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On the Shape and Rheology of Linear Micelles in Dilute Solutions

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Abstract. — We calculate steady state properties of linear (wormlike) micelles modeled as flexible bead–spring chains from both microscopic and mesoscopic models. The latter model is based on an expression for the free energy of Gaussian chains, modified by a term which takes into account a finite scission energy in order to describe micelles, or breakable polymer chains. In equilibrium, the length distribution then depends on two parameters, namely the micellar concentration and the scission energy. Results of this approach are compared both with previous mesoscopic descriptions and Molecular Dynamics (MD) computer simulation results of the FENE–C model of linear micellar solutions (Phys. Rev. E 53 (1995) 2531). The mesoscopic model is extended to describe flow situations. Implications are discussed and compared with NonEquilibrium MD (NEMD) computer simulation results for the length distribution and flow alignment of linear micelles as well as the corresponding rheological behavior. For the case of steady shear flow both models do predict a decrease of the average micellar size with increasing shear rate.

1. Introduction

In order to predict the macroscopic behavior of wormlike micelles in equilibrium, the length distribution of living model chains has been calculated, e.g., by Cates [1] on the basis of a mean–field argument. The consequence of a flow field on the size of rod–like micellar aggregates has been considered for the first time by Wang et al. [2]. In this article we will use two formalisms also based on statistical mechanics which can be applied for general nonequilibrium situations to study the length distribution of living and flexible model chains under shear flow. The first treatment (now called mesoscopic approach) exhibits similarities to the calculation of products in polymerization kinetics and to association theory [3–5]. The second approach (now called

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microscopic approach) has been used in a recent computer simulation study [6] and is based on the multiple bead–spring FENE–C model (Sect. 3, Eq. (24)).

Both approaches lead to expressions for the average length of micelles as well as for the distribution of lengths, and the rheological behavior as functions of the micellar concentration, the scission energy and the parameters of the applied flow field. Moreover the microscopic approach provides every information on the intermolecular correlations as represented by pair correlation functions or structure factors. Most of the microscopic quantities cannot be detected in a direct way from experiments, even if there exist experimental studies of the micellar structure via neutron scattering methods, see e.g. [7].

For the case of steady shear flow, inserting the features of Gaussian chains (Rouse model) into the mesoscopic equations, we discuss the flow–induced alignment of aggregates and rheological behavior. We compare it successfully with the results obtained from the microscopic model for which the rheological behavior is calculated without any assumptions apart from the definition of the model potentials.

This paper is divided as follows. In Section 1 we will develop the mesoscopic model and calculate the related macroscopic quantities. Section 2 gives a brief description of the microscopic model. The results of both approaches will be discussed and compared in Section 3.

2. Mesoscopic Model

2.1. Expression for the Free Energy. — Consider an ideal solution of linear chains (micelles) which are modeled as bead–spring chains [5,8,9]. We assume that each bead can have two bonds and we exclude ring formation. The micellar solution of concentration \( \phi \) is modeled by \( N_b \) beads. In general a bead may represent a number of (typically 2–20) chemical units. Let \( N_M \equiv \phi N_b \) be the number of beads which are able to form linear chains ("M–beads") and which can associate and dissociate, and \( N_S \equiv (1 - \phi)N_b \) the number of solvent particles ("S–beads"). The system is then characterized by the number \( n_i \) of micellar chains made of \( i \) beads and the concentration. Now at equilibrium the distribution of chains results from the grand canonical partition function \( \Xi \)

\[
\Xi = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \frac{(q_1 \lambda_1)^{n_1}}{n_1!} \frac{(q_2 \lambda_2)^{n_2}}{n_2!} \cdots \frac{(q_N \lambda_N)^{n_N}}{n_N!} = \prod_{i=1}^{N} q_i^{n_i} \lambda_i ,
\]

where \( q_i \) is the partition function of an \( i \)-chain ("subsystem" \( i \)), \( \lambda_i = \exp(\beta \mu_i) \), where \( \beta = 1/(k_BT) \) and \( \mu_i \) is the activity of subsystem \( i \). For the average number of \( i \)-chains one has \( \langle n_i \rangle = \lambda_i \partial (\ln \Xi) / \partial \lambda_i = \lambda_i q_i \). Let us require that the various subsystems are in a chemical equilibrium with each other, i.e., \( \mu_i = i \mu_1 \) [4]. Thus with the abbreviation \( \lambda \equiv \lambda_1 \) we have \( \langle n_i \rangle = \lambda q_i \). For an \( i \)-chain the Hamiltonian \( \mathcal{H} \) is formulated in terms of momentum and space coordinate of the center of mass, \( p_c \) and \( r_c \), respectively, and \( i - 1 \) internal momenta and coordinates \( p_k, q_k \) with \( (k = 1, \ldots, i - 1) \). We choose the internal coordinates such that \( Q_k \) denotes the \( k \)th bond vector between beads \( k \) and \( k + 1 \). Carrying out the integration over momenta (Maxwell distribution) and coordinates yields [8] \( \int \exp (\beta \mathcal{H}) \, dp_c dP^{i-1} dr_c dQ^{i-1} = (2\pi mk_BT)^{3i/2} V q_i^{\text{int}} \), where \( m \) is the mass of a single bead and \( V \) is the total volume of the solution, \( q_i^{\text{int}} \) denotes the internal configurational integral, hence we can write \( q_i = \sqrt[\lambda]{q_i^{\text{int}}} \), with the thermal de Broglie wavelength of a bead \( \Lambda \). In order to simplify the structure of the following equations we equal the masses of \( M - \) and \( S - \)beads. For the calculation of the configurational integral we introduce a configurational distribution function \( \psi \). The configurational integral is related to the free energy via [5,8] \( q_i^{\text{int}} = \exp(-\beta A_i^{\text{int}}) \),
with

$$A^\text{int}_i = \int dQ^{i-1} \psi_i(k_B T \ln \psi_i + U_i),$$  \hspace{1cm} (2)

where $U_i$ denotes the internal energy of an $i$–chain.

2.2. **GAUsSiAN CHAIN STATisTics.** — We now assume, as for the classical \(^1\) Rouse model, that the distribution functions are Gaussian \([5,8,9]\)

$$\psi_i(Q^{[i-1]}) = \frac{1}{(2\pi)^{3(i-1)/2}} \frac{1}{|C_{i-1}^{-1}|^{1/2}} \exp \left( -\frac{1}{2} Q^{[i-1]} \cdot C_{i-1}^{-1} Q^{[i-1]} \right)$$  \hspace{1cm} (3)

with $Q^{[i-1]} \equiv (Q_1, Q_2, \ldots, Q_{i-1})$. The $3(i-1) \times 3(i-1)$ matrix of covariances is given by $C_{i-1}^{-1} = (B_i)$ with

$$B_i = \begin{pmatrix}
Q_1 Q_1 & Q_1 Q_2 & Q_1 Q_{i-1} \\
Q_2 Q_1 & Q_2 Q_2 & Q_2 Q_{i-1} \\
Q_{i-1} Q_1 & Q_{i-1} Q_2 & Q_{i-1} Q_{i-1}
\end{pmatrix},$$  \hspace{1cm} (4)

with $|\cdot|$ denoting a determinant. In the “slow reaction limit” in which changes in micellar size occur on a time scale which is long compared to orientational diffusion of the segments in presence of flow, one can assert that the deformation energy can be added to the micellar free energy. The internal energy of $i$–chains is then given by

$$U = -(i - 1)E_{sc} + \sum_{j=1}^{i-1} \frac{1}{2} k(Q_j^2)$$  \hspace{1cm} (5)

where $E_{sc}$ is the scission energy, i.e. $E_{sc}$ is the energy required to break a chain (independent of its length, for a more general case see \([10]\)) and $k = 3k_B T/a^2$ is the spring constant of the Rouse model with bond length $a$. Inserting equations (3, 5) in (2) and performing the integration over $Q$ yields

$$A^\text{int}_i = -\frac{3}{2} (i - 1)k_B T - \frac{3}{2} (i - 1)k_B T \ln(2\pi) - \frac{1}{2} k_B T \ln|\langle B_i \rangle| - (i - 1)E_{sc} + \frac{1}{2} \sum_{j=1}^{i-1} (Q_j^2).$$  \hspace{1cm} (6)

Equation (6) is comparable to an expression given by Booij \([11]\). Note that the last term on the rhs is proportional to the trace of the pressure tensor for an $i$–chain within the Rouse model, $\frac{1}{2} k \sum_{j=1}^{i-1} (Q_j^2) = \frac{V}{2} \text{Tr}(P_i)$. Inserting the expressions from the previous subsection into (5, 6) we get

$$\langle n_i \rangle = V \left( \frac{\lambda}{A^3} \right)^i (2\pi)^{3(i-1)/2} |\langle B_i \rangle|^{1/2} \exp \left( (i - 1) \left( \beta E_{sc} + \frac{3}{2} \right) - \beta \frac{V}{2} \text{Tr}(P_i) \right).$$  \hspace{1cm} (7)

This expression provides our basis to analyze the length distribution for the equilibrium state as well as for nonequilibrium situations.

\(^1\) Here we will call polymers which are not allowed to break: “classical” polymers.
2.3. Equilibrium Results Based on the Rouse Model. — We now evaluate the expression (7) for the equilibrium state (no external fields) by making use of expressions resulting from the Rouse model [8, 9, 12]. In this model there are no orientation correlations between bond vectors. Let us label equilibrium averages as ⟨ ⟩0, e.g., \( \mathbf{P}^0 \) denotes the (isotropic) pressure tensor. We then use

\[
\langle \mathbf{Q}_k \mathbf{Q}_l \rangle_0 = \frac{1}{3} a^2 \delta_{kl} \mathbf{I} \equiv \langle \mathbf{Q} \mathbf{Q} \rangle_0 \delta_{kl},
\]

(8)

\[
|\langle \mathbf{B}_2 \rangle_0|^{1/2} = \langle \mathbf{Q} \mathbf{Q} \rangle_0^{(i-1)/2} = \left( \frac{a^2}{3} \right)^{(i-1)/2},
\]

(9)

and

\[
\frac{V}{2} \text{Tr} (\mathbf{P}^0) = \frac{3}{2} (i - 1) k_B T.
\]

(10)

\( \mathbf{I} \) is the rank 2 unit tensor. The number of \( i \)-chains is given by

\[
\langle n_i \rangle_0 = V \left( \frac{1}{\lambda^3} \right)^{1} z^{i-1},
\]

(11)

where

\[
z \equiv (2\pi)^{3/2} \langle \mathbf{Q} \mathbf{Q} \rangle_0^{1/2} \exp(\beta E_{sc}) = \left( \frac{2\pi a^2}{3} \right)^{3/2} \exp(\beta E_{sc})
\]

(12)

inherits the scission energy and represents an apparent volume of a bead. For the number density of micellar \( i \)-chains \( \rho_i \equiv \langle n_i \rangle_0 / V \) we finally have:

\[
\rho_i = \rho_1^i z^{i-1}
\]

(13)

Through the constraint of conserved total density of beads \( \rho = N_b / V \) the density \( \rho_1 \) of 1-chains can be expressed in terms of the concentration \( \phi \) and \( z \) in (12) by use of a sum rule for geometric series (11) as

\[
\rho_1 \equiv \sum_{i=1}^{N} i \rho_i = \frac{\rho_1}{(1 - \rho_1 z)^2}.
\]

(14)

Thus, the length distribution in equilibrium is determined by the scission energy and concentration. Equation (13) coincides with results obtained from association theory [3, 4] and may also be rewritten in exponential form, \( \langle n_i \rangle_0 / \langle n_{i-1} \rangle_0 = \rho_i / \rho_{i-1} = \rho_1 z \). Thus, the normalized equilibrium distribution function \( C_0(L) \) of \( L \)-chains is equivalent to the expression given in [1, 5] and reads

\[
C_0(L) = \frac{1}{\langle L \rangle_0} \exp \left( -\frac{L}{\langle L \rangle_0} \right).
\]

(15)

From (13) we get the average length (number of beads) \( \langle L \rangle_0 \) of the micelles

\[
\langle L \rangle_0 \equiv \frac{\sum_{i=1}^{N} i \rho_i}{\sum_{i=1}^{N} \rho_i} = \frac{1}{1 - \rho_1 z}.
\]

(16)

Solving (16) for \( \rho_1 \) and inserting it into (14) leads to the relation

\[
\langle L \rangle_0^2 - \langle L \rangle_0 = z \rho \phi,
\]

(17)
which is solved (for positive lengths \( L \)) by

\[
\langle L \rangle_0 = \frac{1}{2} + \left( \frac{1}{4} + z\rho \phi \right)^{1/2}
\]

(18)

For a simple fluid which is, within this framework, modeled by an infinitely large negative scission energy, we get the correct result \( \langle L \rangle_0 = 1 \) which we call a generalization of the square root dependence obtained earlier, e.g., in [1]. Our generalization is indeed important in reproducing the results from the microscopic model as well as to describe experimental results, for which at low concentrations the dependence of the micellar length on concentration seems to be quite weak.

2.4. Extension to Non–Harmonic Model Potentials. — For the case of “Finitely Extendable Nonlinear Elastic” spring force (FENE) chains [13] the expressions in (8–10) are altered, e.g., the isotropic pressure becomes [5,13]

\[
\frac{V}{2} \text{Tr}(\mathbf{P}_0^0) = \frac{1}{2} \frac{b(i + 1)}{(i + b + 3)} k_B T,
\]

(19)

with \( b = kR_0^2/k_B T \). For dumbbells \( (i = 2) \) and \( b \to \infty \) (19) reduces to the expression for Hookean dumbbells (10). For this case we have

\[
\rho_i = \rho_1^i z^{i-1} \exp \left[ \frac{1}{2} \left( 3(i - 1) - \frac{b(i + 1)}{3(i + b + 3)} \right) \right]
\]

(20)

for which the terms \( \sum_{i=1}^{N} i^\alpha \rho_i \) with \( \alpha = 0, 1 \) needed to calculate the average length \( \langle L \rangle_0 \) have to be evaluated numerically as function of concentration \( \phi \), FENE parameter \( b \) and scission energy \( E_{sc} \). The ratio \( \rho_i/\rho_{i-1} \) then increases weakly with \( i \) and therefore the length distribution \( C_0(L) \) decreases more weak than exponential with \( L \). The concentration dependence of the average micellar length \( \langle L \rangle_0 \) is more pronounced than the square root behavior given in (18).

2.5. Shear Flow. — The formalism presented is extendable to homogeneous flow fields and allows to calculate the variation of the length distribution with the flow rate. Under flow the evaluation of the above expressions within the mesoscopic model complicates considerably due to correlations between the bond vectors [9,14] and the dependence of the pressure tensor on flow parameters. The resulting expressions have then to be evaluated numerically, the alignment tensors \( <QQ> \) (Eq. (8)) become anisotropic. A simplified approach is to neglect the variation of the determinant of the covariance matrix (4) with the shear rate. Such an approximation was used in [11] for (classical) polymers and is justified by the fact that the determinant is of the order of \( \gamma^{1/2} \) which is small compared with the exponential of the trace of the pressure tensor. From the approximation follows an increase of the scalar pressure \( p = \text{Tr}(\mathbf{P}_1)/3 \) with shear rate \( \gamma \), i.e. \( \partial p/\partial \gamma > 0 \) which influences the given result (7) as if one would decrease the scission energy (see Eqs. (6, 7)). A decrease of that energy is connected with a decrease of the average length according to (12,18) and hence with a decrease of the viscosity [5]. At high shear rates and for the general case of multibead spring models the terms embodying the pressure tensor must be explicitly taken into account. Rheological quantities are then derived by use of a constitutive equation which connects the pressure tensor with the length distribution and the flow alignment of linear chains.

Let us denote the deviation of the trace of the (partial) pressure tensor from its equilibrium value \( \mathbf{P}_i^0 \) as function of shear rate by \( \Delta P_i = \text{Tr}(\mathbf{P}_i - \mathbf{P}_i^0) \). The density of \( i \)-chains depends on
the shear rate and reads, according to equation (7),
\[
\rho_i(\gamma) = \rho_1(\gamma)^{1+z} \exp(-\beta \Delta P_i)^{1/\sqrt{|\langle B_i \rangle|/|\langle B_i \rangle_0|},}
\]
with \(z\) defined in (12). Obviously, the equilibrium distribution \(\rho_0\) is equal to the nonequilibrium distribution \(\rho_0(\gamma = 0)\), since \(\Delta\) and \(|\langle B_i \rangle|/|\langle B_i \rangle_0|\) characterize deviations from equilibrium. The covariance matrix \(|\langle B_i \rangle|\) represents the shear induced orientation of segments. The stretching of segments is reflected by the pressure increase \(\Delta P\). The concentration \(\phi\) is obtained by the summation in (14) which now has to be performed numerically.

2.6. Shear Flow Results Based on the Rouse Model. — The approximate treatment mentioned above reproduces the crude overall features of the length distribution but cannot reveal the subtleties that are due to the determinant. Here, we examine the complete expression in a most simple approach, i.e. we will use results of the Rouse model. The lowest order correction of the trace of the pressure tensor \(\Delta P\) under weak shear rates \(\gamma\) then reads \([4,9]\)
\[
\Delta P_i = (i-1)^4 a^4 \zeta^2 \gamma^2 / (1620 k_B T),
\]
where \(\zeta\) is the friction coefficient of a monomer. The equilibrium value \(P_0^0\) is given by \((10)\). The covariance matrix can be found in the literature \([9]\), using it, the densities \(\rho_i\) are obtained. In discussing the results and their implications for rheological quantities we introduce a dimensionless shear rate \(\gamma^*\) and scission energy \(E_{sc}^*\) via
\[
\gamma^* \equiv \gamma \tau \quad \text{with} \quad \tau \equiv \frac{a^2 \zeta}{3 \pi^2 k_B T} = \frac{\zeta}{k \pi^2},
\]
\[
E_{sc}^* \equiv \beta E_{sc}.
\]

The coefficient \(\tau\) is equal to the orientational relaxation time of a dumbbell in the Rouse model. If no ambiguities can arise in the following we will replace \(\gamma^*\) and \(E_{sc}^*\) by \(\gamma\) and \(E_{sc}\), respectively, when dimensionless quantities are used within our approach. The contribution of an \(i\)-chain to the (total) shear viscosity and the first viscometric function, \(\eta\) and \(\Psi_1\), respectively, are given by \([4,9]\): \(\eta^{(i)} = (i-1)^4 G \tau\), with the shear modulus \(G = c k_B T / 12\) and orientational relaxation time of a dumbbell \(\tau = \zeta / \pi^2 k\) (Eq. (22)), and \(\Psi_1^{(i)} = (i-1)^4 G \tau^2 \pi^2 / 15 = 4 \eta^{(i)} / (5 c k B T)\).

Hence, by definition, 1-chains (free beads) will not contribute to the viscosity. To obtain the values of the viscosities, e.g. the sum \(\eta = V \sum_i \rho_i \eta^{(i)}\) must be taken over all \(i\)-chains and the summations \(\sum_{i=1}^\infty(i-1)^4 \rho_i(\gamma)\) have to be evaluated with \(\alpha = 2\) and \(\alpha = 4\). Since \(\exp(-\beta \Delta P_i)\) decreases strongly with the shear rate, the width of the length distribution decreases rapidly which, in turn, promotes shear thinning. Varying the shear rate a maximum in the distribution of micellar lengths \(C(L)\) occurs (see Fig. 3d), which would not be visible within the simplified approach. It results directly from taking into account all elements of the covariance matrix in performing its determinant. The flow alignment angle \(\chi\) can be determined from the viscosities under the assumption of the validity of the stress optic rule which is fulfilled for the Rouse model. The flow alignment angle is available via flow birefringence measurements \([5,15]\) \(\chi = \pi/4 + \tan^{-1}[\gamma \Psi_1 / (2\eta)]\). We evaluate the material quantities \(\eta, \Psi_1, \chi\) from equation (21) numerically as functions of the dimensionless parameters (22). Figure 1 displays the dependence of the average length \(\langle L \rangle\) on shear rate, concentration and scission energy in two different representations.

In Figure 2a the flow alignment angle is plotted vs. shear rate for a specific concentration. A change in concentration does not qualitatively affect the result. Notice that even for high scission energies the alignment angle does not decrease with increasing shear rate towards zero, because, in opposite to “died” polymers, here the average length of chains decreases. This
behavior virtually increases the flow alignment angle at a specified shear rate. The rheological quantities vs. shear rate for two fixed concentrations as function of scission energy are plotted in Figure 2b (shear viscosity $\eta$) and Figure 2c (first viscometric function $\Psi_1$), respectively.

At the highest shear rates for which the model may be appropriate (the above approximation for the stress becomes nonvalid for strong flows), the power laws for the rheological quantities are: $\eta \propto \gamma^{-2/3}$ and $\Psi_1 \propto \gamma^{-5/3}$. At moderate shear rates these values are only realized for high scission energies (see Figs. 2c-f) and are then independent of concentration, since the product $\phi \exp(-\beta E_{sc})$ plays a key role throughout this calculation, according to the summation procedure which is used for $z$ (12), and $z$ contains the product.

The flow–induced changes of the distribution $C(L)$ of micellar lengths $L$ for four sets of pairs of concentration/scission energy are visualized in Figure 3. Since in equilibrium the distribution function is monoexponential (cf. Eq. (15)), with increasing shear rate a maximum evolves which is shifted to shorter chain length with increasing shear rate. Additionally the distribution becomes less broad with increasing rate.

All results will be compared with simulation data for a microscopic model in the next section.
Fig. 2. — (a): Flow–alignment angle $\chi$ vs. shear rate for linear micelles with different scission energies $E_{sc}^*=0(\cdot),2,4,6,8,10,12(\cdot)$. (b): Shear viscosity and (c): first viscometric function vs. shear rate for $\phi = 4\%$ parametrized in the scission energy. The curves are calculated from (21, 14) and the defining formula for $\eta$ and $\Psi_1$ given in Section 2. For the Rouse model the second viscometric function vanishes.

3. Microscopic Model

In this section we will epitomize the Finitely Extendable Nonlinear Elastic force (FENE) multibead linear chain model [16, 17] with finite Cut-off distance (FENE–C) as introduced
Fig. 3. — Flow–induced changes of the distribution of micellar length $C(L)$ for different concentrations and scission energies. a) $\phi = 4\%$, $E_{sc} = 4$; b) $\phi = 15\%$, $E_{sc} = 4$; c) $\phi = 4\%$, $E_{sc} = 6$; d) $\phi = 15\%$, $E_{sc} = 6$.

Fig. 4. — Model potential specifying the microscopic FENE–C model (see Eqs. (24)).

in [6]. The micellar solution of concentration $\phi$ is modeled by $N_b$ beads, which interact via two–body potentials (Fig. 4). As above let $\phi N_b$ be the number of beads, which are able to form wormlike chains of monomers ("M–beads") and $(1-\phi) N_b$ the number of solvent particles ("S–particles"). All particles of the system ("M" and "S") have the same mass and interact
via the purely repulsive part of the Lennard–Jones (LJ) potential [18,19]

\[
U_{ij}^{LJ} = \begin{cases} 
4 \varepsilon \left[ (r_{ij}^*)^{-12} - (r_{ij}^*)^{-6} + 1/4 \right] & \text{for } r_{ij}^* \leq r_{\text{cut}} = 2^{1/6} \\
0 & \text{for } r_{ij}^* > r_{\text{cut}} 
\end{cases}
\] (23)

with \( r_{ij}^* = r_{ij}/\sigma \) being the distance between beads \( i \) and \( j \). All quantities resulting from the simulations are reduced to LJ units (and labeled with an asterisk if otherwise ambiguities could arise) which provides the energy (by \( \varepsilon \)) and length scale (by \( \sigma \)) of the system; the monomeric mass gives the third unit. All M–beads are able to form transient bonds which all other M–beads — except with those of the same chain — and every M–bead can have at maximum two bonds at the same time. Within this limitations, which ensure that only end–end–recombinations and therefore no branched structures do occur, all M–beads interact via the following “FENE–C” potential:

\[
U_{ij}^{\text{FENE–C}} = \begin{cases} 
-0.5k^*R_0^2 \ln[1 - (r_{ij}^*/R_0)^2] & \text{for } r_{ij}^* \leq \min(R_C, R_0) \\
-0.5k^*R_0^2 \ln[1 - (R_C/R_0)^2] & \text{for } r_{ij}^* \geq R_C 
\end{cases}
\] (24)

as introduced in [6] with parameters \( R_0 \) (maximum bond length), \( R_C \) (cut–off radius) and \( k^* \) (strength of spring). All results we present here from molecular dynamics simulations are for systems with bead number density \( \rho^* = 0.84 \) and temperature \( T^* = 1 \) as in [6,19]. The scission energy \( E_{sc}/k_B T \) corresponding to the model potential is connected with the cut–off radius \( R_C \) via the difference between \( U^{\text{bond}}(r \to \infty) \) and the energy at the minimum of the bonding potential (see Fig. 4). The original FENE potential [13] for a “Finitely Extendable Nonlinear Elastic” spring is obtained from the FENE–C potential by setting \( R_C = R_0 \) where \( R_0 \) is the maximum bond length.

4. Comparison between Meso- and Microscopic Model

In the simulations of the FENE–C model the bead number density is chosen as \( n^* = 0.84 \) (dense fluid near the critical point), the bead number concentrations of M–beads (in percent but denoted by \( \phi \) for convenience) are \( \phi = 4\%, 15\%, 100\% \) where a system with \( \phi = 100\% \) corresponds to a melt with no S–beads present. The temperature is kept constant at \( k_B T/\varepsilon = 1 \), the cutoff radius of the FENE–C potential has been chosen as \( R_0 = 1.13\sigma \), which implies \( E_{sc} = 8.09 \), in order to study our presently largest treatable system containing “long” chains and totally 16800 beads. In real systems scission energies take values around 3–10\( k_B T \). Note that the computing time increases with the length of chains to a power of around 7/2 [20]. The average bond length in equilibrium is \( a \approx 0.94\sigma \) which is close to the minimum distance provided by the bond potential \( U = U^{LJ} + U^{\text{FENE–C}} \) Together with a bead friction coefficient which has been estimated to be \( \zeta^* \approx 40 \) from the simulations the dimensionless parameter of the mesoscopic model should be \( \tau \approx 4.8 \). As an arbitrary “well” behaving function the bond potential can be approximated by a harmonic function around its minimum, thus the Rouse model should provide an approximate description close to equilibrium at moderate temperatures.
4.1. Equilibrium. — Having these specifications of the microscopic model the results of the micro- and mesoscopic models can be plotted as done in Figures 5–7 without any other adjustable parameter. As can be seen clearly from Figure 6 only the dependence of average length $\langle L \rangle$ divided by $E_{sc}$ (representation motivated by Eq. (18)) on concentration is not in perfect agreement, but a tendency to a small slope at low concentrations is obvious. The slope at high concentrations is around 0.8 for the systems studied here. All other quantities are described well.

4.2. Shear Flow. — For the case of shear flow with shear rate $\gamma$ the microscopic model is studied by performing NEMD simulations which make use of the homogeneous shear algorithm of Evans [17, 21] without introducing any new assumptions into the microscopic model.
Fig. 7. — MD results for the normalized equilibrium distribution of micellar length $C_0(L)$ for three samples at different concentrations $\phi$. Lines: the mesoscopic result (15) with same parameters as for the microscopic model.

Fig. 8. — Both NEMD and mesoscopic results for the non–Newtonian shear viscosity $\eta$, the viscometric function $\Psi_1$ vs. the shear rate $\gamma$. All quantities are given in Lennard–Jones (LJ) units.

We plot the numerical solution of the mesoscopic model under shear (see Figs. 1–3) together with the NEMD results for a micellar solution ($\phi = 4\%$, $R_C = 1.13$) in Figures 8–11. Notice that in these figures all quantities are expressed in terms of the usual Lennard–Jones units [19] in order to be able to compare these plots with results from computer simulation studies of
the corresponding classical polymers. Again, the main characteristics are in very good mutual agreement. A single refinement was needed to get all results in accordance. The NEMD first viscometric function is a factor of around 3 higher than expected from the adapted Rouse model. In Figure 8 we compared both viscometric functions by multiplying the theoretical result by 3. This change does also affect directly the flow alignment angle in Figure 11 (compare with Fig. 2). We have not yet a convincing argument for introducing this factor. Straightforward application of the Rouse model within our approach seems to underestimate the flow-induced alignment of chains in direction of flow.
5. Summary and Conclusions

The length and length distribution of micelles as modeled as bead–spring chains have been calculated from both microscopic and mesoscopic models. Within the framework of statistical mechanics an expression for the free energy is given for which the ratio between number of micelles $n_i$ with $i$ beads over number of micelles $n_{i-1}$ does not depend on $i$ if Gaussian chains are considered. The length distribution in equilibrium then only depends on two parameters, namely the total number of beads (micellar concentration) and the scission energy. We get a concentration dependent relationship between average length and scission energy which is not monoexponential at small concentrations (see Fig. 1b and Fig. 6). Results from this approach were successfully compared with the results as calculated for the microscopic FENE-C model by MD computer simulations.

Both approaches were then extended to study the length distribution, the flow–alignment and the rheological behavior under shear flow. We provide an expression for the number density of $i$–chains as function of scalar pressure and orientation of segments. Both dependencies describe the coupling of the shape of micelles to the flow parameters. The model predicts shear thinning resulting from the decrease of average micellar lengths. The distribution of lengths is no longer monoexponential under flow. A maximum occurs whose evolution with shear rate has been described. The influence of the concentration and scission energy on the power law behavior of the shear viscosity and the normal stress difference, respectively, and its influence on the flow alignment angle has been reported. These results are in very good agreement with our NEMD computer simulation results. The similarities validate the rough model assumption; the mesoscopic model assumes independent Gaussian (Rouse) chains whereas the microscopic model calculates properties for phantom chains in a theta solvent (FENE+LJ chains), including hydrodynamic interactions. Entanglements should be rare for the lengths considered here.
Also, the results imply how to modify the approaches in order to obtain models with the opposite behavior in, e.g., \( (L) \) as function of shear rate, for which experimental evidence does exist.

The mesoscopic model has to be extended if one wants to account for concentration effects related to intermolecular interactions, e.g., by introducing a mean field potential into the free energy. A proper prediction of the non–Newtonian behavior of the micellar systems requires to leave the analytical equations of the Rouse model and to perform the calculations for nonharmonic potentials, as outlined here for the FENE model [22].

Through (7) a phase separation between the short chain and long chain systems can be expected if the sign of \( \partial p/\partial \gamma \) depends on the length of chains as it has been detected for the microscopic FENE model polymers [17]. Various hints for such a phase separation exist, e.g., under shear, a shear banding structure has been observed by one of us [23]. Theoretical studies on the latter phenomenon have been already performed [24–26].

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