Nonlinear kinetics of fast relaxation in solutions with short and lengthy micelles

M. S. Kshevetskiy[a)] and A. K. Shchekin[b)]

Department of Statistical Physics, St. Petersburg State University, Ulyanovskaya St. 1,
Petrodvorets, St. Petersburg 198504, Russia

An analytical treatment of the nonlinear kinetic equations for fast relaxation of coexisting short and lengthy micelles in surfactant solutions is presented. The kinetic equations can be written as a hierarchical set of differential equations for the moments of the aggregation number distribution function of micelles. It is shown that the moment equations can be successively integrated. As examples of the general approach, particular cases of short spherical micelles, lengthy cylindrical micelles, and coexisting short and lengthy micelles have been considered and compared to the results of linear kinetic theory of micellar fast relaxation. The results show that there is a strong interplay between coexisting short and lengthy micelles, even in the case when the total number of surfactant molecules aggregated in short micelles is small in comparison with that in lengthy micelles. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3204699]

I. INTRODUCTION

Speaking of fast relaxation in surfactant solution above the critical micelle concentration (cmc), which is defined by the condition that the total number of surfactant molecules in micelles is about 10% of the number of surfactant monomers, we assume a stepwise relaxation process with a fixed total number of micelles and a time scale much smaller than that for slow relaxation to the final equilibrium. As a result of fast relaxation, the quasi-equilibrium distributions of subcritical premicellar aggregates and micelles (as stable molecular aggregates) have been established separately, but their mutual equilibrium has not yet been reached. The quasi-equilibrium distributions are the separate local (in terms of the aggregation number) equilibrium distributions of aggregates in the aggregation number axis with the parameters varying in time relatively slowly. These local distributions evolve on the stage of slow relaxation to a final one-piece equilibrium distribution of molecular aggregates covering all aggregation numbers.

The foundations of the kinetic theory of fast relaxation in micellar solutions were build by Aniansson and Wall,[1,2] Almgren *et al.*,[3] Kahlweit,[4] and Kahlweit and Teubner.[5] A modern review on the subject is given by Zana.[6] Aniansson and co-workers[1–3] proposed a procedure of solution of the kinetic equations of micellization by finding the time-dependent coefficients of expansion of the linearized (with respect to the Gauss local equilibrium distribution) nonequilibrium distribution function of spherical micelles in the Hermitian polynomials. This procedure allowed them to obtain a hierarchical set of the specific times of the fast relaxation in solutions with spherical micelles. An extension of the linear theory to the case of spherical micelles and lengthy micelles

with the fusion-fission mechanism of micelle formation was done by Kahlweit,[4] Kahlweit and Teubner,[5] and Waton.[7] A generalization of the linear kinetic theory to the case of lengthy cylindrical micelles with the stepwise molecular mechanism of micelle formation was proposed by Shchekin *et al.*[8] using an expansion in the Laguerre polynomials. Fast relaxation of coexisting spherical and cylindrical micelles was recently studied within the same framework in Ref. 9.

The characteristic feature of the approaches from Refs. 1–3, 8, and 9 is considering only the final stage of fast relaxation where the deviations from the local quasi-equilibrium distributions are small and the relaxation has a pure exponential character. This justifies the linearization of the kinetic equation for the aggregation number distribution function of aggregates and using for solving the corresponding linear kinetic equation a technique of separating variables with the help of appropriate polynomials. The technique cannot be applied for the solution of the kinetic equation on the arbitrary stage of fast relaxation with nonsmall deviations from the local quasi-equilibrium distributions.

We use in this paper a moment approach to find a solution of the nonlinear kinetic equations for a stepwise fast relaxation in micellar solutions. The nonlinearity of the kinetic equations is provided by the dependence of a rate coefficient in the equation on the surfactant monomer concentration.

The moment approach is one of the standard methods in the theory of kinetic equations and it had been used for study of slow relaxation in micellar systems with the stepwise molecular mechanism of micelle formation[1–3,10,11] and with the fusion-fission mechanism also.[7] The moment approach to the nonlinear kinetic equations of aggregation allows us to consider the fast relaxation from the beginning to the end, starting from the initial arbitrary disturbance of the micellar system and finishing by the exponential approaching a quasi-

---

a)Electronic mail: kl@stat.phys.spbu.ru.
b)Electronic mail: akshch@list.ru. URL: http://stat.phys.spbu.ru/personal/en-shchekin.html.

equilibrium state. The central idea of the approach is that the kinetic equations of aggregation can be written as a hierarchical set of differential equations for the moments of the aggregation number distribution function of micelles. Although these moment equations can be nonlinear too, it is possible to integrate them successively (even in an analytical form in particular cases). Because only the moments of the distribution function can be observable in kinetic experiment, the information on their time dependence obtained from the integration will be sufficient for describing the whole behavior of a nonequilibrium distribution function.

As examples of the general moment approach in the nonlinear kinetics of fast relaxation in micellar solutions, we will consider particular cases of short spherical micelles, lengthy cylindrical micelles, and coexisting short and lengthy micelles. The results will be compared to the results of linear kinetic theory of micellar fast relaxation.[1–3,8,9]

II. KINETIC EQUATION OF MICELLIZATION AND QUASI-EQUILIBRIUM DISTRIBUTIONS

Let us consider a micellar solution above the second critical cmc (cmc$_2$, which is defined by the condition that the total number of molecules in lengthy micelles is about 10% of the total number of surfactant monomers) with coexisting short and lengthy molecular aggregates of surfactant. The kinetic equation describing the stepwise evolution in time t of the distribution function $c_n(t)$ of molecular aggregates in aggregation number n is the Becker–Döring master equation

$$\frac{\partial c_n}{\partial t} = -(J_n - J_{n-1}),$$ (1)

where

$$J_n = j_n^+ c_n - j_{n+1}^- c_{n+1}$$ (2)

is the flux of aggregates in the aggregation number axis between numbers n and $n+1$. Here j_n^+ is the monomer capture rate (the number of surfactant monomers captured out the solution per unit of time by the aggregate with aggregation number n) and j_{n+1}^- is the monomer emission rate (the number of surfactant monomers emitted into the solution per unit of time by the aggregate with aggregation number $n+1$). The rate j_{n+1}^- is independent of the surfactant concentration in the solution and can be determined with the help of the monomer capture rate $\breve{j}_n^+$ at quasi-equilibrium state. Denoting the quantities at the quasi-equilibrium state with a breve and recognizing that the flux J_n turns to zero at this state, we have

$$j_{n+1}^- = \breve{j}_n^+ \frac{\breve{c}_n}{\breve{c}_{n+1}}.$$ (3)

The rate j_n^+ is directly proportional to the surfactant monomer concentration c_1, so we can write

$$j_n^+ = \breve{j}_n^+ \frac{c_1}{\breve{c}_1}.$$ (4)

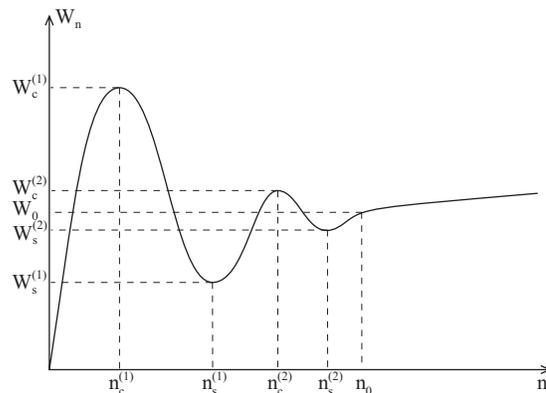Substituting Eqs. (3) and (4) to Eq. (2), we finally get

FIG. 1. A typical aggregation work W_n of surfactant aggregate as a function of the aggregation number n at total surfactant concentration in solution above the cmc$_2$. The upper indices (1) and (2) number the corresponding maxima and minima points. The lower indices s and c refer to stable and critical micelles, respectively. The index 0 indicates the beginning of linear dependence of W_n on n.

$$J_n = \breve{j}_n^+ \breve{c}_n \left(\frac{c_1 c_n}{\breve{c}_1 \breve{c}_n} - \frac{c_{n+1}}{\breve{c}_{n+1}} \right).$$ (5)

Instead of distribution $c_n(t)$, it is more convenient to use a relative deviation $\xi_n(t)$ of the distribution function $c_n(t)$ from the quasi-equilibrium distribution $\breve{c}_n$,

$$\xi_n = \frac{c_n - \breve{c}_n}{\breve{c}_n}, \quad c_n = \breve{c}_n(1 + \xi_n).$$ (6)

Below we will be interested mostly in monomers and rather large aggregates with aggregation numbers $n \gg 1$. Using Eq. (6) in Eq. (5) and replacing $\xi_{n+1} - \xi_n$ with $\partial \xi_n / \partial n$ at $n \gg 1$, we get

$$J_n = \breve{j}_n^+ \breve{c}_n \left(\xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right).$$ (7)

Replacing $J_n - J_{n-1}$ with $\partial J_n / \partial n$ at $n \gg 1$ and substituting Eq. (7) in Eq. (1) yields

$$\breve{c}_n \frac{\partial \xi_n}{\partial t} = -\frac{\partial}{\partial n} \left[\breve{j}_n^+ \breve{c}_n \left(\xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right) \right].$$ (8)

The nonlinear term $\xi_1 \xi_n$ on the right-hand side of Eq. (8) had usually been neglected in the previous analysis of fast relaxation[1–3,8,9] under assumptions $\xi_n \ll 1$, $\xi_1 \ll 1$. These assumptions are satisfied on the final stage of fast relaxation only. To describe the very early and the intermediate stages of fast relaxation, we need to keep this term in the kinetic Eq. (8). The corresponding peculiarities will be in the focus of our investigation below.

Let us turn now to analysis of the profile of the dimensionless (expressed in thermal units $k_B T$, where k_B is the Boltzmann constant and T is the temperature of the solution) aggregation work W_n as a function of aggregation number n. A typical plot[12–14] of the work at surfactant concentration in solution above cmc$_2$ is shown in Fig. 1. We will not consider here the case when globular and spherocylindrical micelles are simultaneously present in the solution and the depen-

dence of aggregation work on the aggregation number of surfactant monomers in micelles is divided into two branches.[11]

There are droplet and quasidroplet models for the work of micelle formation which determine every contribution to the work as a function of the aggregation number n.[14–19] These models give a behavior of the work of droplet formation that is consistent with the plot shown in Fig. 1. We will not consider in this paper such detailed models and restrict themselves only with most general peculiarities of the plot in Fig. 1.

There are first and second maxima and first and second minima in the plot in Fig. 1. The quantities corresponding to these extrema are denoted with superscripts (1) and (2). With the help of subscripts c and s we distinguish the maxima and the minima. The vicinity of the first minimum corresponds to the range of aggregation numbers where short micelles accumulate (the term "short micelles" refers to spherical or quasispherical micelles). We will assume that the corresponding potential well is sufficiently narrow, and quasi-equilibrium distribution of short micelles in the well can be described by a Gaussian.

Lengthy micelles (they may be cylindrical or disklike micelles) are located at $n > n_c^{(2)}$. It is known[12,15,16] that the behavior of the aggregation work above the cmc$_2$ becomes linear starting from some aggregation number. We denote this number in Fig. 1 by n_0. The behavior of the aggregation work W_n with the distinguished maxima and minima (shown in Fig. 1) allows us to write relaxation equations for fast relaxation after initial disturbance separately for short and lengthy micelles. It will be done in Secs. III and IV.

III. MOMENT EQUATIONS FOR SHORT MICELLES

First, we will consider fast relaxation of short micelles accumulated within the first potential well in the work of aggregate formation in Fig. 1. Let us multiply both parts of Eq. (8) by n^k where $k = 0, 1, 2, \ldots$ and sum the result over the first potential well. Passing from summing to integration at $n \gg 1$ yields

$$\int_{\substack{\text{short}\\\text{micelles}}} n^k \check{c}_n \frac{\partial \xi_n}{\partial t} dn = - \int_{\substack{\text{short}\\\text{micelles}}} n^k \frac{\partial}{\partial n} \\ \times \left[\check{j}_n^+ \check{c}_n \left(\xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right) \right] dn. \quad (9)$$

The words *short micelles* in the lower limit of integration indicate the region of the first potential well.

Integrating the right-hand side of Eq. (9) by parts and using the natural for fast relaxation conditions that the flux J_n and deviation $\xi_n(t)$ tend to zero at the boundaries of the first potential well, we find

$$\int_{\substack{\text{short}\\\text{micelles}}} n^k \check{c}_n \frac{\partial \xi_n}{\partial t} dn = k \xi_1 \int_{\substack{\text{short}\\\text{micelles}}} n^{k-1} \check{j}_n^+ \check{c}_n (1 + \xi_n) dn \\ + k \int_{\substack{\text{short}\\\text{micelles}}} \xi_n \frac{\partial}{\partial n} (n^{k-1} \check{j}_n^+ \check{c}_n) dn. \quad (10)$$

We used integration by parts twice to obtain the second term

on the right-hand side of Eq. (10). Thus we completely eliminate the derivatives of unknown function ξ_n with respect to n from the equation. This will facilitate our next task.

We will assume that the potential well for short micelles and the corresponding quasi-equilibrium distribution in aggregation numbers are sufficiently narrow, so we can use a quadratic approximation for the aggregation work $\check{W}_n$,

$$\check{W}_n = \check{W}_s^{(1)} + \frac{1}{2} \left(\frac{n - \check{n}_s^{(1)}}{\Delta \check{n}_s^{(1)}} \right)^2,$$

$$\check{n}_s^{(1)} - \Delta \check{n}_s^{(1)} \le n \le \check{n}_s^{(1)} + \Delta \check{n}_s^{(1)}, \quad \Delta \check{n}_s^{(1)} \ll \check{n}_s^{(1)}. \quad (11)$$

Here $\check{n}_s^{(1)}$ is the location (in the aggregation number axis) of the aggregation work minimum for short micelles in the quasi-equilibrium state (see first potential well in Fig. 1), $\check{W}_s^{(1)} \equiv \check{W}_n|_{n=\check{n}_s^{(1)}}$, $\Delta \check{n}_s^{(1)} \equiv (d^2 \check{W}_n / dn^2|_{n=\check{n}_s^{(1)}})^{-1/2}$.

According to the Boltzmann principle, the quasi-equilibrium distribution $\check{c}_n$ can be written in the potential well for short micelles as

$$\check{c}_n = \check{c}_s^{(1)} e^{-(\check{W}_n - \check{W}_s^{(1)})}, \quad (12)$$

where $\check{c}_s^{(1)} \equiv \check{c}_n|_{n=\check{n}_s^{(1)}}$. In view of Eqs. (11) and (12), the quasi-equilibrium distribution of short micelles in the first potential well has the form of the Gauss distribution,

$$\check{c}_n = \check{c}_s^{(1)} \exp\left[-\frac{1}{2} \left(\frac{n - \check{n}_s^{(1)}}{\Delta \check{n}_s^{(1)}} \right)^2 \right],$$

$$\check{n}_s^{(1)} - \Delta \check{n}_s^{(1)} \le n \le \check{n}_s^{(1)} + \Delta \check{n}_s^{(1)}. \quad (13)$$

The total concentration $\check{c}_M^{(1)}$ of short micelles, their average aggregation number $\check{n}_M^{(1)}$, and dispersion $\Delta \check{n}_M^{(1)}$ of aggregation numbers are determined at the quasi-equilibrium state as

$$\check{c}_M^{(1)} \equiv \int_{\substack{\text{short}\\\text{micelles}}} \check{c}_n dn, \quad (14)$$

$$\check{n}_M^{(1)} \equiv \frac{1}{\check{c}_M^{(1)}} \int_{\substack{\text{short}\\\text{micelles}}} n \check{c}_n dn = \check{n}_s^{(1)}, \quad (15)$$

$$(\Delta \check{n}_M^{(1)})^2 \equiv \frac{1}{\check{c}_M^{(1)}} \int_{\substack{\text{short}\\\text{micelles}}} (n - \check{n}_M^{(1)})^2 \check{c}_n dn = (\Delta \check{n}_s^{(1)})^2. \quad (16)$$

It is clear from Eq. (13) and definitions (14)–(16) that the location of the aggregation work minimum for short micelles and the quantity $\Delta \check{n}_s^{(1)}$ coincides with the average aggregation number and the aggregation number dispersion, respectively.

The rate $\check{j}_n^+$ is proportional to the probability of collision between monomer and aggregate with the aggregation number n. As a consequence, it should be proportional to the collision cross section, i.e., in the case of spherical aggregates, to the surface area of the aggregate which depends on n as $n^{2/3}$. Thus $\check{j}_n^+ \propto n^{2/3}$. This is a regular assumption on $\check{j}_n^+$ in the kinetics of nucleation[20–22] in the absence of a controlled diffusion process onto aggregate.

Taking into account Eq. (13) and strong inequality $\Delta \breve{n}_s^{(1)} \ll \breve{n}_s^{(1)}$, which characterizes the relative narrowness of the first potential well, we can use an approximation

$$\breve{j}_n^+ \simeq \breve{j}_n^+|_{n=\breve{n}_s^{(1)}} \equiv \breve{j}_M^{(1)}, \quad \breve{n}_s^{(1)} - \Delta \breve{n}_s^{(1)} \leq n \leq \breve{n}_s^{(1)} + \Delta \breve{n}_s^{(1)} \tag{17}$$

in the integrand of Eq. (10). Substituting Eqs. (13) and (11) into Eq. (10) and taking into account Eqs. (15)–(17), we get

$$\int_{\substack{\text{short} \\ \text{micelles}}} n^k \breve{c}_n \frac{\partial \xi_n}{\partial t} dn = k \breve{j}_M^{(1)} \left[\xi_1 \int_{\substack{\text{short} \\ \text{micelles}}} n^{k-1} \breve{c}_n (1 + \xi_n) dn \right.$$
$$+ (k-1) \int_{\substack{\text{short} \\ \text{micelles}}} n^{k-2} \breve{c}_n \xi_n dn$$
$$\left. - \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \int_{\substack{\text{short} \\ \text{micelles}}} n^{k-1} \breve{c}_n \xi_n (n - \breve{n}_M^{(1)}) dn \right]. \tag{18}$$

Let us now define

$$M_k^{(1)} \equiv \frac{1}{\breve{c}_1} \int_{\substack{\text{short} \\ \text{micelles}}} n^k \breve{c}_n dn, \tag{19}$$

$$\Delta M_k^{(1)}(t) \equiv \frac{1}{\breve{c}_1} \int_{\substack{\text{short} \\ \text{micelles}}} n^k \breve{c}_n \xi_n(t) dn. \tag{20}$$

It is evident that the time-independent quantities $M_k^{(1)}$ are the moments of the quasi-equilibrium distribution $\breve{c}_n$ of short micelles. According to definitions (14)–(16), we can link the moments $M_k^{(1)}$ with the total concentration of short micelles, their average aggregation number, and their aggregation number dispersion by the relations

$$M_0^{(1)} = \frac{\breve{c}_M^{(1)}}{\breve{c}_1}, \quad M_1^{(1)} = \frac{\breve{c}_M^{(1)}}{\breve{c}_1} \breve{n}_M^{(1)}, \quad M_2^{(1)} = \frac{\breve{c}_M^{(1)}}{\breve{c}_1} [(\breve{n}_M^{(1)})^2 + (\Delta \breve{n}_M^{(1)})^2]. \tag{21}$$

The time-dependent quantities $\Delta M_k^{(1)}$ ($k = 0, 1, 2, \ldots$) describe the deviations of the moments of nonequilibrium distribution c_n from their quasi-equilibrium values $M_k^{(1)}$. Substituting Eqs. (19) and (20) into Eq. (18), we get

$$\frac{d}{dt} \Delta M_k^{(1)} = -k \breve{j}_M^{(1)} \left[\frac{\Delta M_k^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} - \left(\frac{\breve{n}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} + \xi_1(t) \right) \Delta M_{k-1}^{(1)} \right.$$
$$\left. - (k-1) \Delta M_{k-2}^{(1)} - \xi_1(t) M_{k-1}^{(1)} \right]. \tag{22}$$

We keep the third term in the square brackets on the right-hand side of Eq. (22) in view of the factor $k-1$ at large k. It can be shown that if we take into account in Eq. (10) the second term in the expansion of the coefficient $\breve{j}_n^+$ in powers of $n - \breve{n}_s^{(1)}$, it will bring a small (less than 1%) rescaling of the quantity $\breve{n}_M^{(1)}/(\Delta \breve{n}_M^{(1)})^2$ in the second term in the square brackets on the right-hand side of Eq. (22). It justifies the accuracy used in deriving Eq. (22).

Equations (22) at different $k = 0, 1, 2, \ldots$ form a system of coupled hierarchical equations which can be completed by adding the balance equation of surfactant matter in the solution. This procedure will be considered in Secs. V and VII.

IV. MOMENT EQUATIONS FOR LENGTHY MICELLES

Now we will consider fast relaxation of lengthy micelles in the interval $[n_c^{(2)}, \infty]$ of aggregation numbers in Fig. 1. According to previous theoretical and experimental data,[10,12–15] we assume that the transition zone from short to lengthy micelles lies in the interval $[n_c^{(2)}, \breve{n}_0]$, and the aggregation work $\breve{W}_n$ becomes linear starting from $n = \breve{n}_0$. Multiplying both parts of Eq. (8) by n^k, where $k = 0, 1, 2, \ldots$, and integrating the result over the interval $n > \breve{n}_0$ (lengthy micelles region) yields

$$\int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \breve{c}_n \frac{\partial \xi_n}{\partial t} dn$$
$$= - \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \frac{\partial}{\partial n} \left[\breve{j}_n^+ \breve{c}_n \left(\xi_1 (1 + \xi_n) - \frac{\partial \xi_n}{\partial n} \right) \right] dn. \tag{23}$$

The words *lengthy micelles* in the lower limit of integration indicate the lengthy micelles region.

Similar to the case of short micelles, we can integrate the right-hand side of Eq. (23) by parts and use the boundary conditions for the flux J_n and deviation $\xi_n(t)$. One of the boundary conditions requires that J_n and $\xi_n(t)$ tend to zero as $n \to \infty$, but J_n and $\xi_n(t)$ can be nonzero at $n = \breve{n}_0$. It means that additional integration terms appear in Eq. (23), but we can neglect them because other terms are much larger (the interval $[n_c^{(2)}, \breve{n}_0]$ is much shorter than the lengthy micelles region). Thus, integrating by parts twice, we can write

$$\int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \breve{c}_n \frac{\partial \xi_n}{\partial t} dn = k \xi_1 \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^{k-1} \breve{j}_n^+ \breve{c}_n (1 + \xi_n) dn$$
$$+ k \int_{\substack{\text{lengthy} \\ \text{micelles}}} \xi_n \frac{\partial}{\partial n} (n^{k-1} \breve{j}_n^+ \breve{c}_n) dn. \tag{24}$$

The linearity of the aggregation work $\breve{W}_n$ as a function of aggregation number at $n > \breve{n}_0$ means

$$\breve{W}_n = \breve{W}_{\breve{n}_0} + \frac{n - \breve{n}_0}{\triangle \breve{n}_l}, \quad n \geq \breve{n}_0. \tag{25}$$

Here $\breve{W}_{\breve{n}_0} \equiv \breve{W}_n|_{n=\breve{n}_0}$, $\Delta \breve{n}_l \equiv (d\breve{W}_n/dn|_{n=\breve{n}_0})^{-1}$, the physical meaning of the quantity $\Delta \breve{n}_l$ we will clarify below.

According to the Boltzmann principle, the quasi-equilibrium distribution $\breve{c}_n$ can be written at $n > \breve{n}_0$ as

$$\breve{c}_n = \breve{c}_{\breve{n}_0} e^{-(\breve{W}_n - \breve{W}_{\breve{n}_0})}, \tag{26}$$

where $\breve{c}_{\breve{n}_0} \equiv \breve{c}_n|_{n=\breve{n}_0}$. In view of Eqs. (25) and (26), we have a pure exponential law for the dependence of quasi-equilibrium distribution on aggregation number n,

$$\breve{c}_n = \breve{c}_{\breve{n}_0} \exp \left[- \frac{n - \breve{n}_0}{\Delta \breve{n}_l} \right], \quad n > \breve{n}_0. \tag{27}$$

The total concentration $\check{c}_M^{(2)}$ of lengthy micelles, their average aggregation number $\check{n}_M^{(2)}$, and dispersion $\Delta\check{n}_M^{(2)}$ of aggregation numbers are determined in the quasi-equilibrium state as

$$\check{c}_M^{(2)} \equiv \int_{\substack{\text{lengthy} \\ \text{micelles}}} \check{c}_n dn, \tag{28}$$

$$\check{n}_M^{(2)} \equiv \frac{1}{\check{c}_M^{(2)}} \int_{\substack{\text{lengthy} \\ \text{micelles}}} n\check{c}_n dn = \check{n}_0 + \Delta\check{n}_l, \tag{29}$$

$$(\Delta\check{n}_M^{(2)})^2 \equiv \frac{1}{\check{c}_M^{(2)}} \int_{\substack{\text{lengthy} \\ \text{micelles}}} (n - \check{n}_M^{(2)})^2 \check{c}_n dn = (\Delta\check{n}_l)^2. \tag{30}$$

It is clear from Eq. (27) and definitions (28)–(30) that the quantity $\Delta\check{n}_l$ coincides with the aggregation number dispersion. It should be noted that $\Delta\check{n}_l$ may be much larger than $\check{n}_0$ for lengthy micelles.

Similar to the case of short micelles, the rate $\check{j}_n^+$ for lengthy micelles should be proportional to the cross section of the molecular collision with the micelle. Evidently, this cross section will be proportional to the total surface area of the micelle. Taking into account the linearity of the micelle surface area in the aggregate number at $n \geq \check{n}_0$ and neglecting the possible deviations in absorption and emission of monomers by micelle endcaps for comparatively large micelles, we can use an approximation

$$\check{j}_n^+ = \check{j}_M^{(2)} \frac{n}{\check{n}_M^{(2)}}, \quad n \geq \check{n}_0, \tag{31}$$

where $\check{j}_M^{(2)} = \check{j}_n^+|_{n=\check{n}_M^{(2)}}$. Note again that it is true in the absence of a controlled diffusion process onto aggregate.

Substituting Eqs. (27) and (31) into Eq. (24) and taking into account Eq. (30) yields

$$\int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \check{c}_n \frac{\partial \xi_n}{\partial t} dn = k \frac{\check{j}_M^{(2)}}{\check{n}_M^{(2)}} \left[\xi_1 \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \check{c}_n (1 + \xi_n) dn \right.$$
$$+ k \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^{k-1} \check{c}_n \xi_n dn$$
$$\left. - \frac{1}{\Delta\check{n}_M^{(2)}} \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \check{c}_n \xi_n dn \right]. \tag{32}$$

Let us now define

$$M_k^{(2)} \equiv \frac{1}{\check{c}_1} \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \check{c}_n dn, \tag{33}$$

$$\Delta M_k^{(2)}(t) \equiv \frac{1}{\check{c}_1} \int_{\substack{\text{lengthy} \\ \text{micelles}}} n^k \check{c}_n \xi_n(t) dn. \tag{34}$$

It is evident that time-independent quantities $M_k^{(2)}$ are the moments of the quasi-equilibrium distribution $\check{c}_n$ of lengthy micelles. According to definitions (28) and (30), we can link the moments $M_k^{(2)}$ with the total concentration of lengthy micelles, their average aggregation number, and their aggregation number dispersion by the relations

$$M_0^{(2)} = \frac{\check{c}_M^{(2)}}{\check{c}_1}, \quad M_1^{(2)} = \frac{\check{c}_M^{(2)}}{\check{c}_1} \check{n}_M^{(2)}, \quad M_2^{(2)} = \frac{\check{c}_M^{(2)}}{\check{c}_1} [(\check{n}_M^{(2)})^2 + (\Delta\check{n}_M^{(2)})^2]. \tag{35}$$

The time-dependent quantities $\Delta M_k^{(2)}$ ($k=0,1,2,\ldots$) describe the deviations of the moments of nonequilibrium distribution c_n from their quasi-equilibrium values $M_k^{(2)}$. Substituting Eqs. (33) and (34) into Eq. (32), we get

$$\frac{d}{dt} \Delta M_k^{(2)} = -k \frac{\check{j}_M^{(2)}}{\check{n}_M^{(2)}} \left[\left(\frac{1}{\Delta\check{n}_M^{(2)}} - \xi_1(t) \right) \Delta M_k^{(2)} - k\Delta M_{k-1}^{(2)} \right.$$
$$\left. - \xi_1(t) M_k^{(2)} \right]. \tag{36}$$

Equation (36) at different $k=0,1,2,\ldots$ forms a system of coupled hierarchical equations which can be completed by adding the balance equation of surfactant matter in the solution. This procedure will be considered in Secs. VI and VII.

V. SOLUTION OF THE MOMENT EQUATIONS FOR SHORT MICELLES

We will study in this section a special case when the aggregation work (see Fig. 1) has only one potential well which corresponds to the short micelles. This case is realized at total surfactant concentrations in solution between cmc and cmc$_2$, when the work $\check{W}_n$ of micelle formation tends to infinity at $n > \check{n}_s^{(1)}$ and lengthy micelles are absent.

As we already noticed, Eq. (22) represents a system of coupled equations at different $k=0,1,2,\ldots$. If we knew $\xi_1(t)$, the system can be easily solved step by step from lower- to higher-order moments $\Delta M_k^{(1)}$. In order to find $\xi_1(t)$, we may use the material balance equation for surfactant in the solution in the form

$$c_1(t) + \int_{\substack{\text{short} \\ \text{micelles}}} n c_n(t) dn = c, \tag{37}$$

where c is the total surfactant concentration. Using Eq. (6) and taking into account that Eq. (37) is valid also in the quasi-equilibrium state, we can rewrite Eq. (37) in the following form:

$$\xi_1(t) + \frac{1}{\check{c}_1} \int_{\substack{\text{short} \\ \text{micelles}}} n \check{c}_n \xi_n(t) dn = 0. \tag{38}$$

Recalling the definition (20) $\Delta M_1^{(1)}$, we finally get from Eq. (38) an important relation,

$$\xi_1(t) = -\Delta M_1^{(1)}. \tag{39}$$

Let us now turn back to system (22). Setting $k=0$ in Eq. (22), we have

$$\frac{d}{dt} \Delta M_0^{(1)} = 0.$$

Thus $\Delta M_0^{(1)}$ is constant in time (on the stage of fast relaxation). Because in view of Eq. (20), $\Delta M_0^{(1)}$ is related to change in total concentration of short micelles and this concentration does not change in fast relaxation, we conclude

$$\Delta M_0^{(1)}(t) = 0. \tag{40}$$

Setting $k = 1, 2, \ldots$ in Eq. (22) and using Eqs. (39) and (40), we can find first, second, and higher moments $\Delta M_k^{(1)}(t)$. As a result, we get

$$\frac{d}{dt} \Delta M_1^{(1)} = -\breve{j}_M^{(1)} \left[\frac{\breve{c}_M^{(1)}}{\breve{c}_1} + \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right] \Delta M_1^{(1)}, \tag{41}$$

$$\frac{d}{dt} \Delta M_2^{(1)} = -2\breve{j}_M^{(1)} \left\{ \frac{\Delta M_2^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} \right.$$
$$\left. + \breve{n}_M^{(1)} \left[\frac{\breve{c}_M^{(1)}}{\breve{c}_1} - \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right] \Delta M_1^{(1)} + (\Delta M_1^{(1)})^2 \right\}, \tag{42}$$

the equations for higher moments are similar to Eq. (42). All the equations at $k = 2, \ldots$ turn to be linear but inhomogeneous. Because only the behavior of average aggregation number and dispersion of micelles can be observable in experiment, we will not consider the details of the time dependence of higher moments.

Solving Eqs. (41) and (42) yields

$$\Delta M_1^{(1)}(t) = C_1^{(1)} \exp\left\{ -\breve{j}_M^{(1)} \left[\frac{\breve{c}_M^{(1)}}{\breve{c}_1} + \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right] t \right\}, \tag{43}$$

$$\Delta M_2^{(1)}(t) = C_2^{(1)} \exp\left(-\frac{2\breve{j}_M^{(1)} t}{(\Delta \breve{n}_M^{(1)})^2} \right) + 2\breve{n}_M^{(1)} \Delta M_1^{(1)}(t)$$
$$+ \frac{\breve{c}_1}{\breve{c}_M^{(1)}} (\Delta M_1^{(1)}(t))^2, \tag{44}$$

where integration constants $C_1^{(1)}$ and $C_2^{(1)}$ can be determined with the help of initial conditions for $\Delta M_1^{(1)}(0)$ and $\Delta M_2^{(1)}(0)$. The laws of time dependence given by Eqs. (43) and (44) are pure exponential, and the characteristic times for fast relaxation of short micelles are

$$t_1^{(1)} = \left[\breve{j}_M^{(1)} \left(\frac{\breve{c}_M^{(1)}}{\breve{c}_1} + \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right) \right]^{-1}, \tag{45}$$

$$t_2^{(1)} = \left[\frac{2\breve{j}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} \right]^{-1}, \quad t_2'^{(1)} = \left[2\breve{j}_M^{(1)} \left(\frac{\breve{c}_M^{(1)}}{\breve{c}_1} + \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right) \right]^{-1}. \tag{46}$$

Comparing these times to the times from Refs. 1, 22, and 23 for nonionic spherical micelles, we see that times $t_1^{(1)}$ and $t_2^{(1)}$ are the same in the linear and nonlinear theories, but time $t_2'^{(1)}$ appears only in the nonlinear theory. As follows from Eqs. (22), (39), (43), and (44), any moment $\Delta M_k^{(1)}(t)$ ($k = 1, 2, \ldots$) can be represented as a finite sum of exponentials.

Let us introduce the central moments for short micelles,

$$\bar{M}_k^{(1)}(t) = \frac{1}{\breve{c}_1} \int_{\substack{\text{short} \\ \text{micelles}}} (n - n_M^{(1)}(t))^k c_n(t) dn, \quad k = 0, 1, 2, \ldots, \tag{47}$$

where $n_M^{(1)}(t)$ is the current value of the average aggregation number in a short micelle. It is clear that $\bar{M}_0^{(1)}(t) = M_0^{(1)} = \breve{c}_M^{(1)}/\breve{c}_1$ and $\bar{M}_1^{(1)}(t) \equiv 0$. In view of definitions (19) and (20) we can write

$$n_M^{(1)}(t) = \frac{M_1^{(1)} + \Delta M_1^{(1)}(t)}{M_0^{(1)} + \Delta M_0^{(1)}(t)}. \tag{48}$$

Taking into account Eqs. (21), (39), and (40), we get

$$n_M^{(1)}(t) = \breve{n}_M^{(1)} - \frac{\breve{c}_1}{\breve{c}_M^{(1)}} \xi_1(t), \tag{49}$$

Repeating the procedure of reducing the kinetic Eq. (8) to a set of evolution equations for central moments (47) at $k = 1, 2, 3, 4$ yields

$$\frac{d}{dt} \xi_1(t) = -\frac{\breve{j}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} \left(1 + \frac{\breve{c}_M^{(1)}}{\breve{c}_1} (\Delta \breve{n}_M^{(1)})^2 \right) \xi_1(t), \tag{50}$$

$$\frac{d}{dt} \bar{M}_2^{(1)}(t) = -\frac{2\breve{j}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} \left(\bar{M}_2^{(1)}(t) - \frac{\breve{c}_M^{(1)}}{\breve{c}_1} (\Delta \breve{n}_M^{(1)})^2 \right), \tag{51}$$

$$\frac{d}{dt} \bar{M}_3^{(1)}(t) = -\frac{3\breve{j}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} \bar{M}_3^{(1)}(t), \tag{52}$$

$$\frac{d}{dt} \bar{M}_4^{(1)}(t) = -\frac{4\breve{j}_M^{(1)}}{(\Delta \breve{n}_M^{(1)})^2} (\bar{M}_4^{(1)}(t) - 3(\Delta \breve{n}_M^{(1)})^2 \bar{M}_2^{(1)}(t)). \tag{53}$$

In view of Eq. (39), Eq. (50) coincides with Eq. (41). Other Eqs. (51)–(53) for central moments are equivalent to that for the moments defined according to Eqs. (19) and (20), but are much simpler and convenient in the treatment of evolution of the potential well profile. Using the central moments allows us to exclude the effects of displacement of the well as whole in the aggregation axes. It is clearly seen, for example, from Eqs. (51) and (52) describing changing in time of the distribution dispersion and asymmetry.

VI. SOLUTION OF THE MOMENT EQUATIONS FOR LENGTHY MICELLES

We will study in this section another special case when the aggregation work (see Fig. 1) has no first minimum for short micelles at all. There are lengthy micelles only in the surfactant solution in this case.

The material balance equation for surfactant in solution in the special case considered here has the form

$$c_1(t) + \int_{\substack{\text{lengthy} \\ \text{micelles}}} n c_n(t) dn = c, \tag{54}$$

where c, as in Sec. V, is the total surfactant concentration. As well as in the Sec. IV, we neglect the small term corresponding to the interval $[\breve{n}_c^{(2)}, \breve{n}_0]$ in Fig. 1. Using Eq. (6) and taking into account that Eq. (54) is valid also in the quasi-

equilibrium state of lengthy micelles, we can rewrite Eq. (54) as

$$\xi_1(t) + \frac{1}{\check{c}_1}\int_{\substack{\text{lengthy}\\\text{micelles}}} n\check{c}_n \xi_n(t)\,dn = 0. \tag{55}$$

Recalling the definition (34) of $\Delta M_1^{(2)}$, we finally get from Eq. (55) an important relation,

$$\xi_1(t) = -\Delta M_1^{(2)}. \tag{56}$$

Let us turn to the system of coupled equations given by Eq. (36). Setting $k=0$ in Eq. (36), we have

$$\frac{d}{dt}\Delta M_0^{(2)} = 0.$$

Thus $\Delta M_0^{(2)}$ is constant in time. Because in view of Eq. (34), $\Delta M_0^{(2)}$ is referred to change in total concentration of lengthy micelles and this concentration does not change in fast relaxation, we conclude

$$\Delta M_0^{(2)}(t) = 0. \tag{57}$$

Setting $k=1,2,\ldots$ in Eq. (36) and using Eqs. (56) and (57), we can find first, second, and higher moments $\Delta M_k^{(2)}(t)$. As a result, we get

$$\frac{d}{dt}\Delta M_1^{(2)} = -\frac{\breve{j}_M^{(2)}}{\breve{n}_M^{(2)}}\left[\left(\frac{\breve{c}_M^{(2)}}{\check{c}_1}\breve{n}_M^{(2)} + \frac{1}{\Delta\breve{n}_M^{(2)}}\right)\Delta M_1^{(2)} + (\Delta M_1^{(2)})^2\right], \tag{58}$$

$$\frac{d}{dt}\Delta M_2^{(2)} = -2\frac{\breve{j}_M^{(2)}}{\breve{n}_M^{(2)}}\left[\left(\Delta M_1^{(2)} + \frac{1}{\Delta\breve{n}_M^{(2)}}\right)\Delta M_2^{(2)} \right.$$
$$\left. + \left(\frac{\breve{c}_M^{(2)}}{\check{c}_1}[(\breve{n}_M^{(2)})^2 + (\Delta\breve{n}_M^{(2)})^2] - 2\right)\Delta M_1^{(2)}\right], \tag{59}$$

the equations for higher moments are similar to Eq. (59). Equation (58) for $\Delta M_1^{(2)}$ is nonlinear, all the equations for $\Delta M_k^{(2)}$ at $k\geq 2$ turn to be inhomogeneous linear equations with variable coefficients. Because only the behavior of average aggregation number and dispersion of micelles can be observable in experiment, and these characteristics, as follows from Eqs. (58) and (59), do not depend on higher moments, we will not consider the details of the time dependence of higher moments.

The variables in the differential Eq. (58) can be easily separated. Note that there is a singular point

$$\Delta M_{1,\text{sp}}^{(2)} = -\left(\frac{\breve{c}_M^{(2)}}{\check{c}_1}\breve{n}_M^{(2)} + \frac{1}{\Delta\breve{n}_M^{(2)}}\right) \tag{60}$$

in this equation. Nevertheless, this point does not cause a problem. Indeed, the total moment $M_1^{(2)}(t) = M_1^{(2)} + \Delta M_1^{(2)}(t)$ (as well as any other full moment $M_k^{(2)}(t)$, $k=0,1,2,\ldots$) at any moment of time should be positive. In view of Eqs. (35) and (60), it means that $\Delta M_1^{(2)}(t) > -(\breve{c}_M^{(2)}/\check{c}_1)\breve{n}_M^{(2)} > \Delta M_{1,\text{sp}}^{(2)}$ at any t.

Solving Eqs. (58) and (59) yields

$$\Delta M_1^{(2)}(t) = \frac{\breve{n}_M^{(2)}\left[\dfrac{\breve{c}_M^{(2)}}{\check{c}_1} + \dfrac{1}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right]}{C_1^{(2)}\exp\left(\breve{j}_M^{(2)}\left[\dfrac{\breve{c}_M^{(2)}}{\check{c}_1} + \dfrac{1}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right]t\right) - 1}. \tag{61}$$

$$\Delta M_2^{(2)}(t) = C_2^{(2)}\left[\Delta M_1^{(2)}(t)\exp\left(\breve{j}_M^{(2)}\frac{\breve{c}_M^{(2)}}{\check{c}_1}t\right)\right]^2$$
$$+ \frac{\dfrac{\breve{c}_M^{(2)}}{\check{c}_1}[(\breve{n}_M^{(2)})^2 + (\Delta\breve{n}_M^{(2)})^2] - 2}{\dfrac{\breve{c}_M^{(2)}}{\check{c}_1}\left[\dfrac{\breve{c}_M^{(2)}}{\check{c}_1} - \dfrac{1}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right](\breve{n}_M^{(2)})^2}$$
$$\times\left(\Delta M_1^{(2)}(t) + 2\frac{\breve{c}_M^{(2)}}{\check{c}_1}\breve{n}_M^{(2)}\right)\Delta M_1^{(2)}(t), \tag{62}$$

where integration constants $C_1^{(2)}$ and $C_2^{(2)}$ can be determined with the help of initial conditions for $\Delta M_1^{(2)}(0)$ and $\Delta M_2^{(2)}(0)$. The laws of time dependence given by Eqs. (61) and (62) become pure exponential as $t\to\infty$, and the characteristic times for fast relaxation of lengthy micelles are

$$t_1^{(2)} = \left[\breve{j}_M^{(2)}\left(\frac{\breve{c}_M^{(2)}}{\check{c}_1} + \frac{1}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right)\right]^{-1}, \tag{63}$$

$$t_2^{(2)} = \left[\frac{2\breve{j}_M^{(2)}}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right]^{-1}, \quad t_2'^{(2)} = \left[2\breve{j}_M^{(2)}\left(\frac{\breve{c}_M^{(2)}}{\check{c}_1} + \frac{1}{\breve{n}_M^{(2)}\Delta\breve{n}_M^{(2)}}\right)\right]^{-1}. \tag{64}$$

Comparing these times to the characteristic times of linear theory from Ref. 8 for cylindrical micelles, we see that times $t_1^{(2)}$ and $t_2^{(2)}$ are present in both linear and nonlinear theories at $\breve{n}_M^{(2)} \approx \Delta\breve{n}_M^{(2)}$, but time $t_2'^{(2)}$ appears only in the nonlinear theory. By contrast to the case of short micelles, none of moments $\Delta M_k^{(2)}(t)$ $(k=1,2,\ldots)$ can be represented as a finite sum of exponentials. Because Eqs. (61) and (62) are more complicated than Eqs. (43) and (44), passing to the central moments for lengthy micelles does not simplify the relaxation equations.

VII. SOLUTION OF THE MOMENT EQUATIONS FOR COEXISTING SHORT AND LENGTHY MICELLES

Now we are ready to study a more complex case when short and lengthy micelles coexist in the surfactant solution. As we have seen, Eqs. (22) and (36) form two independent sets of nonuniform first-order differential equations for moments $\Delta M_k^{(1)}(t)$ or $\Delta M_k^{(2)}(t)$ of the aggregate distribution function. These sets can be easily solved for any moment starting from $k=2$ if we know $\xi_1(t)$ and all previous moments $\Delta M_i^{(1)}(t)$ and $\Delta M_i^{(2)}(t)$ $(i=0,1,\ldots,k-1)$. Thus we see that it is sufficient to find $\Delta M_0^{(1)}(t)$, $\Delta M_1^{(1)}(t)$, $\Delta M_0^{(2)}(t)$, and $\Delta M_1^{(2)}(t)$.

It is evident that the material balance equation for surfactant in solution with coexisting short and lengthy micelles can be written in the form

$$c_1(t) + \int_{\substack{\text{short} \\ \text{micelles}}} nc_n(t)dn + \int_{\substack{\text{lengthy} \\ \text{micelles}}} nc_n(t)dn = c, \qquad (65)$$

where c is (as before) the total surfactant concentration. Like in the Section IV, we neglect in Eq. (65) a small term that corresponds to the interval $[\breve{n}_c^{(2)}, \breve{n}_0]$. Note that this approximation imposes additional conditions on the depths and widths of the first and the second potential wells and the heights of the first and the second potential peaks of the aggregation work at surfactant concentrations above the cmc$_2$. These conditions require that the first well should contain a considerable number of spherical micelles, while the second well should be insignificant, and the difference between the heights of the potential peaks and potential well should be at least several $k_B T$. Using Eq. (6) and taking into account that Eq. (65) is valid for the quasi-equilibrium states also, we can rewrite Eq. (65) in the following form:

$$\xi_1(t) + \frac{1}{\breve{c}_1} \int_{\substack{\text{short} \\ \text{micelles}}} n\breve{c}_n \xi_n(t)dn + \frac{1}{\breve{c}_1} \int_{\substack{\text{lengthy} \\ \text{micelles}}} n\breve{c}_n \xi_n(t)dn = 0. \qquad (66)$$

Recalling definitions (20) and (34) of $\Delta M_1^{(1)}$ and $\Delta M_1^{(2)}$, we finally get from Eq. (66)

$$\xi_1(t) = -\Delta M_1^{(1)} - \Delta M_1^{(2)}. \qquad (67)$$

Following Eqs. (22) and (36), we have the same equations and solutions for the moments $\Delta M_0^{(1)}(t)$ and $\Delta M_0^{(2)}(t)$ as in Secs. V and VI,

$$\frac{d}{dt}\Delta M_0^{(1)} = 0, \quad \frac{d}{dt}\Delta M_0^{(2)} = 0,$$

$$\Delta M_0^{(1)}(t) = 0, \quad \Delta M_0^{(2)}(t) = 0. \qquad (68)$$

Substituting $k=1$ into Eqs. (22) and (36) and using Eqs. (67) and (68) leads to two coupled equations for the moments $\Delta M_1^{(1)}(t)$ and $\Delta M_1^{(2)}(t)$,

$$\frac{d}{dt}\Delta M_1^{(1)} = -\breve{j}_M^{(1)}\left[\left(\frac{\breve{c}_M^{(1)}}{\breve{c}_1} + \frac{1}{(\Delta \breve{n}_M^{(1)})^2} \right) \Delta M_1^{(1)} + \frac{\breve{c}_M^{(1)}}{\breve{c}_1} \Delta M_1^{(2)} \right], \qquad (69)$$

$$\frac{d}{dt}\Delta M_1^{(2)} = -\frac{\breve{j}_M^{(2)}}{\breve{n}_M^{(2)}}\left[\left(\frac{\breve{c}_M^{(2)}}{\breve{c}_1}\breve{n}_M^{(2)} + \frac{1}{\Delta \breve{n}_M^{(2)}} \right) \Delta M_1^{(2)} + (\Delta M_1^{(2)})^2 \right.$$
$$\left. + \left(\frac{\breve{c}_M^{(2)}}{\breve{c}_1}\breve{n}_M^{(2)} + \Delta M_1^{(2)} \right) \Delta M_1^{(1)} \right]. \qquad (70)$$

At a first glance, it seems that Eqs. (69) and (70) can be solved analytically in the case when the number of surfactant molecules in short micelles is much less than that in lengthy micelles. It sounds like one can neglect the last term in Eq. (69) in this case. However, the numerical analysis shows that such approach may be erroneous because the total number of micelles is more important for changing monomer concentration in fast relaxation than the total number of surfactant molecules in the micelles.
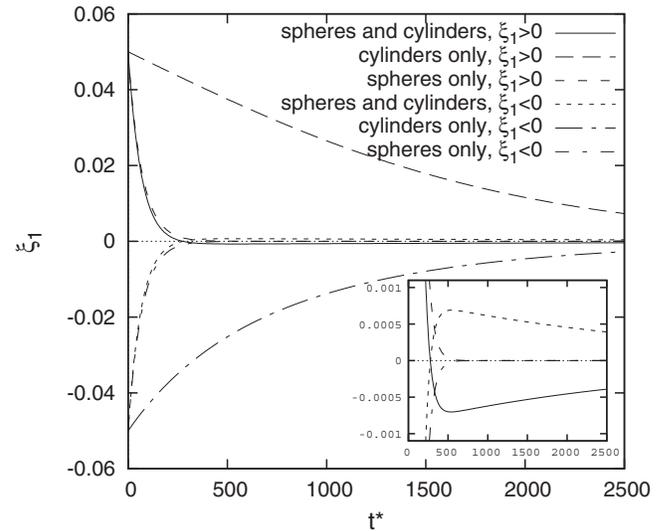

FIG. 2. Relative deviation ξ_1 of monomer concentration c_1 from its quasi-equilibrium value $\breve{c}_1$ (near cmc$_2$) as a function of dimensionless time $t^* = t\breve{j}_M^{(1)}$.

In order to demonstrate the specific roles of short and lengthy micelles in solutions above the cmc$_2$, we have solved Eqs. (69) and (70) numerically, considering short micelles as spherical and lengthy micelles as cylindrical. The results are shown in Figs. 2–7.

Although there are two rates $\breve{j}_M^{(1)}$ and $\breve{j}_M^{(2)}$ in Eqs. (69) and (70), we represent time dependences in Figs. 2–7 using only one dimensionless time $t^* = t\breve{j}_M^{(1)}$. The aggregate capture rates $\breve{j}_M^{(1)}$ (for spherical micelles) and $\breve{j}_M^{(2)}$ (for cylindrical micelles) are linked by relation

$$\breve{j}_M^{(2)} \simeq \frac{2}{3}\breve{j}_M^{(1)}\frac{\breve{n}_M^{(2)}}{\breve{n}_M^{(1)}}\frac{R_s^{(1)}}{R_{\text{cyl}}}, \qquad (71)$$
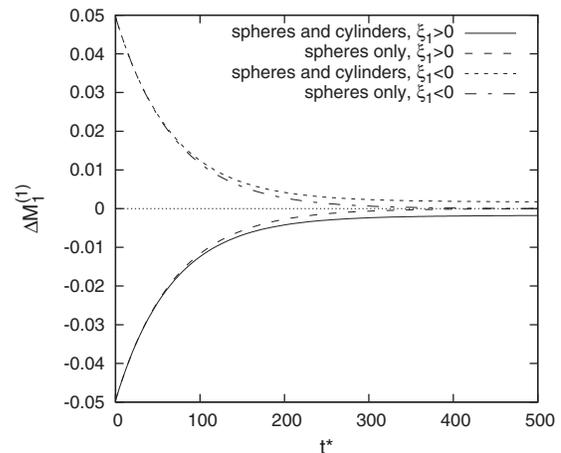

FIG. 3. Moment $\Delta M_1^{(1)}$ as a function of dimensionless time $t^* = t\breve{j}_M^{(1)}$ in the presence and absence of cylindrical micelles (near cmc$_2$).
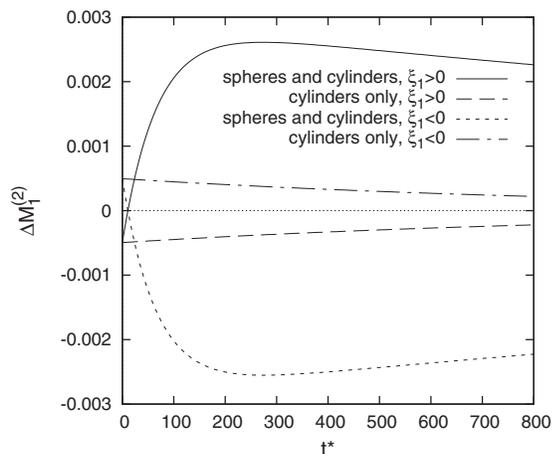
FIG. 4. Moment $\Delta M_1^{(2)}$ as a function of dimensionless time $t^*=t\breve{j}_M^{(1)}$ in the presence and absence of spherical micelles (near cmc_2).

where $R_s^{(1)}$ is the radius of spherical micelles at $n=\breve{n}_M^{(1)}$ and R_{cyl} is the radius of the micelle cylindrical body. Since the factor $(2/3)(R_s^{(1)}/R_{cyl})$ lies in the interval of 0.3–1.0, we may use a simplified relation $\breve{j}_M^{(2)}=\breve{j}_M^{(1)}(\breve{n}_M^{(2)}/\breve{n}_M^{(1)})$ in computations.

Parameters in Eqs. (69) and (70) were taken owing to the following arguments. As was shown in Ref. 10, the monomer concentration and the total concentration of spherical micelles become "frozen" above cmc_2. Indeed, they slightly change with increasing the total surfactant concentration above cmc_2 but not significantly. As a result, the corresponding change in the values of $\breve{n}_M^{(1)}$ and $\Delta\breve{n}_M^{(1)}$ should be small. One may expect that corresponding change in large values of $\breve{n}_M^{(2)}$ and $\Delta\breve{n}_M^{(2)}$ will be relatively small as well. Thus we may choose for fast relaxation near cmc_2 (when the total number of cylindrical micelles is small) and markedly above cmc_2 (when the cylindrical micelles accumulate almost all the surfactants) the next values
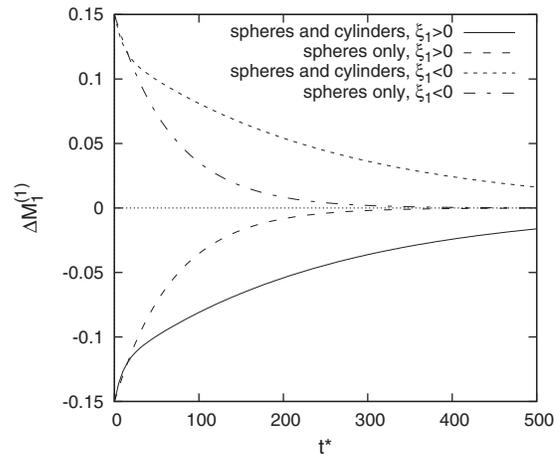

FIG. 5. Relative deviation ξ_1 of monomer concentration c_1 from its quasi-equilibrium value $\breve{c}_1$ (markedly above cmc_2) as a function of dimensionless time $t^*=t\breve{j}_M^{(1)}$.

FIG. 6. Moment $\Delta M_1^{(1)}$ as a function of dimensionless time $t^*=t\breve{j}_M^{(1)}$ in the presence and absence of cylindrical micelles (markedly above cmc_2).

$$\breve{n}_M^{(1)}=100, \quad \Delta\breve{n}_M^{(1)}=15, \quad \breve{n}_M^{(2)}=1000,$$
$$\Delta\breve{n}_M^{(2)}=850, \quad \breve{c}_M^{(1)}=0.01\breve{c}_1,$$
$$\breve{c}_M^{(2)}=0.0001\breve{c}_1 (\text{near } cmc_2),$$
$$\breve{c}_M^{(2)}=0.01\breve{c}_1 (\text{markedly above } cmc_2).$$
(72)

Indeed, this values are generally consistent with the plot on Fig. 1 because $\Delta\breve{n}_M^{(1)}/\breve{n}_M^{(1)}\ll1$ (this is compatible with the Gauss distributions of spherical micelles), $\breve{n}_M^{(2)}\approx\Delta\breve{n}_M^{(2)}$ (this is compatible with exponential size distribution of cylindrical micelles), $\breve{n}_M^{(1)}\breve{c}_M^{(1)}=\breve{c}_1$ (it means that total surfactant concentration is above cmc_1), and $\breve{c}_M^{(2)}\breve{n}_M^{(2)}=0.1$ (it means that total surfactant concentration is slightly above cmc_2).

Figure 2 illustrates the behavior of surfactant monomer concentration at total concentration near cmc_2. The corresponding curves are denoted as "spheres and cylinders." For comparison, we added here (as well as in subsequent figures) also two particular cases with $\breve{n}_M^{(1)}=0$ ("cylinders only") and with $\breve{n}_M^{(2)}=0$ ("spheres only"), other parameters were kept the same. First of all, we see that relaxation of monomer con-
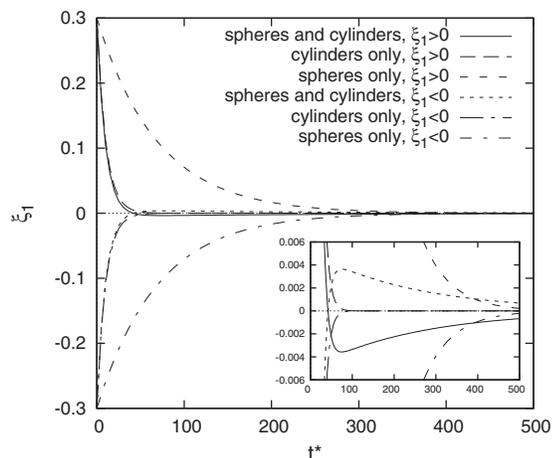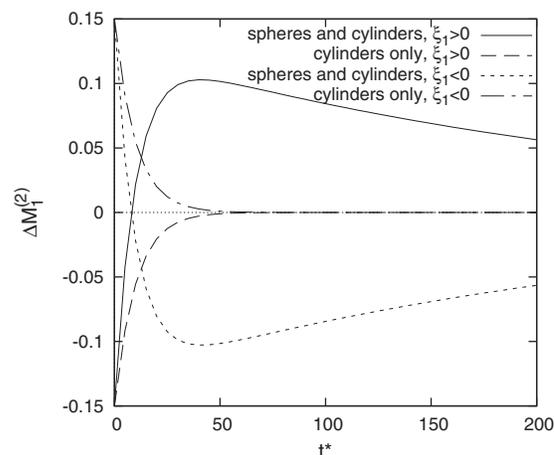

FIG. 7. Moment $\Delta M_1^{(2)}$ as a function of dimensionless time $t^*=t\breve{j}_M^{(1)}$ in the presence and absence of spherical micelles (markedly above cmc_2).

centration is monotonous when only one modification of micelles (spherical or cylindrical) is present in the solution. Note that the monomer relaxation curves for solution with cylindrical micelles depend on the sign of initial deviation while there is no such dependence for solution with spherical micelles. For solution with coexisting spherical and cylindrical micelles, the relaxation curves demonstrate nonmonotonous behavior and even change in the deviation sign.

Figures 3 and 4 allow us to compare the fast relaxation curves for the average aggregation number in spherical and cylindrical micelles at parameters corresponding to the total concentration near cmc$_2$ from Eq. (72). We see that relaxation of spherical micelles is markedly slowed down in the presence of cylindrical micelles. At the beginning of relaxation, the effect is almost invisible, but later it becomes significant. The effect of spherical micelles on relaxation of cylindrical micelles is different. At the beginning, the average aggregation number of cylindrical micelles rapidly increases in amplitude and changes its sign, but later it becomes flat descending (similar to the behavior without spherical micelles).

Figures 5–7 illustrate the influence of increasing the total surfactant concentration in solution markedly above cmc$_2$. As we can see, the general behavior of the curves is similar to the case of lower total concentration near cmc$_2$. Nevertheless the effect of cylindrical micelles on relaxation of spherical micelles becomes more pronounced due to increase in cylindrical cmc, but we still cannot neglect the backward effect of spherical micelles on cylindrical micelles. It still brings changing the sign of deviation of average aggregation number of cylindrical micelles due to a large number of spherical micelles. This fact reveals the reasons why the condition of smallness of total amount of surfactant in spherical micelles is not sufficient to neglect their effects.

VIII. CONCLUSION

As we have seen in Secs. I–VII, the proposed approach allows one to find the time dependence of any moment of the distribution function of molecular aggregates in the micellar solution on the stage of fast relaxation. This approach is based on the specific model assumptions that (i) short micelles satisfy a Gaussian length distribution, (ii) there is a narrow range of intermediate aggregates lying between short and lengthy micelles which can be neglected in comparison with the major part of lengthy micelles, (iii) lengthy micelles satisfy an exponential length distribution, and (iv) the probability of the capture of free surfactant monomers by the lengthy micelles is proportional to the aggregation number of these micelles.

Equations (22) and (39) together with formulas (43) and (44) determine the time behavior in the case of existence of short micelles only, Eqs. (36) and (56) together with formulas (61) and (62) determine the time behavior in the case of existence of lengthy micelles only, and Eqs. (22), (36), and (67)–(70) determine the time behavior of moments for coex-

isting short and lengthy micelles. These results, for the first time, take into account the influence of initial conditions at fast relaxation.

The higher-order moments of the distribution function of molecular aggregates depend on the lower-order moments but have also their own contributions. Thus there are specific times of fast relaxation for every higher-order moment. This behavior is similar to that predicted by the linear kinetic theory in Refs. 1, 2, 4, 5, 8, and 9, but the set of specific times in the nonlinear theory is richer.

It has been shown that there is a strong interplay between coexisting short and lengthy micelles even in the case when the total number of surfactant molecules aggregated in short micelles is small in comparison with that in lengthy micelles.

[1] E. A. G. Aniansson and S. N. Wall, J. Phys. Chem. **78**, 1024 (1974).
[2] S. N. Wall and E. A. G. Aniansson, J. Phys. Chem. **84**, 727 (1980).
[3] M. Almgren, E. A. G. Aniansson, and K. Holmaker, Chem. Phys. **19**, 1 (1977).
[4] M. Kahlweit, Pure Appl. Chem. **53**, 2069 (1981).
[5] M. Kahlweit and M. Teubner, Adv. Colloid Interface Sci. **13**, 1 (1980).
[6] R. Zana, in *Dynamics of Surfactant Self-Assembles, Micelles, Microemulsions, Vesicles, and Lyotrophic Phases*, Surfactant Science Series Vol. 125, edited by R. Zana (Taylor & Francis, Boca Raton, 2005), Chap 3, p. 75.
[7] G. Waton, J. Phys. Chem. B **101**, 9727 (1997).
[8] A. K. Shchekin, F. M. Kuni, A. P. Grinin, and A. I. Rusanov, Colloid J. **68**, 248 (2006).
[9] A. K. Shchekin, F. M. Kuni, A. P. Grinin, and A. I. Rusanov, Russ. J. Phys. Chem. **82**, 101 (2008).
[10] F. M. Kuni, A. K. Shchekin, A. I. Rusanov, and A. P. Grinin, Langmuir **22**, 1534 (2006).
[11] M. S. Kshevetskii, A. K. Shchekin, and F. M. Kuni, Colloid J. **70**, 455 (2008).
[12] G. Porte, Y. Poggi, J. Appell, and G. Maret, J. Phys. Chem. **88**, 5713 (1984).
[13] S. May and A. Ben-Shaul, J. Phys. Chem. B **105**, 630 (2001).
[14] M. S. Kshevetskiy and A. K. Shchekin, Colloid J. **67**, 324 (2005).
[15] R. Nagarajan and E. Ruckenstein, in *Equation of State for Fluids and Fluid Mixtures*, edited by J. V. Sengers, R. F. Kayser, and H. J. White, Jr., (Elsevier Science B.V., The Netherlands, 2000), p. 589.
[16] R. Nagarajan, in *Structure Performance Relationships in Surfactants: Second Edition, Revised and Expanded*, Surfactant Science Series Vol. 112, edited by K. Esumi and M. Ueno (Taylor & Francis, London, 2003), p. 1.
[17] A. I. Rusanov, F. M. Kuni, A. P. Grinin, and A. K. Shchekin, Colloid J. **64**, 605 (2002).
[18] A. I. Rusanov, A. P. Grinin, F. M. Kuni, and A. K. Shchekin, Russ. J. Gen. Chem. **72**, 607 (2002).
[19] A. P. Grinin, A. I. Rusanov, F. M. Kuni, and A. K. Shchekin, Colloid J. **65**, 145 (2003).
[20] M. Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden, 1939).
[21] D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth, Washington, DC, 2000).
[22] A. K. Shchekin, F. M. Kuni, A. P. Grinin, and A. I. Rusanov, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer (Wiley, New York, 2005), p. 397.
[23] F. M. Kuni, A. I. Rusanov, A. K. Shchekin, and A. P. Grinin, Russ. J. Phys. Chem. **79**, 833 (2005).