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ON THE PRESENCE OF LOOPS IN LINEAR SELF-ASSEMBLING SYSTEMS. STATISTICAL METHODS AND BROWNIAN DYNAMICS

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Abstract: In this note we present i) a microscopic model for the self-assembly of linear wormlike micelles for which loop formation is allowed, and ii) an analytical mesoscopic description of such systems. Both approaches predict the extent of loop formation under different conditions. As a matter of fact, even if loop formation is unfavorable under certain conditions, e.g., for stiff micelles and low end cap energies, they have to be treated correctly in any statistical approach to their behavior, since their presence can significantly affect the relaxation time spectrum, the rheological behavior and correlation function of various types.

Résumé: Dans cette note nous présentons: i) un modèle microscopique de l'auto-assemblage des micelles vermiculaires pour lequelles on permet la formation de cycles; ii) une description analytique de ces même systèmes à une èchelle mesoscopique. Les deux approches permettent de prédire le nombre de cycles formés dans des conditions données. La formation de cycles est peu favorable, notemment dans le cas de micelles rigides et d'énergies de scission faibles. Mais, ces cycles doivent être pris en compte dans toute approche statistique visantà décrire le comportement des micelles vermiculaires. Elles peut affecter de facon notable comportement rheologique, spectre de relaxation et diverses fonctions de correlations. [1]

I. INTRODUCTION

It is usually argued that the population of closed loops (or rings) in wormlike micellar systems is always small and can be neglected at all practical concentrations [1]. But at least in Brownian dynamics simulations we do observe loop formation, which is – for a positive end-cap energy – an energetically favored, but entropically disfavored state of the system. How much it is disfavored at first glance should depend mainly on i) the ratio between average length and persistence length of the chains and ii) the end-cap energy. The average length in turn depends on the end-cap energy and concentration, since the flexibility which is an intrinsic quantity, is

Keywords: linear wormlike micelles, loops, Brownian dynamics

affected by concentration. We will demonstrate it later. Hence, if the end-cap energy is large, on one hand loop formation is preferred, on the other hand the ratio between average length and persistence length becomes large. For the same reason the limiting case of no ring formation is not simply obtained for very small end-cap energies, since then this ratio becomes small. In together, we have two concurrent mechanisms which are affected by the end-cap energy. With increasing concentration the average length increases, but the chains usually become more flexible, such that we do not expect an universal increase or decrease of the ratio between average length and persistence length with concentration. For concentrated systems the end-cap energy should play a more important role for loop formation than in the dilute case.
In the following we study the length distribution of linear wormlike micelles and related quantities by using a functional integral approach in connection with methods provided by the statistical thermodynamics of Amphiphile self-assembly. [1,2]. The analytical results are in agreement with findings from our Brownian dynamics computer simulations. The treatment presented here is more general than the ones in [3,4] for polymers since it takes into account semiflexibility and scission/recombination of micelles.

II. MESOSCOPIC MODEL

Chemical potential for self-assembling systems

Let us denote the chemical potential of a cluster (which has to be identified with a linear chain) of size N in configuration s by $\mu_s^{(N)} = E_s^{(N)} + k_B T \rho_s^{(N)}$, where $E_s^{(N)}$ denotes its energy and $\rho_s^{(N)}$ stands for the number density of clusters of size N in configuration s. In chemical equilibrium, where all reactions $NA_1 = A_N$ as well as linear combinations of these reactions take place simultaneously, one usually requires, for all s: $N\mu^{(1)} = \mu_s^{(N)}$ [1]. Hence we can express the number densities of configurations s as

$$\rho_s^{(N)} \propto e^{\beta N \mu^{(1)}} e^{-\beta E_s^{(N)}}. \tag{1}$$

The number density of clusters of size N is then

$$\rho^{(N)} = \sum_s \rho_s^{(N)} = \frac{q^{(N)}}{q^{(1)}} [\rho^{(1)}]^N \propto q^{(N)} e^{N\beta(\mu^{(1)}+E_0)}, \tag{2}$$

where the configurational integral

$$q^{(N)} = \sum_s e^{-\beta \triangle E_s^{(N)}} \tag{3}$$

has been introduced. The densities are subject to the constraint of fixed number of beads of the total system, or alternatively, the bead concentration $\phi = \sum_N N\rho^{(N)}$. Within the context of the following dimensionless analysis, ϕ has to be interpreted as the extent of contour length per volume, measured in units of the width of the wormlike micelles. Obviously, the aim becomes to calculate the configurational integral $q^{(N)}$ of a cluster of size N.
In order to estimate the probability of finding loops, we split the configurational integral of linear chains of size N as

$$q^{(N)} = q_{\text{open}}^{(N)} [1 + \frac{q_{\text{loop}}^{(N)}}{q_{\text{open}}^{(N)}}] = q_{\text{open}}^{(N)} [1 + \frac{g_N^{\text{loop}}}{g_N^{\text{open}}} e^{E_2}], \tag{4}$$

where $g_{\ddot{N}}$ abbreviates the degeneracy of configurations with same energy and same size N. The expression involves the ratio of degeneracies of linear chains with and without loops times the Boltzmann factor according to the energy difference between a closed and open chain of size N. respectively.

Statistics of the wormlike chain

The wormlike chain model was first proposed by Kratky and Porod [5] and extended to the continuum model (functional integrals) by Saitô, Takahashi and Yunoki [6] and Freed [7], which is described by the statistical weighting factor $p[\mathbf{r}(s)]$ where the wormlike chain is described by a continuous curve in three-dimensional space $\mathbf{r}(s)$. Here, s measures the contour length along the chain, $0 \leq s \leq L$, κ is the bending elastic coefficient and $\mathbf{u}(s) = \partial \mathbf{r}(s)/\partial s$ the differential (tangent) of the curve $\mathbf{r}(s)$, and A a normalization constant which is equal to the inverse of the partition function.

$$p[\mathbf{r}(s)] = A e \left[-\frac{3}{2l} \int_0^L \mathbf{u}^2(s)\, ds - \frac{1}{2}\kappa \int_0^L (\mathbf{u}')^2(s)\, ds \right]. \tag{5}$$

The stretching coefficient l will be related to κ below. So far, this model does not take into account concentration effects, i.e., we should at least regard an effective κ, being a function of concentration (see Tab. 1). But notice that the model works also in both limits, flexible chains ($\kappa < L$) as well as stiff chains ($\kappa > L$). Using the constraint $|\mathbf{u}(s)| = 1$ which means that the polymer chains cannot be stretched, Saitô et al. derived a approximate (series) solution for the tangent distribution function (Green's function). There are many other contributions in this field but no analytical solutions for all κ and the case of $|\mathbf{u}(s)| = 1$ are available. We follow here the most recent approach of Zhao, Sun and Zhang. They got analytical solutions for any type of correlation function for the model (5) by studying the configurational statistics by functional integrals in quasi-momentum space [8]. A fundamental quantity is the correlation function

$$C(\mathbf{R}, s) \propto \langle \delta(\mathbf{r}(s_1) - \mathbf{r}(s_2) - \mathbf{R}) \rangle\,, \tag{6}$$

where $s = s_1 - s_2$, $0 \leq s_1, s_2 \leq L$ and $\langle ... \rangle$ means the statistical average over various configurations of the chain by functional integrals. In [8] it was stressed out that the correlation functions are actually more fundamental than the end-to-end distribution functions for wormlike chains. As pointed out in [9], the end-to-end distribution function gives the mean end-to-end distance as $\left\langle R^2 \right\rangle = lL$ in the long chain limit, which in fact is only valid for ideal Gaussian chains. For the average end-to-end distance they obtain, by making use of an additional condition of the average length of the chain being L, which leads to the relationship $l = 4\kappa/3$ [3,10]

$$\begin{aligned} \left\langle \mathbf{R}^2 \right\rangle &= l[L - \frac{l}{2}(1 - e^{-2L/l})], \\ \left\langle \mathbf{R}^2 \right\rangle &= lL \qquad \text{for } \kappa \to 0 \quad \text{(Gaussian)}, \quad \left\langle \mathbf{R}^2 \right\rangle = L^2 \qquad \text{for } \kappa \to \infty \quad \text{(rodlike)}. \end{aligned} \tag{7}$$

Other reasonable constraints can be formulated and lead to slightly different relationships between l and κ, e.g., $l = 3\pi^2\kappa/16$ (for $|\mathbf{u}^2| = 1$), $l = \kappa/3$ [7] or also $l = 4\kappa/3$ by taking a limit on $C(\mathbf{R}, s)$ which reads [8]

$$C(\mathbf{R}, s) = Ae^{-R^2/4a_1(s)} \tag{8}$$

where

$$a_1(s) = \frac{l}{6}\left[s - \frac{1}{\alpha}(1 - e^{-s\alpha})\right], \text{ and } \alpha \equiv \sqrt{\frac{3}{\kappa l}} = \frac{3}{2\kappa}. \tag{9}$$

Using (8) we get the average monomer-monomer distance (distinguished from the end-to-end distance) separated by the contour distance s, for the wormlike chain model

$$\left\langle \mathbf{R^2} \right\rangle (s) = l\left[s - \frac{1}{\alpha}(1 - e^{-s\alpha})\right], \tag{10}$$

from which (7) follows under the additional condition cited above, since $\left\langle \mathbf{R}^2 \right\rangle \equiv \left\langle \mathbf{R^2} \right\rangle (L)$. From the correlation function the persistence length $l_p(s)$ for finite contour distance s is derived as

$$l_p(s) = \frac{1}{\alpha}(1 - e^{-s\alpha}), \quad l_p \equiv l_p(1) \tag{11}$$

Probability of loop formation

Now, to get the probability of finding the ends of a linear multibead chain with contour length L or alternatively N beads ($L = aN$ with bond length $a \equiv 1$ in order to use the same notation as used in a computational study of a discretized version of the wormlike chain model) within a finite interaction distance $r_c \approx a = 1$, we have to carry out the appropriate integral over $C(\mathbf{R}, s)$

$$\begin{aligned} \frac{g_N^{\text{loop}}}{g_N^{\text{open}}} &= [\int_0^{|\mathbf{R}|\le r_c} C(\mathbf{R}, L) d^3\mathbf{R}]/[\int_0^{|\mathbf{R}|\le L} C(\mathbf{R}, L) d^3\mathbf{R}] \\ &= [\int_0^{r_c} R^2 C(R, L)\, dR]/[\int_0^{L} R^2 C(R, L)\, dR] \end{aligned} \tag{12}$$

Two plots are given in Fig. 1. We find the following scaling behavior $(r_c = 1)$

$$\begin{aligned} \frac{g_N^{\text{loop}}}{g_N^{\text{open}}} &\approx (\kappa N)^{-\zeta} \quad \text{for } N > \zeta\kappa, \\ \frac{g_N^{\text{loop}}}{g_N^{\text{open}}} &\approx \zeta^\zeta \kappa^0 N^{-2\zeta} \quad \text{for } N \le \zeta\kappa, \quad \text{with } \zeta = \frac{3}{2}, \end{aligned} \tag{13}$$

which is valid for classical polymers too [11]. To derive the number density of living chains of size N, i.e., N beads, one has to determine the coefficient of proportionality in (2) from the constraint of fixed concentration ϕ (by making use of Eq. 17)

$$\begin{aligned} \phi &= \sum_N N\rho^{(N)} = \sum_N N\frac{q^{(N)}}{q^{(1)}}(\rho^{(1)})^N \\ &= e^{-\delta}\sum_N N e^{-N\alpha_o}[1 + \frac{g_N^{\text{loop}}}{g_N^{\text{open}}} e^{E_2}] \\ &= e^{-\delta}\alpha_o^{-2} + \omega^{-1}\sum_N N e^{-N\alpha_o}\frac{g_N^{\text{loop}}}{g_N^{\text{open}}} \end{aligned} \tag{14}$$

with $\alpha_o = -\log\rho^{(1)} - \delta$, $\delta \equiv E_2 + \log\omega$ and $q^{(N)}_{\rm open} = \omega^{N-1}e^{E_2(N-1)}$, where ω is independent of N for open chains [1]. An approximate expression for ω as function of the bending coefficient κ we relate to the bending potential $U(\vartheta)$ (see next section)

$$\log\omega = \int_0^\pi \sin\vartheta e^{-\kappa(1-\cos\vartheta)}\, d\vartheta = \frac{1}{\kappa}(1-e^{-2\kappa}), \tag{15}$$

i.e., $\omega \to e^{2(1-\kappa)}$ and $\omega \to e^{\kappa^{-1}}$ for flexible and stiff chains, respectively. The expression (15) reflects a scaling of the configurational integral with the contour length in units of the persistence length. Inserting (13) into (14), with $r_c = 1$, we have

$$\phi = e^{-\delta}\alpha_o^{-2} + \omega^{-1}\zeta^{\zeta}\sum_{N\le\zeta\kappa} N^{-2}e^{-N\alpha_o} + \omega^{-1}\kappa^{-\zeta}\sum_{N>\zeta\kappa} N^{-1/2}e^{-N\alpha_o}. \tag{16}$$

Before we proceed we should recall relationships, which will be frequently used in the following (for any $k+2>0, \alpha>0$):

$$\begin{aligned} M_k &\equiv \sum_{N=1}^{\infty} N^{k+1}e^{-\alpha N} \approx \int_{N=1}^{\infty} N^{k+1}e^{-\alpha N}\,{\rm d}N = \Gamma(k+2)\alpha^{-(k+2)}, \\ M_{k+1}/M_k &= \frac{\Gamma(k+3)}{\Gamma(k+2)}1/\alpha = (k+2)/\alpha, \end{aligned} \tag{17}$$

where $\Gamma(k) = (k-1)!$, if k is an integer. E.g., for linear chains without loops the density ϕ is proportional to the quantity M_k with $k=0$ and the number and weight averaged sizes of linear micelles are expressed through the M's as [1]

$$\langle n\rangle_{\#} \equiv \phi/[\textstyle\sum \rho^{(N)}] = M_k/M_{k-1}, \qquad \langle n\rangle_w \equiv M_{k+1}/M_k. \tag{18}$$

Obviously, in the classical case the ratio between weight and number average size is readily evaluated as $M_{k+1}M_{k-1}/M_k^2 = (k+2)/(k+1) = 2$. In opposite, evaluating the bounded sums in (16) which involve N^{k+1} with $k+2<0$ is more complicated. For example, we have for $\alpha_o > 0$

$$\begin{aligned} \bar{M}_{(-3/2)} \equiv \sum_{N=\zeta\kappa}^{\infty} N^{-1/2}e^{-\alpha_o N} &= \sqrt{\frac{\pi}{\alpha_o}}(1-{\rm Erf}[\sqrt{\alpha_o\zeta\kappa}]) \overset{\alpha_o\zeta\kappa<1}{\approx} \sqrt{\frac{\pi}{\alpha_o}} - 2\sqrt{\zeta\kappa} \\ \underline{M}_{(-3)} \equiv \sum_{N=1}^{\zeta\kappa} N^{-2}e^{-\alpha_o N} &= e^{-\alpha_o} - \frac{e^{-\alpha_o\zeta\kappa}}{\zeta\kappa} + \alpha_o[{\rm Ei}(-\alpha_o) - {\rm Ei}(-\alpha_o\zeta\kappa)] \end{aligned} \tag{19}$$

with the the error function ${\rm Erf}(..)$ and the exponential integral function ${\rm Ei}(..)$. Here, we will only treat extreme cases.

Analytical results

Quite stiff semiflexible chains To proceed with (16) in case of quite stiff chains, for which $\zeta\kappa\alpha_o > 1$ is required, we find

$$\begin{aligned} \alpha_o &= \phi^{-1/2}e^{-\delta/2} \\ \rho^{(N\le\zeta\kappa)} &= e^{-N\phi^{-1/2}e^{-\delta/2}-\delta}[1+\zeta^{\zeta}\kappa^0 N^{-2\zeta}e^{E_2}] \\ \rho^{(N>\zeta\kappa)} &= e^{-N\phi^{-1/2}e^{-\delta/2}-\delta}[1+(\kappa N)^{-\zeta}e^{E_2}] \approx e^{-N\phi^{-1/2}e^{-\delta/2}-\delta} \\ \langle n\rangle_{\#} &= \phi^{1/2}e^{\delta/2} = \phi^{1/2}e^{E_2/2}\sqrt{\omega}. \end{aligned} \tag{20}$$

As expected, in case of stiff chains and few loops we recover the classical result.

Flexible non-ideal chains In case of flexible chains, i.e., for $\kappa \to 0$, or even for $\kappa\zeta < 1$ the second term in (16) vanishes – $N \leq \zeta\kappa$ cannot be fulfilled – and the remaining terms read

$$\phi = e^{-\delta}\alpha_o^{-2} + \omega^{-1}\kappa^{-\zeta}\sqrt{\frac{\pi}{\alpha_o}} \tag{21}$$

In case that loop formation is preferred, i.e., if the second term on the rhs of (21) dominates, e.g., at large end-cap energies E_2, for the size distribution and average weight size we get a result which is now independent of E_2

$$\begin{aligned} \alpha_o &= (\phi\omega)^{-2}\pi\kappa^{-3} \\ \rho^{(N)} &= \omega^{-1}\kappa^{-\zeta}e^{-N\alpha_o}N^{-\zeta}, \\ \langle n\rangle_w &= \Gamma(3/2)\alpha_o^{-1} = (\phi\omega)^2\kappa^3(4\pi)^{-1/2}. \end{aligned} \tag{22}$$

Semiflexible chains In general, for chains with finite semiflexibility the nonlinear equation for α_o and the expression for the size distribution read

$$\begin{aligned} \phi &= e^{-\delta}\alpha_o^{-2} + \omega^{-1}\left[\zeta^{\zeta}\underline{M}_{(-3)} + \kappa^{-\zeta}\bar{M}_{(-3/2)}\right] \\ \rho^{(N)} &= e^{-\delta}e^{-N\alpha_o}[1 + \frac{g_N^{\text{loop}}}{g_N^{\text{open}}}e^{E_2}], \end{aligned} \tag{23}$$

The rich scaling behavior of $\langle n\rangle_{\#,w}$ follows directly by inserting the solution for α_o of (23a) into Eqs. 13,19,18,23b. The number and weight averages involve also the symbols $\bar{M}_{(-1/2)}, \bar{M}_{(1/2)}$ and $\underline{M}_{(-2)}$ and $\underline{M}_{(-1)}$.

II. A BROWNIAN MOLECULAR DYNAMICS STUDY

As we mentioned before, the reason to study the probabilities of loop formation stemmed from our observation of loops in model wormlike micellar systems. We will briefly introduce this method and will concentrate on the equilibrium results, although the rheological properties of the samples under study are also known [13], as studied within the framework of generally branched self-assembling systems by an extended version of the algorithm, a so called Nonequilibrium Brownian dynamics computer simulation.

The Brownian dynamics method solves a many particle system numerically by adding stochastic forces to the deterministic part of the equation of motions in accordance with the fluctuation dissipation theorem. Typically, we study 500-5000 particles. The deterministic part of the motion of our particles is completely determined by the model potentials. The first one is a Lennard-Jones potential which acts between all pairs of beads.

end-cap energy $E_2 = 4.7$

ϕ	κ	$\log_{10}\frac{p^{\text{loop}}}{p^{\text{open}}}$	$\langle n\rangle_w$	$\langle n\rangle_\#$	l_p
0.05	1	-1.26	3.98	2.66	0.53
0.05	2	-1.48	4.91	3.07	1.00
0.05	3	-1.67	5.05	2.91	1.44
0.05	5	-2.67	5.37	3.02	3.58
0.05	10	-3.17	5.46	3.06	7.54
0.05	20	-3.43	5.04	2.95	13.5
0.05	50	-3.99	5.20	2.52	31.2
0.05	100	-4.22	5.17	2.22	62.6
0.05	200	-5.10	4.06	1.94	94.2
0.10	1	-1.27	5.74	3.67	0.63
0.10	2	-1.55	7.73	4.19	1.19
0.10	3	-2.25	8.94	4.48	2.11
0.10	5	-2.71	9.28	4.78	3.43
0.10	10	-2.89	10.1	4.84	6.84
0.10	20	-2.90	11.4	4.89	12.0
0.10	50	-3.09	12.4	4.80	21.1
0.10	100	-4.31	12.7	3.99	54.9
0.10	200	-6.22	21.1	3.49	103.
0.20	1	-1.65	12.9	6.70	0.96
0.20	2	-1.83	11.9	6.40	1.38
0.20	3	-2.38	14.2	7.17	2.02
0.20	5	-3.39	14.9	7.63	3.37
0.20	10	-3.17	16.5	7.87	5.73
0.20	20	-4.47	21.0	8.72	10.3
0.20	50	-3.39	22.9	7.98	23.3
0.20	100	-2.81	23.0	6.94	39.8
0.20	200	-3.50	30.9	8.02	61.9

end-cap energy $E_2 = 8.1$

ϕ	κ	$\log_{10}\frac{p^{\text{loop}}}{p^{\text{open}}}$	$\langle n\rangle_w$	$\langle n\rangle_\#$	l_p
0.01	0	-0.63	3.41	2.79	0.90
0.01	5	-1.76	7.88	4.64	2.69
0.01	20	-2.39	8.49	4.60	13.6
0.01	100	-2.71	5.01	2.38	57.8
0.02	0	-0.62	3.69	3.07	0.40
0.02	5	-1.93	13.5	6.57	3.53
0.02	20	-2.94	14.6	8.98	18.6
0.02	100	-4.51	11.5	3.95	83.4
0.05	0	-0.67	5.13	3.79	0.47
0.05	5	-2.25	20.0	10.0	3.80
0.05	20	-2.70	21.5	12.7	17.1
0.05	100	-3.40	34.4	12.8	75.0
0.10	0	-0.79	10.0	4.59	0.41
0.10	5	-2.29	35.5	18.6	3.82
0.10	20	-2.80	38.4	21.9	14.5
0.10	100	-3.50	33.9	18.7	59.6
0.15	0	-1.01	19.2	6.82	0.41
0.15	5	-2.39	43.0	21.9	3.89
0.15	20	-2.69	39.4	23.8	13.1
0.15	100	-3.19	34.7	18.5	38.0
0.20	0	-1.15	22.2	8.41	0.52
0.20	5	-2.69	40.8	22.4	3.68
0.20	20	-2.81	57.8	30.3	13.2
0.20	100	-3.29	69.1	16.9	28.1
0.30	0	-1.25	47.2	11.2	0.57
0.30	5	-1.60	49.3	23.1	2.95
0.30	20	-2.60	73.1	28.8	11.1
0.30	100	-3.41	53.3	23.9	21.7

$\log_{10}\frac{p^{\text{loop}}}{p^{\text{open}}}$ $(E_2 = 8.1)$

ϕ	$\kappa = 0$	5	20	100
0.01	-0.63	-1.76	-2.39	-2.71
0.02	-0.62	-1.93	-2.94	-4.51
0.05	-0.67	-2.25	-2.70	-3.40
0.10	-0.79	-2.29	-2.80	-3.50
0.15	-1.01	-2.39	-2.69	-3.19
0.20	-1.15	-2.69	-2.81	-3.29
0.30	-1.25	-1.60	-2.60	-3.41

$\log_{10}\frac{p^{\text{loop}}}{p^{\text{open}}}$ $(E_2 = 4.7)$

ϕ	$\kappa = 1$	2	3	5	10	20	50	100	200
0.05	-1.26	-1.48	-1.67	-2.67	-3.17	-3.43	-3.99	-4.22	-5.10
0.10	-1.27	-1.55	-2.25	-2.71	-2.89	-2.90	-3.09	-4.31	-6.22
0.20	-1.65	-1.83	-2.38	-3.39	-3.17	-4.47	-3.39	-2.81	-3.50

Tab. 1. Preliminary results from a Brownian dynamics computer simulation of linear wormlike micelles. Given are extracted values for the number and weight size averages $\langle n\rangle_{\#,w}$ as well as the number of loops per bead and the measured persistence length l_p for different bead number concentrations ϕ, end-cap energies E_2 and bending coefficients κ.

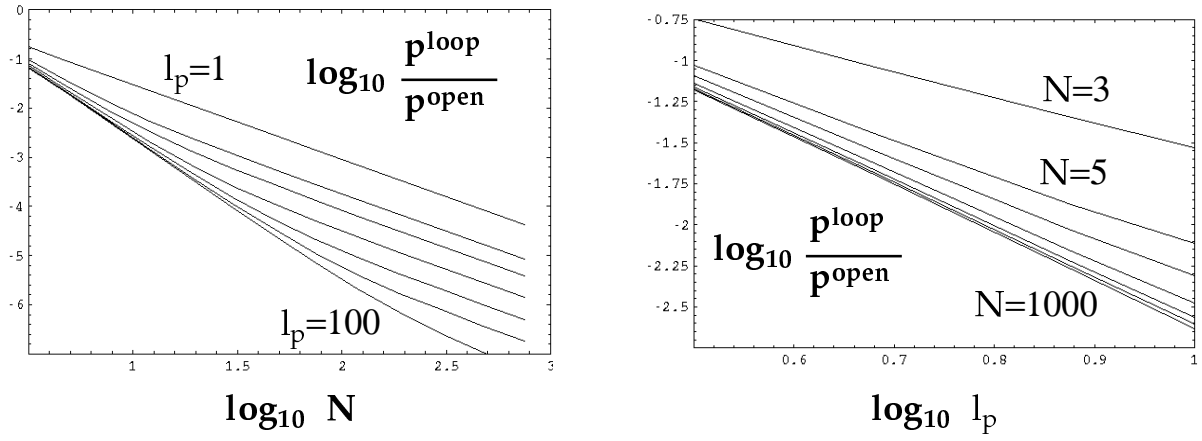

Fig. 1. Analytic results for the probability of loop formation as function of the length of a wormlike chain ($N = L/a$) and the persistence length. The results for wormlike micellar (living) chains incorporate the nature of scission and are discussed in the text. They depend on the end-cap energy and concentration too. The persistence length l_p and N are measured in units of the width of the wormlike chain. Left: $l_p = 1, 3, 5, 10, 20, 30, 50, 100$. Right: $N = 3, 5, 10, 20, 50, 100, 1000$.

Second, in order to form chains, an attractive nonlinear spring force (FENE-C potential, introduced in [14]) acts between all pairs of beads (whose spatial distance is below a certain threshold value) as long as both beads have only one or two interacting neighbors. Such a transient bond between connected beads defines the chain itself as well as its contour and it breaks if any bond length exceeds the threshold value. The parameters of the FENE-C potential define the end-cap energy E_2 of our model.
Moreover, we apply a bending potential which makes it possible to study chains with different flexibilities, it is a bending potential between neighboring bonds within chains of the form $U(\vartheta) = \kappa[1 - \cos(\vartheta)]$, where κ is the bending coefficient and ϑ is the angle between connected bonds, such that $\vartheta = 0$ for a stretched chain. Here, we present results of a Brownian dynamics simulation which does not take into account hydrodynamic interactions [15]. Some results are collected in Tab. 1. The agreement with the theoretical predictions is good for all concentrations, if the effect of concentration is incorporated into the bending coefficient.

III. CONCLUSIONS

In this note we presented a route to the study of the statics and dynamics of loop formation in wormlike micellar systems. As shown, the probability of finding loops depends only on the end-cap energy and the persistence length, as the effect of concentration can be incorporated into a relationship between elastic bending coefficient and persistence length. With increasing concentration the persistence length increases until loop formation becomes very unprobable, at high concentration the persistence length and hence the effective bending coefficient decrease due to collisions which occur on a length scale which is comparable to the mesh size. Hence, for

real systems, if the persistence length and the probability of loops has been determined, e.g., by optical methods [16], the end-cap energy and the size distribution of micelles can be estimated by using the above formulas. We did not estimate the effect of branching on the number of loops here. A more complete discussion, which treats also branchings will be available soon [13].

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