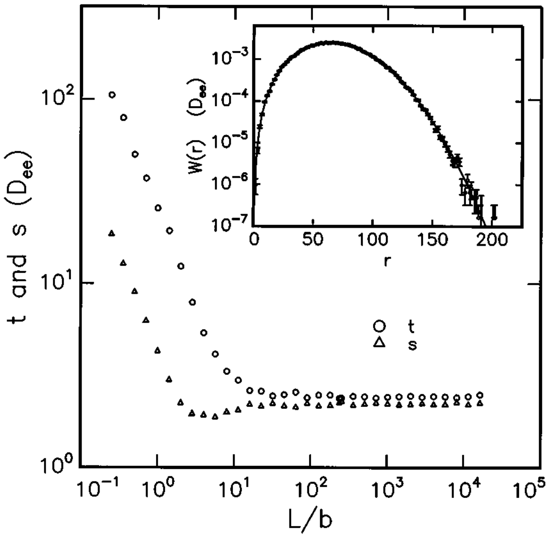

FIG. 2. Results for s and t in the Mazur function for D_{ee} for chains with excluded volume interactions. Inset: fit to the distribution function for $L/b=2048$.

viation less than 0.3% for $10 \leqslant L/b \leqslant 16384$, which is of the same magnitude as the statistical errors on the simulation results.

The distribution functions of D_{ee}, D_{em}, and D_{ii} have been analyzed using the function suggested by Mazur [7]: $W(r)=Cr^s\exp[-(r/\sigma)^t]$, with $C^{-1}=(\sigma^{s+1}/t)\Gamma[(s+1)/t]$ and $\sigma^2=\overline{D_{xy}}^2\Gamma[(s+1)/t]/\Gamma[(s+3)/t]$, where $\overline{D_{xy}}^2$ is the mean-square value of one of the distances and $\Gamma(x)$ is the gamma function. This function gives relatively good fits to the distributions in the full range of L/b both with and without excluded volume interactions with almost perfect agreement for $L/b>10$ (see Fig. 2). The parameters s and t for D_{ee} for excluded volume effects obtained from fits to the individual distributions are displayed in Fig. 2. For $L/b \rightarrow 0$, s and $t \rightarrow \infty$, which reflects that the distribution function approaches a δ function at $r=L/b$ due to the local stiffness of the chain. For $L/b \rightarrow \infty$, t and s approach constant values of about 2.43 and 2.22, respectively.

In order to get accurate estimates of the parameters in the asymptotic limit $L/b \rightarrow \infty$, the 42 distribution functions of D_{ee}, D_{em}, and D_{ii} were analyzed by an approach in which all the distributions for $L/b>200$ were fitted simultaneously. The expression (1) was used for the expansion factors with ϵ and Δ fixed at the values determined by fitting the expansion factors. Using $t=2/(1-\epsilon)$ [8], one has only nine fitting parameters (A_1, A_2, and s, for each of the parameters D_{ee}, D_{em}, and D_{ii}, for fitting 42 distributions [23]. We obtained an excellent fit to the distribution functions, which shows that the distributions follow the suggested behavior within the statistical errors. The values for s were 2.224 ± 0.006, 2.412 ± 0.006, and 2.714 ± 0.006 for D_{ee}, D_{em}, and D_{ii}, respectively. These values are very close to those found by renormalization-group calculations [9]: 2.273 ± 0.004, 2.459 ± 0.003, and 2.71 ± 0.05, respectively. Monte Carlo simulations on relatively short flexible chains with $R/b=0.28$ [13] give 2.27 ± 0.01, 2.55 ± 0.06, and 2.60 ± 0.15, respectively, whereas lattice simulations give 2.262 ± 0.015 for D_{ee} [11] and 2.419 ± 0.003 for D_{em} [12,27].

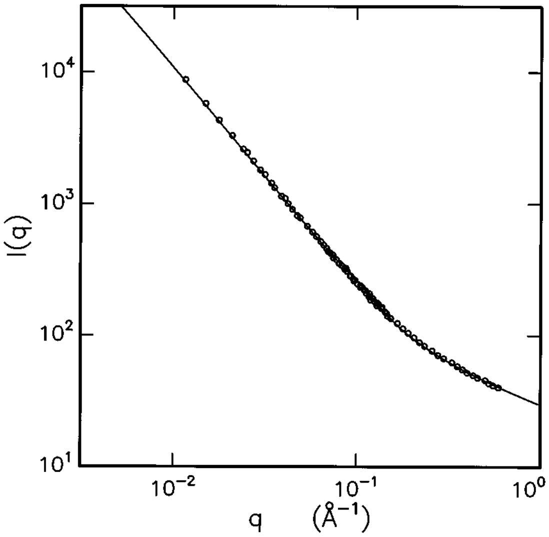

FIG. 3. Scattering data for PS in carbon disulfide [33]. The curve is a fit using the parametrized functions with excluded volume interactions.

In the present work, the strength of the excluded volume interactions is expressed through the parameter R/b. However, in most theoretical studies [28] it is more frequently done by giving the value of the reduced binary cluster integral B. In order to get the value of B corresponding to $R/b=0.1$ we have analyzed the results for R_g and D_{ee} by the Yamakawa-Stockmayer-Shimada (YSS) theory [4]. A simultaneous fit to the simulation results for R_g and D_{ee} gives $B=0.30 \pm 0.01$ for $L/b<500$. The fits to the simulation data deviate significantly for $L/b>1000$ due to the assumed value $\epsilon=0.200$ in the YSS theory. The value for B is quite similar to the value determined for polystyrene (PS) in benzene ($B=0.23$) [4,29] and PS in toluene [30] ($B=0.26$), which means that the simulation results should also be applicable to PS in good solvents. This is further demonstrated in the following.

The scattering functions $S(q)$ have been determined for $L/b=0.3-640$. For $qb>5$, $S(q)$ follows the $1/q$ behavior of a straight cylinder and at lower q it follows the expected $q^{-2/(1+\epsilon)}$ behavior for chains with excluded volume interactions. The scattering functions have been parameterized for use in least-squares analysis of SLS and SANS data [31,32] and in the following an application to the SANS data from atactic PS in the good solvent carbon disulfide is described [33]. Figure 3 shows the scattering data for PS with a molecular weight of about 1.6×10^6 deuterated only at the backbone. With this labeling the chains are effectively infinitely thin in the SANS experiment and the scattering function is directly observed. The data show the expected $q^{-2/(1+\epsilon)}$ and q^{-1} behavior; however, a crossover to a constant intensity is not observed at low q due to the large R_g of the chains. The full curve in Fig. 3 is the parametrized scattering function calculated for $b=25$ Å and with L determined from the molecular weight. The agreement between the curve and the data is excellent.

In this paper, we have presented a Monte Carlo model for simulating single chain properties of polymerlike micelles with excluded volume interactions. The study provides important understanding of the excluded volume effects in such micelles. The results for, e.g., the expansion factors are essential for the correct interpretation, in particular of scattering experiments. A simultaneous analysis of a large amount of simulation results for different chain lengths has provided accurate exponents in scaling laws and very accurate parameters for the distribution functions, which have been found to be in good agreement with the predictions of renormalization-group calculations. We have, in addition, made connections to the standard models and theories for polymers and demonstrated that the results are applicable to polymers in a good solvent. Finally, we have obtained parametrized scattering functions, which we have successfully applied to PS in a good solvent and which we can use for analyzing scattering data from polymerlike micelles in the future.

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