

## 17 Nonlinear Fast Relaxation of Coexisting Short and Lengthy Micelles

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**God does not care about our mathematical difficulties.  
He integrates empirically.**

**Albert Einstein**

### Abstract

A direct way of deriving an analytic solution of nonlinear kinetic equation for fast relaxation of the distribution function of molecular aggregates in aggregation number in surfactant solutions with coexisting short and lengthy micelles has been proposed. It has been shown that the kinetic equation can be reduced to a complete set of differential evolution equations for the moments of the distribution function. The equations for higher-order moments include the same and lower-order moments only. It allows one to integrate these equations and establish a total time dependence of any moment of the distribution function at the stage of fast relaxation. The separate cases when only short (usually spherical) or only lengthy (usually cylindrical) micelles are present have also been considered. The results are compared with the results of linear kinetic theory of micellar fast relaxation.

### 17.1 Introduction

Speaking on fast relaxation, we assume usually the relaxation process in surfactant solution above the critical micelle concentration (cmc) with a time scale much smaller than that for total micellar relaxation. As a result of this process, the

quasi-equilibrium distributions of subcritical premicellar aggregates and micelles as stable molecular aggregates are established separately. The quasi-equilibrium distributions refer to the local equilibrium state with the parameters varying in time relatively slow. These distributions evolve at the stage of slow relaxation to a final single equilibrium distribution.

The foundations of the theory of fast relaxation in micellar solutions were built by Aniansson, Wall [1, 2], Kahlweit [3], Kahlweit and Teubner [4]. Initially the theory was formulated for solutions with spherical micelles characterized by a narrow distribution in aggregation numbers. A generalization of this theory to the case of lengthy cylindrical micelles was proposed by Shchekin et al. [5]. Fast relaxation of coexisting spherical and cylindrical micelles was recently studied within the same framework in Ref. 6. The characteristic feature of the approaches from [1 - 6] is considering only the final stage of fast relaxation where the deviations from the quasi-equilibrium distributions are small. So one can linearize the kinetic equation for distribution function of aggregates and use for solving a corresponding linear equation the technique of separating variables with appropriate polynomials.

We present in this paper an approach which allows us to construct an analytic solution of the nonlinear kinetic equation for fast relaxation. The approach works as well as in the separate cases of existence of only short or only lengthy micelles and in the most general case of coexisting short and lengthy micelles. The central idea of the approach is that the kinetic equation for distribution function of molecular aggregates in aggregation number can be reduced to a complete set of differential evolution equations for the moments of the distribution function. Although these equations can be nonlinear too, it is possible to integrate them in an analytical form and establish the total time dependence of any moment of the distribution function at the stage of fast relaxation.

## 17.2 Kinetic Equation of Micellization and Quasi-equilibrium Distributions

Let us consider a micellar solution above the second critical micelle concentration ( $\text{cmc}_2$ ) with coexisting short and lengthy molecular aggregates of surfactant. The kinetic equation describing the evolution of the distribution function  $c_n(t)$  of molecular aggregates in aggregation number  $n$  in time  $t$  is the Becker-Döring master equation which can be written as

$$\frac{\partial c_n}{\partial t} = -\frac{\partial}{\partial n} J_n, \quad (17.1)$$

where

$$J_n = j_n^+ c_n - j_{n+1}^- c_{n+1} \quad (17.2)$$

is the flux of aggregates along the aggregation number axis between states  $n - 1$  and  $n$ . Here  $j_n^+$  is the number of surfactant monomers captured per unit of time out of the solution by the aggregate with aggregation number  $n$ ,  $j_{n+1}^-$  is the number of surfactant monomers emitted per unit of time into solution by the aggregate with aggregation number  $n + 1$ . The rate  $j_{n+1}^-$  is independent of the solution state and can be determined with the help of the rate  $\hat{j}_n^+$  at equilibrium or quasi-equilibrium state. Denoting the quantities at the quasi-equilibrium state with upper hat and recognising that the flux  $J_n$  turns to zero at this state, we have

$$j_{n+1}^- = \hat{j}^+ \frac{\hat{c}_n}{\hat{c}_{n+1}}. \quad (17.3)$$

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

$$j_n^+ = \hat{j}^+ \frac{c_1}{\hat{c}_1}. \quad (17.4)$$

Substituting Eqs. (17.3) and (17.4) into Eq. (17.2), we finally get

$$J_n = \hat{j}^+ \hat{c}_n \left( \frac{c_1 c_n}{\hat{c}_1 \hat{c}_n} - \frac{c_{n+1}}{\hat{c}_{n+1}} \right). \quad (17.5)$$

It is more convenient to go over from the distribution  $c_n(t)$  to the relative deviation  $\xi_n(t)$  of the distribution function  $c_n(t)$  from quasi-equilibrium distribution  $\hat{c}_n$

$$\xi_n = \frac{c_n - \hat{c}_n}{\hat{c}_n}, \quad c_n = \hat{c}_n(1 + \xi_n). \quad (17.6)$$

Using Eq. (17.6) in Eq. (17.5) and replacing  $\xi_{n+1} - \xi_n$  by  $\partial \xi_n / \partial n$  at  $n \gg 1$ , we get

$$J_n = \hat{j}_n^+ \hat{c}_n \left( \xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right). \quad (17.7)$$

Substituting Eq. (17.7) into Eq. (17.1) yields

$$\hat{c}_n \frac{\partial \xi_n}{\partial t} = - \frac{\partial}{\partial n} \left[ \hat{j}_n^+ \hat{c}_n \left( \xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right) \right]. \quad (17.8)$$

The non-linear term  $\xi_1 \xi_n$  on the right hand side of Eq. (17.8) was usually neglected at assumption  $\xi_n \ll 1$ ,  $\xi_1 \ll 1$  in the previous analysis of fast relaxation [1, 5, 6]. This assumption is satisfied at final stage of fast relaxation only. To describe the very early stages of fast relaxation, we need to keep this term in kinetic equation Eq. (17.8). This will be in the focus of our investigation below.

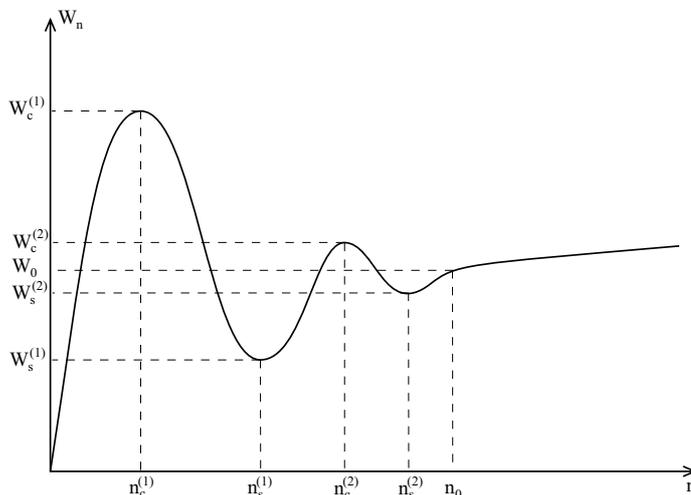


Fig. 17.1 A typical shape of the aggregation work  $W_n$  of surfactant aggregate as a function of the aggregation number  $n$  at overall surfactant concentration in solution above the  $\text{cmc}_2$ . The upper indices (1) and (2) denote the corresponding maxima and minima points. The lower indices  $s$  and  $c$  refer to stable and critical micelles respectively. The index 0 indicates the beginning of linear dependence of  $W_n$  on  $n$ .

Let us turn now to analysis of the profile of the aggregation work  $W_n$  as a function of aggregation number  $n$ . A typical plot [7, 9] of the work at surfactant concentration in solution above  $\text{cmc}_2$  is shown in Fig. 17.1. There are first and second maxima and first and second minima in the plot. The quantities corresponding to these extrema are denoted with upper indices (1) and (2). With the help of lower indices  $c$  and  $s$  we distinguish maxima and minima. The vicinity of first minimum corresponds to the range of aggregation numbers where short micelles accumulate. The lengthy micelles are located at  $n > n_c^{(2)}$ . It is known [7, 8] that the behavior of the aggregation work becomes linear starting from some aggregation number. We denote this number in Fig. 17.1 by  $n_0$ . The behavior of the aggregation work  $W_n$  with distinguished maxima and minima shown in Fig. 17.1 allows us to consider fast relaxation after initial disturbance separately for short and lengthy micelles.

### 17.3 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. 17.1. Multiplying both parts of Eq. (17.8) by  $n^k$ , where  $k = 0, 1, 2, \dots$  and integrating the result over the first potential well yields

$$\int_{\text{sh-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} dn = - \int_{\text{sh-mic}} n^k \frac{\partial}{\partial n} \left[ \widehat{j}_n^+ \widehat{c}_n \left( \xi_1 + \xi_1 \xi_n - \frac{\partial \xi_n}{\partial n} \right) \right] dn . \quad (17.9)$$

The abbreviation "sh-mic" for the words *short micelles* in the lower limits to the integrals indicates the region of integration.

Integrating the right-hand side of Eq. (17.9) by parts and using the natural conditions that  $\xi_n(t)$  tends to zero at the boundaries of the first potential well, we find

$$\begin{aligned} \int_{\text{sh-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} dn &= k \xi_1 \int_{\text{sh-mic}} n^{k-1} \widehat{j}_n^+ \widehat{c}_n (1 + \xi_n) dn + \\ &+ k \int_{\text{sh-mic}} \xi_n \frac{\partial}{\partial n} \left( n^{k-1} \widehat{j}_n^+ \widehat{c}_n \right) dn . \end{aligned} \quad (17.10)$$

We used integration by parts twice to find the second term on the right-hand side of Eq. (17.10). Thus we completely eliminate the derivatives of unknown function  $\xi_n$  with respect to  $n$  from the equation. This will facilitate our next task.

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

$$\begin{aligned} \widehat{W}_n &= \widehat{W}_s^{(1)} + \frac{1}{2} \left( \frac{n - \widehat{n}_s^{(1)}}{\Delta \widehat{n}_s^{(1)}} \right)^2 , \\ \widehat{n}_s^{(1)} - \Delta \widehat{n}_s^{(1)} &\leq n \leq \widehat{n}_s^{(1)} + \Delta \widehat{n}_s^{(1)}, \quad \Delta \widehat{n}_s^{(1)} \ll \widehat{n}_s^{(1)} . \end{aligned} \quad (17.11)$$

Here  $\widehat{n}_s^{(1)}$  is the location of the minimum in the aggregation work for short micelles (see first potential well in Fig. 17.1) at the quasiequilibrium state,

$$\widehat{W}_s^{(1)} \equiv \widehat{W}_n \Big|_{n=\widehat{n}_s^{(1)}} , \quad \Delta \widehat{n}_s^{(1)} \equiv \left( d^2 \widehat{W}_n / dn^2 \Big|_{n=\widehat{n}_s^{(1)}} \right)^{-1/2} . \quad (17.12)$$

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

$$\widehat{c}_n = \widehat{c}_s^{(1)} e^{-(\widehat{W}_n - \widehat{W}_s^{(1)})}, \quad \text{where} \quad \widehat{c}_s^{(1)} \equiv \widehat{c}_n|_{n=\widehat{n}_s^{(1)}}. \quad (17.13)$$

In view of Eqs. (17.11) and (17.13), the quasi-equilibrium distribution of short micelles in the first potential well has the form of the Gauss distribution:

$$\widehat{c}_n = \widehat{c}_s^{(1)} \exp \left[ -\frac{1}{2} \left( \frac{n - \widehat{n}_s^{(1)}}{\Delta \widehat{n}_s^{(1)}} \right)^2 \right], \quad (17.14)$$

$$\widehat{n}_s^{(1)} - \Delta \widehat{n}_s^{(1)} \leq n \leq \widehat{n}_s^{(1)} + \Delta \widehat{n}_s^{(1)}.$$

With the use of statistical definitions and Eq. (17.14), the total concentration  $\widehat{c}_M^{(1)}$  of short micelles, their average aggregation number  $\widehat{n}_M^{(1)}$  and dispersion  $\Delta \widehat{n}_M^{(1)}$  of aggregation numbers are determined at the quasi-equilibrium state as

$$\widehat{c}_M^{(1)} \equiv \int_{\text{sh-mic}} \widehat{c}_n dn, \quad (17.15)$$

$$\widehat{n}_M^{(1)} \equiv \frac{1}{\widehat{c}_M^{(1)}} \int_{\text{sh-mic}} n \widehat{c}_n dn = \widehat{n}_s^{(1)}, \quad (17.16)$$

$$\left( \Delta \widehat{n}_M^{(1)} \right)^2 \equiv \frac{1}{\widehat{c}_M^{(1)}} \int_{\text{sh-mic}} \left( n - \widehat{n}_M^{(1)} \right)^2 \widehat{c}_n dn = \left( \Delta \widehat{n}_s^{(1)} \right)^2. \quad (17.17)$$

It is clear from Eq. (17.14) and the definitions, Eqs. (17.15)–(17.17), that the location of the minimum of the aggregation work for the short micelles and the quantity  $\Delta \widehat{n}_s^{(1)}$  coincide with the average aggregation number and the aggregation number dispersion, respectively.

Taking into account Eq. (17.14) and the strong inequality  $\Delta \widehat{n}_s^{(1)} \ll \widehat{n}_s^{(1)}$ , which characterizes the narrowness of the first potential well, we can use the approximation

$$\widehat{j}_n^+ \simeq \widehat{j}_M^+ \equiv \widehat{j}_n^+ \Big|_{n=\widehat{n}_s^{(1)}}, \quad \widehat{n}_s^{(1)} - \Delta \widehat{n}_s^{(1)} \leq n \leq \widehat{n}_s^{(1)} + \Delta \widehat{n}_s^{(1)} \quad (17.18)$$

in the integrand of Eq. (17.10). Substituting Eqs. (17.14) and (17.11) into Eq. (17.10) and taking into account Eqs. (17.16)–(17.18), we get

$$\int_{\text{sh-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} dn = k \widehat{j}_M^{(1)} \left[ \xi_1 \int_{\text{sh-mic}} n^{k-1} \widehat{c}_n (1 + \xi_n) dn + \right. \\ \left. + (k-1) \int_{\text{sh-mic}} n^{k-2} \widehat{c}_n \xi_n dn - \frac{1}{\left(\Delta \widehat{n}_M^{(1)}\right)^2} \int_{\text{sh-mic}} n^{k-1} \widehat{c}_n \xi_n \left(n - \widehat{n}_M^{(1)}\right) dn \right]. \quad (17.19)$$

Let us now define

$$M_k^{(1)} \equiv \frac{1}{\widehat{c}_1} \int_{\text{sh-mic}} n^k \widehat{c}_n dn, \quad (17.20)$$

$$\Delta M_k^{(1)}(t) \equiv \frac{1}{\widehat{c}_1} \int_{\text{sh-mic}} n^k \widehat{c}_n \xi_n(t) dn. \quad (17.21)$$

It is evident that the time-independent quantities  $M_k^{(1)}$  are the moments of the quasi-equilibrium distribution  $\widehat{c}_n$  of short micelles.

According to the definitions Eqs. (17.15)–(17.17), 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

$$M_0^{(1)} = \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1}, \quad M_1^{(1)} = \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1} \widehat{n}_M^{(1)}, \quad (17.22)$$

$$M_2^{(1)} = \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1} \left[ \left(\widehat{n}_M^{(1)}\right)^2 + \left(\Delta \widehat{n}_M^{(1)}\right)^2 \right].$$

The time-dependent quantities  $\Delta M_k^{(1)}$  ( $k = 0, 1, 2, \dots$ ) describe the deviations of the moments of non-equilibrium distribution  $c_n$  from their quasi-equilibrium values  $M_k^{(1)}$ .

Substituting Eqs. (17.20) and (17.21) into Eq. (17.19), we get

$$\frac{d}{dt} \Delta M_k^{(1)} = -k \widehat{j}_M^{(1)} \left[ \frac{\Delta M_k^{(1)}}{(\Delta \widehat{n}_M^{(1)})^2} - \left( \frac{\widehat{n}_M^{(1)}}{(\Delta \widehat{n}_M^{(1)})^2} + \xi_1(t) \right) \Delta M_{k-1}^{(1)} - (k-1) \Delta M_{k-2}^{(1)} - \xi_1(t) M_{k-1}^{(1)} \right]. \quad (17.23)$$

Eqs. (17.23) at different  $k = 0, 1, 2, \dots$  form a system of linked equations which can be completed with the help of balance equation of surfactant matter in the solution.

## 17.4 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. 17.1. According to previous theoretical and experimental data [7 - 10], we assume that the transition zone from short to lengthy micelles lies in the interval  $[n_c^{(2)}, \widehat{n}_0]$  and the aggregation work  $\widehat{W}_n$  becomes linear starting from  $n = \widehat{n}_0$ . Multiplying both parts of Eq. (17.8) by  $n^k$ , where  $k = 0, 1, 2, \dots$  and integrating the result over the interval  $n > \widehat{n}_0$  (linear micelles region) yields

$$\int_{\text{lin-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} dn = - \int_{\text{lin-mic}} n^k \frac{\partial}{\partial n} \left[ \widehat{j}_n^+ \widehat{c}_n \left( \xi_1(1 + \xi_n) - \frac{\partial \xi_n}{\partial n} \right) \right] dn. \quad (17.24)$$

The abbreviation "lin-mic" for the words *linear micelles* in the lower limits to the integrals indicates the region of integration.

Similarly to the case of short micelles, we can integrate the right-hand side of Eq. (17.24) and use the boundary conditions. The condition at  $n \rightarrow \infty$  requires that  $\xi_n(t)$  tends to zero, but  $\xi_n(t)$  is nonzero at  $n = \widehat{n}_0$ . It means that an additional term remains in the equations, but we can neglect this term because other terms are much larger (the interval  $[n_c^{(2)}, \widehat{n}_0]$  is much shorter than the linear micelles region). Thus, integrating by parts twice, we can write

$$\int_{\text{lin-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} dn = k \xi_1 \int_{\text{lin-mic}} n^{k-1} \widehat{j}_n^+ \widehat{c}_n (1 + \xi_n) dn +$$

$$\begin{aligned}
& + k \int_{\text{lin-mic}} \xi_n \frac{\partial}{\partial n} \left( n^{k-1} \widehat{J}_n^+ \widehat{c}_n \right) dn . \\
& \hspace{15em} (17.25)
\end{aligned}$$

The linearity of the aggregation work  $\widehat{W}_n$  as a function of aggregation number at  $n > \widehat{n}_0$  can be expressed as

$$\widehat{W}_n = \widehat{W}_{\widehat{n}_0} + \frac{n - \widehat{n}_0}{\Delta \widehat{n}_l} , \quad n \geq \widehat{n}_0 , \quad (17.26)$$

where the notations

$$\widehat{W}_{\widehat{n}_0} \equiv \widehat{W}_n \Big|_{n=\widehat{n}_0} , \quad \Delta \widehat{n}_l \equiv \left( d\widehat{W}_n / dn \Big|_{n=\widehat{n}_0} \right)^{-1} \quad (17.27)$$

have been introduced. The physical meaning of the quantity  $\Delta \widehat{n}_l$  we will clarify below.

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

$$\widehat{c}_n = \widehat{c}_{\widehat{n}_0} \exp \left\{ - \left( \widehat{W}_n - \widehat{W}_{\widehat{n}_0} \right) \right\} , \quad (17.28)$$

where  $\widehat{c}_{\widehat{n}_0} \equiv \widehat{c}_n \Big|_{n=\widehat{n}_0}$ . In view of Eqs. (17.26) and (17.28), we have a pure exponential law for the dependence of quasi-equilibrium distribution on aggregation number  $n$ :

$$\widehat{c}_n = \widehat{c}_{\widehat{n}_0} \exp \left[ - \frac{n - \widehat{n}_0}{\Delta \widehat{n}_l} \right] , \quad n > \widehat{n}_0 . \quad (17.29)$$

With use of the statistical definitions and Eq. (17.29), the total concentration  $\widehat{c}_M^{(2)}$  of lengthy micelles, their average aggregation number  $\widehat{n}_M^{(2)}$  and dispersion  $\Delta \widehat{n}_M^{(2)}$  of aggregation numbers are determined at the quasi-equilibrium state as

$$\widehat{c}_M^{(2)} \equiv \int_{\text{lin-mic}} \widehat{c}_n dn , \quad (17.30)$$

$$\widehat{n}_M^{(2)} \equiv \frac{1}{\widehat{c}_M^{(2)}} \int_{\text{lin-mic}} n \widehat{c}_n dn = \widehat{n}_0 + \Delta \widehat{n}_l , \quad (17.31)$$

$$\left(\Delta\widehat{n}_M^{(2)}\right)^2 \equiv \frac{1}{\widehat{c}_M^{(2)}} \int_{\text{lin-mic}} \left(n - \widehat{n}_M^{(2)}\right)^2 \widehat{c}_n \, dn = (\Delta\widehat{n}_l)^2. \quad (17.32)$$

As follows from Eq. (17.32), the quantity  $\Delta\widehat{n}_l$  coincides with the aggregation number dispersion. It should be noted that  $\Delta\widehat{n}_l$  may be much larger than  $\widehat{n}_0$  for the lengthy micelles.

Taking into account the definition of  $\widehat{j}_n^+$  and the linearity of micelle length in the aggregate number, we can write

$$\widehat{j}_n^+ = \widehat{j}_M^{(2)} \frac{n}{\widehat{n}_M^{(2)}}, \quad n \geq \widehat{n}_0, \quad (17.33)$$

where  $\widehat{j}_M^{(2)} = \widehat{j}_n^+ \Big|_{n=\widehat{n}_M^{(2)}}$ . Substituting Eqs. (17.29) and (17.33) into Eq. (17.25) and taking into account Eq. (17.32) yields

$$\int_{\text{lin-mic}} n^k \widehat{c}_n \frac{\partial \xi_n}{\partial t} \, dn = k \frac{\widehat{j}_M^{(2)}}{\widehat{n}_M^{(2)}} \left[ \xi_1 \int_{\text{lin-mic}} n^k \widehat{c}_n (1 + \xi_n) \, dn + \right. \\ \left. + k \int_{\text{lin-mic}} n^{k-1} \widehat{c}_n \xi_n \, dn - \frac{1}{\Delta\widehat{n}_M^{(2)}} \int_{\text{lin-mic}} n^k \widehat{c}_n \xi_n \, dn \right]. \quad (17.34)$$

Let us now define

$$M_k^{(2)} \equiv \frac{1}{\widehat{c}_1} \int_{\text{lin-mic}} n^k \widehat{c}_n \, dn, \quad (17.35)$$

$$\Delta M_k^{(2)}(t) \equiv \frac{1}{\widehat{c}_1} \int_{\text{lin-mic}} n^k \widehat{c}_n \xi_n(t) \, dn. \quad (17.36)$$

It is evident that time-independent quantities  $M_k^{(2)}$  are the moments of the quasi-equilibrium distribution  $\widehat{c}_n$  of lengthy micelles.

According to definitions Eqs. (17.30)–(17.32), we can link the moments  $M_k^{(2)}$  with the total concentration of linear micelles, their average aggregation number and their aggregation number dispersion by the relations

$$M_0^{(2)} = \frac{\widehat{c}_M^{(2)}}{\widehat{c}_1}, \quad M_1^{(2)} = \frac{\widehat{c}_M^{(2)}}{\widehat{c}_1} \widehat{n}_M^{(2)}, \quad (17.37)$$

$$M_2^{(2)} = \frac{\widehat{c}_M^{(2)}}{\widehat{c}_1} \left[ \left( \widehat{n}_M^{(2)} \right)^2 + \left( \Delta \widehat{n}_M^{(2)} \right)^2 \right].$$

The time-dependent quantities  $\Delta M_k^{(2)}$  ( $k = 0, 1, 2, \dots$ ) describe the deviations of the moments of non-equilibrium distribution  $c_n$  from their quasi-equilibrium values  $M_k^{(2)}$ .

Substituting Eqs. (17.35) and (17.36) into Eq. (17.34), we get

$$\frac{d\Delta M_k^{(2)}}{dt} = -k \frac{\widehat{J}_M^{(2)}}{\widehat{n}_M^{(2)}} \left[ \left( \frac{1}{\Delta \widehat{n}_M^{(2)}} - \xi_1(t) \right) \Delta M_k^{(2)} - k \Delta M_{k-1}^{(2)} - \xi_1(t) M_k^{(2)} \right]. \quad (17.38)$$

Equations (17.38) at different  $k = 0, 1, 2, \dots$  form a system of linked equations which can be completed with the help of the balance equation of surfactant matter in the solution.

## 17.5 Solution of the Moment Equations for the Short Micelles

We will study in this section a special case, when the aggregation work (see Fig. 17.1) has only one minimum which corresponds to the short micelles. This case realizes at overall surfactant concentrations in solution between  $\text{cmc}$  and  $\text{cmc}_2$ , when the work  $\widehat{W}_n$  of micelles formation tends to infinity at  $n > \widehat{n}_s^{(1)}$  and the lengthy micelles are not present.

As we already noticed, Eqs. (17.23) compose a system of linked equations at different  $k = 0, 1, 2, \dots$ . If we would know  $\xi_1(t)$ , the system can be easily solved step by step from lower- to higher-order moments  $\Delta M_k^{(1)}$ . Using the balance equation for surfactant, we can find  $\xi_1(t)$ . The material balance equation in the special case considered has the form

$$c_1(t) + \int_{\text{sh-mic}} n c_n(t) dn = c, \quad (17.39)$$

where  $c$  is the total surfactant concentration. Substituting  $c_n$  from Eq. (17.6) and taking into account that Eq. (17.39) is fulfilled at quasi-equilibrium state also, we can rewrite Eq. (17.39) in the following form

$$\xi_1(t) + \frac{1}{\widehat{c}_1} \int_{\text{sh-mic}} n \widehat{c}_n \xi_n(t) dn = 0. \quad (17.40)$$

Recalling the definition Eq. (17.21) of  $\Delta M_1^{(1)}$ , we finally get

$$\xi_1(t) = -\Delta M_1^{(1)}. \quad (17.41)$$

Let us now turn back to Eqs. (17.23). Setting  $k = 0$ , we have

$$\frac{d}{dt} \Delta M_0^{(1)} = 0. \quad (17.42)$$

Thus  $\Delta M_0^{(1)}$  is constant in time. Because, in view of Eq. (17.21),  $\Delta M_0^{(1)}$  is referred to change of total concentration of short micelles and this concentration does not change in fast relaxation, we conclude

$$\Delta M_0^{(1)}(t) = 0. \quad (17.43)$$

Setting  $k = 1, 2, \dots$  in Eq. (17.23) and using Eqs. (17.41) and (17.43), we can find first, second and higher moments  $\Delta M_k^{(1)}(t)$ . As a result, we get

$$\frac{d}{dt} \Delta M_1^{(1)} = -\widehat{j}_M^{(1)} \left[ \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1} + \frac{1}{(\Delta \widehat{n}_M^{(1)})^2} \right] \Delta M_1^{(1)}, \quad (17.44)$$

$$\begin{aligned} \frac{d}{dt} \Delta M_2^{(1)} = & -2\widehat{j}_M^{(1)} \left\{ \frac{\Delta M_2^{(1)}}{(\Delta \widehat{n}_M^{(1)})^2} + \right. \\ & \left. + \widehat{n}_M^{(1)} \left[ \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1} - \frac{1}{(\Delta \widehat{n}_M^{(1)})^2} \right] \Delta M_1^{(1)} + (\Delta M_1^{(1)})^2 \right\}, \end{aligned} \quad (17.45)$$

the equations for higher moments are similar to Eq. (17.45). All the equations at  $k = 2, \dots$  turn to be linear but inhomogeneous. Because we are interested mainly

in the behavior of the average aggregation number and dispersion of micelles, we will not consider the details of the time dependence of higher moments.

Solving Eqs. (17.44)–(17.45) yields

$$\Delta M_1^{(1)}(t) = C_1^{(1)} \exp \left\{ -\widehat{j}_M^{(1)} \left[ \frac{\widehat{c}_M^{(1)}}{\widehat{c}_1} + \frac{1}{(\Delta \widehat{n}_M^{(1)})^2} \right] t \right\}. \quad (17.46)$$

$$\begin{aligned} \Delta M_2^{(1)}(t) = C_2^{(1)} \exp \left( -\frac{2\widehat{j}_M^{(1)}t}{(\Delta \widehat{n}_M^{(1)})^2} \right) + \\ + 2\widehat{n}_M^{(1)} \Delta M_1^{(1)}(t) + \frac{\widehat{c}_1}{\widehat{c}_M^{(1)}} \left( \Delta M_1^{(1)}(t) \right)^2, \end{aligned} \quad (17.47)$$

where the integration constants  $C_1^{(1)}$  and  $C_2^{(1)}$  can be determined with the help of initial conditions for fast relaxation. Comparing these results with [1, 11, 12], we see the agreement of non-linear theory with the linear theory based on the Hermite polynomial expansion. The law of time dependence of concentration of monomers or average aggregation number given by Eq. (17.46) is purely exponential, and the characteristic time for fast relaxation for these characteristics of the micellar solution coincides in both theories. Contrary to the linear theory, there is an additional term in Eq. (17.47) which is quadratic in  $\Delta M_1^{(1)}(t)$ . This term provides an additional characteristic time to compare with the linear theory. As we can see,  $\Delta M_2^{(1)}(t)$  is the sum of exponentials with different arguments, thus any moment  $\Delta M_k^{(1)}(t)$ , where  $k = 1, 2, \dots$ , can be represented as a finite sum of exponentials.

## 17.6 Solution of the Moment Equations for the Lengthy Micelles

We will study in this section another special case, when the aggregation work (see Fig. 17.1) has no first minimum for short micelles at all. There are lengthy micelles only in the solution in this case.

As we already noticed, Eqs. (17.38) compose a system of linked equations at different  $k = 0, 1, 2, \dots$ . If we would know  $\xi_1(t)$ , the system can be easily solved step by step from lower- to higher-order moments  $\Delta M_k^{(2)}$ . Using the material

balance equation for surfactant, we can find  $\xi_1(t)$ . The material balance equation in the special case considered has the form

$$c_1(t) + \int_{\text{lin-mic}} n c_n(t) dn = c, \quad (17.48)$$

where  $c$  is the total surfactant concentration. Here we also neglect the small term corresponding to the interval  $[\widehat{n}_c^{(2)}, \widehat{n}_0]$  in Fig. 17.1. Substituting  $c_n$  from Eq. (17.6) and taking into account that Eq. (17.48) is fulfilled at quasi-equilibrium state also, we can rewrite Eq. (17.48) in the following form

$$\xi_1(t) + \frac{1}{\widehat{c}_1} \int_{\text{lin-mic}} n \widehat{c}_n \xi_n(t) dn = 0. \quad (17.49)$$

Recalling the definition Eq. (17.36) of  $\Delta M_1^{(1)}$ , we finally get

$$\xi_1(t) = -\Delta M_1^{(2)}. \quad (17.50)$$

Let us now turn back to Eqs. (17.38). Setting  $k = 0$ , we have

$$\frac{d}{dt} \Delta M_0^{(2)} = 0. \quad (17.51)$$

Thus  $\Delta M_0^{(2)}$  is constant in time. Because, in view of Eq. (17.36),  $\Delta M_0^{(2)}$  is referred to the change of total concentration of lengthy micelles and this concentration does not change in fast relaxation, we conclude

$$\Delta M_0^{(2)}(t) = 0. \quad (17.52)$$

Setting  $k = 1, 2, \dots$  in Eq. (17.38) and using Eqs. (17.50) and (17.52), we can find first, second and higher moments  $\Delta M_k^{(2)}(t)$ . As a result, we get

$$\frac{d}{dt} \Delta M_1^{(2)} = -\frac{\widehat{j}_M^{(2)}}{\widehat{n}_M^{(2)}} \left[ \left( \frac{\widehat{c}_M^{(2)}}{\widehat{c}_1} \widehat{n}_M^{(2)} + \frac{1}{\Delta \widehat{n}_M^{(2)}} \right) \Delta M_1^{(2)} + \left( \Delta M_1^{(2)} \right)^2 \right], \quad (17.53)$$

$$\begin{aligned} \frac{d}{dt} \Delta M_2^{(2)} = & -2 \frac{\widehat{j}_M^{(2)}}{\widehat{n}_M^{(2)}} \left[ \left( \Delta M_1^{(2)} + \frac{1}{\Delta \widehat{n}_M^{(2)}} \right) \Delta M_2^{(2)} + \right. \\ & \left. + \left( \frac{\widehat{c}_M^{(2)}}{\widehat{c}_1} \left[ \left( \widehat{n}_M^{(2)} \right)^2 + \left( \Delta \widehat{n}_M^{(2)} \right)^2 \right] - 2 \right) \Delta M_1^{(2)} \right], \end{aligned} \quad (17.54)$$

the equations for higher moments are similar to Eq. (17.54).

Equation (17.53) for  $\Delta M_1^{(2)}$  is non-linear, all the equations for  $\Delta M_k^{(2)}$  at  $k \geq 2$  turn out to be linear but inhomogeneous with variable coefficients. Because we are interested mainly in behavior of average aggregation number and dispersion of micelles, we will not consider the details of the time dependence of higher moments.

Solving Eqs. (17.53)–(17.54) yields

$$\Delta M_1^{(2)}(t) = \frac{\hat{n}_M^{(2)} \left[ \frac{\hat{c}_M^{(2)}}{\hat{c}_1} + \frac{1}{\hat{n}_M^{(2)} \Delta \hat{n}_M^{(2)}} \right]}{C_1^{(2)} \exp \left( \hat{j}_M^{(2)} \left[ \frac{\hat{c}_M^{(2)}}{\hat{c}_1} + \frac{1}{\hat{n}_M^{(2)} \Delta \hat{n}_M^{(2)}} \right] t \right) - 1}. \quad (17.55)$$

$$\begin{aligned} \Delta M_2^{(2)}(t) = & C_2^{(2)} \left[ \Delta M_1^{(2)}(t) \exp \left( \hat{j}_M^{(2)} \frac{\hat{c}_M^{(2)}}{\hat{c}_1} t \right) \right]^2 + \\ & + \frac{\frac{\hat{c}_M^{(2)}}{\hat{c}_1} \left[ \left( \hat{n}_M^{(2)} \right)^2 + \left( \Delta \hat{n}_M^{(2)} \right)^2 \right] - 2}{\frac{\hat{c}_M^{(2)}}{\hat{c}_1} \left[ \frac{\hat{c}_M^{(2)}}{\hat{c}_1} - \frac{1}{\hat{n}_M^{(2)} \Delta \hat{n}_M^{(2)}} \right] \left( \hat{n}_M^{(2)} \right)^2} \left( \Delta M_1^{(2)}(t) + 2 \frac{\hat{c}_M^{(2)}}{\hat{c}_1} \hat{n}_M^{(2)} \right) \Delta M_1^{(2)}(t), \end{aligned} \quad (17.56)$$

where the integration constants  $C_1^{(2)}$  and  $C_2^{(2)}$  can be determined with the help of the initial conditions for fast relaxation.

Let us compare Eqs. (17.55) and (17.56) with the results of the linear theory based on the Laguerre polynomial expansion [5]. The law of time dependence of concentration of monomers or average aggregation number given by Eq. (17.55) becomes purely exponential as in the linear theory at  $t \rightarrow \infty$  only. The characteristic time for fast relaxation for these characteristics of the micellar solution coincides in both theories at  $t \rightarrow \infty$ .

Contrary to the linear theory, there is an additional term in Eq. (17.56), which is quadratic in  $\Delta M_1^{(2)}(t)$ . This term provides an additional characteristic time to compare with the linear theory. Unlike the short micelles case, the expressions for  $\Delta M_1^{(2)}(t)$  and  $\Delta M_2^{(2)}(t)$  are more complicated. As a consequence, none of the moments  $\Delta M_k^{(2)}(t)$ , where  $k = 1, 2, \dots$ , can be represented as a finite sum of exponentials.

## 17.7 Solution of the Moment Equations for Coexisting Short and Lengthy Micelles

Now we are ready to study more complex case, when the short and lengthy micelles coexist. As we could see, Eqs. (17.23) and (17.38) compose two independent sets of non-uniform differential equations for moments  $\Delta M_k^{(1)}$  or  $\Delta M_k^{(2)}$  of the 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  $\Delta M_i^{(1)}$  and  $\Delta M_i^{(2)}$ , where  $i = 0, 1, \dots, k - 1$ . Let us show that it is sufficient to know  $\Delta M_0^{(1,2)}$  and  $\Delta M_1^{(1,2)}$ .

It follows from the material balance equation that

$$c_1(t) + \int_{\text{sh-mic}} n c_n(t) dn + \int_{\text{lin-mic}} n c_n(t) dn = c, \quad (17.57)$$

where  $c$  is as usually the overall surfactant concentration. Like in the previous section, we neglect here a small term that corresponds to the interval  $[\widehat{n}_c^{(2)}, \widehat{n}_0]$ . Unlike the previous section, this neglect imposes an additional condition on the depths and widths of the first and the second minima of the aggregation work. Substituting  $c_n$  from Eq. (17.6) and taking into account that Eq. (17.57) is fulfilled at quasi-equilibrium states also, we can rewrite Eq. (17.57) in the following form

$$\xi_1(t) + \frac{1}{\widehat{c}_1} \int_{\text{sh-mic}} n \widehat{c}_n \xi_n(t) dn + \frac{1}{\widehat{c}_1} \int_{\text{lin-mic}} n \widehat{c}_n \xi_n(t) dn = 0. \quad (17.58)$$

Recalling the definition Eqs. (17.21) and (17.36) of  $\Delta M_1^{(1)}$  and  $\Delta M_1^{(2)}$ , we finally get

$$\xi_1(t) = -\Delta M_1^{(1)} - \Delta M_1^{(2)}. \quad (17.59)$$

Now we can solve Eqs. (17.23) and (17.38) for the zero moments. Similarly to the previous cases, we get

$$\frac{d}{dt} \Delta M_0^{(1)} = 0, \quad \frac{d}{dt} \Delta M_0^{(2)} = 0, \quad (17.60)$$

$$\Delta M_0^{(1)}(t) = 0, \quad \Delta M_0^{(2)}(t) = 0. \quad (17.61)$$

Substituting  $k = 1$  into Eqs. (17.23) and (17.38) and using Eqs. (17.59) and (17.61) yields equations for the first moments

$$\frac{d}{dt}\Delta M_1^{(1)} = -\hat{j}_M^{(1)} \left[ \left( \frac{\hat{c}_M^{(1)}}{\hat{c}_1} + \frac{1}{(\Delta\hat{n}_M^{(1)})^2} \right) \Delta M_1^{(1)} + \frac{\hat{c}_M^{(1)}}{\hat{c}_1} \Delta M_1^{(2)} \right], \quad (17.62)$$

$$\begin{aligned} \frac{d}{dt}\Delta M_1^{(2)} = & -\frac{\hat{j}_M^{(2)}}{\hat{n}_M^{(2)}} \left[ \left( \frac{\hat{c}_M^{(1)}}{\hat{c}_1} \hat{n}_M^{(2)} + \frac{1}{\Delta\hat{n}_M^{(2)}} \right) \Delta M_1^{(2)} + (\Delta M_1^{(2)})^2 + \right. \\ & \left. + \left( \frac{\hat{c}_M^{(1)}}{\hat{c}_1} \hat{n}_M^{(2)} + \Delta M_1^{(2)} \right) \Delta M_1^{(1)} \right]. \end{aligned} \quad (17.63)$$

Equations (17.62) and (17.63) form a coupled set which can be easily solved numerically. Taking into account that the effect of short micelles on lengthy micelles is rather small, we can neglect the last term in Eq. (17.63). Thus the exact solution for  $\Delta M_1^{(1)}$  and approximate solution for  $\Delta M_1^{(2)}$  can be written as

$$\Delta M_1^{(1)}(t) = C_1^{(1')} \exp \left\{ -\hat{j}_M^{(1)} \left( \frac{\hat{c}_M^{(1)}}{\hat{c}_1} + \frac{1}{(\Delta\hat{n}_M^{(1)})^2} \right) t \right\} - \quad (17.64)$$

$$- \hat{j}_M^{(1)} \frac{\hat{c}_M^{(1)}}{\hat{c}_1} \int_0^t \Delta M_1^{(2)}(t') \exp \left\{ -\hat{j}_M^{(1)} \left( \frac{\hat{c}_M^{(1)}}{\hat{c}_1} + \frac{1}{(\Delta\hat{n}_M^{(1)})^2} \right) (t-t') \right\} dt',$$

$$\Delta M_1^{(2)}(t) \approx \frac{\hat{n}_M^{(2)} \left[ \frac{\hat{c}_M^{(2)}}{\hat{c}_1} + \frac{1}{\hat{n}_M^{(2)} \Delta\hat{n}_M^{(2)}} \right]}{C_1^{(2')} \exp \left( \hat{j}_M^{(2)} \left[ \frac{\hat{c}_M^{(2)}}{\hat{c}_1} + \frac{1}{\hat{n}_M^{(2)} \Delta\hat{n}_M^{(2)}} \right] t \right) - 1}, \quad (17.65)$$

where the integration constants  $C_1^{(1')}$  and  $C_1^{(2')}$  can be determined with the help of initial conditions for fast relaxation.

Equations for higher moments can be solved analytically. As it follows from Eqs. (17.23) and (17.38),

$$\begin{aligned} \Delta M_2^{(1)}(t) = C_2^{(1')} \exp \left\{ -\frac{2\hat{j}_M^{(1)}t}{(\Delta\hat{n}_M^{(1)})^2} \right\} + 2\hat{j}_M^{(1)} \int_0^t \left[ \frac{\hat{n}_M^{(1)}\Delta M_1^{(1)}(t')}{(\Delta\hat{n}_M^{(1)})^2} + \right. \\ \left. + (M_1^{(1)} + \Delta M_1^{(1)}(t')) \xi_1(t') \right] \exp \left\{ -\frac{2\hat{j}_M^{(1)}(t-t')}{(\Delta\hat{n}_M^{(1)})^2} \right\} dt' , \end{aligned} \quad (17.66)$$

$$\begin{aligned} \Delta M_2^{(2)}(t) = C_2^{2'} \exp \left\{ -\frac{2\hat{j}_M^{(2)}}{\hat{n}_M^{(2)}} \int_0^t \left( \frac{1}{\Delta\hat{n}_M^{(2)}} - \xi_1(t') \right) dt' \right\} + \\ + \frac{2\hat{j}_M^{(2)}}{\hat{n}_M^{(2)}} \int_0^t \left( 2\Delta M_1^{(2)}(t') + M_2^{(2)} \xi_1(t') \right) \exp \left\{ -\frac{2\hat{j}_M^{(2)}}{\hat{n}_M^{(2)}} \int_{t'}^t \left( \frac{1}{\Delta\hat{n}_M^{(2)}} - \xi_1(t'') \right) dt'' \right\} dt' , \end{aligned} \quad (17.67)$$

where  $C_2^{(1')}$  and  $C_2^{2'}$  are the corresponding integration constants.

## 17.8 Conclusions

As we could see in the previous sections, the proposed approach allows one to find the complete time dependence of any moment of the distribution function of molecular aggregates in the micellar solution at the stage of fast relaxation. In this way, the approach is equivalent to deriving an analytical solution of nonlinear kinetic equation of micellization for fast relaxation. Equations (17.23) and (17.41) together with Eqs. (17.46) and (17.47) determine the time behaviour in the case of existence of short micelles only, Eqs. (17.38) and (17.50) together with Eqs. (17.55) and (17.56) determine the time behaviour in the case of existence of lengthy micelles only, and Eqs. (17.23), (17.38) and (17.59) together with Eqs. (17.64)–(17.67) determine the time behaviour of moments for coexisting short and lengthy micelles. These results 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 moment. This behaviour is similar to that predicted by the linear kinetic theory in Refs. 1-6, but the set of specific times in the nonlinear theory is richer.

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## 18 Deliquescence and Efflorescence Barriers in Heterogeneous Nucleation in Undersaturated Vapor

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Doch erscheint eine Rückerinnerung an die älteren Erfahrungen,  
die zur Festlegung der gebräuchlichen Begriffe und zur  
Aufstellung oft erwähnter empirischer Regeln geführt haben,  
notwendig, weil sie bei der heutigen Generation grossenteils in  
Vergessenheit geraten sind. Von diesen umfangreichen Arbeiten  
der früheren Zeit . . . ist in die modernen Hand- und Lehrbücher  
fast nichts übergegangen – ein Zeugnis dafür, wie gering die  
Summe vieljähriger rein empirischer Forschung gewertet wird,  
der die Einfügung in das physikalisch-chemische Gesamtbild  
mangelt.

Max Volmer (1939)

### Abstract

The well and the saddle points of the work of droplet formation on a soluble nucleus in undersaturated vapor have been analyzed in their dependence on droplet and nucleus sizes and chemical potential of vapor molecules. The direct (deliquescence) and reversal (efflorescence) activation barriers for transitions of droplets between states with partially and completely dissolved condensation nuclei have been numerically studied. It has been taken into account that the behavior of the work of droplet formation in the vicinity of its saddle point differs essentially in the cases when the vapor chemical potential is

close to its threshold value corresponding to barrierless dissolution of condensation nucleus (deliquescence threshold) and when it is noticeably below this threshold value (but far from reaching the efflorescence threshold). Coefficients of the diagonalized quadratic forms of the work of droplet formation on a soluble nucleus in undersaturated vapor in the neighborhood of the minimum and the saddle points of the work have been numerically studied. Exchange of the roles of thermodynamically stable and thermodynamically unstable variables in transitions over the deliquescence and efflorescence barriers near the deliquescence threshold and noticeably below it has been found and explained.

## 18.1 Introduction

Thermodynamics of thin liquid films plays the key role in understanding the specific features of the deliquescence stage in nucleation on soluble nuclei in supersaturated and undersaturated vapors [1 - 4]. We will rely in the present work upon the basic thermodynamic relations describing the deliquescence stage in nucleation on soluble nuclei. In particular, the conditions of chemical equilibrium of the droplet with partially dissolved nucleus and the expression for the work of droplet formation on a soluble condensation nucleus are of importance [4].

It is known [1 - 5] that there are two specific values of the vapor chemical potential in nucleation on soluble nuclei which are called the deliquescence and efflorescence thresholds. Above the deliquescence threshold, the activation barrier for formation of a droplet around a soluble condensation nucleus vanishes and heterogeneous nucleation occurs intensively with complete dissolution of the nuclei in droplets (i.e. deliquescence proceeds barrierlessly). Below the efflorescence threshold, the activation barrier for crystallization of a salt nucleus within the droplet of solution becomes so small that the nuclei form in the droplets immediately (i.e. efflorescence proceeds very fast).

At the state of internal equilibrium of the droplet with incompletely dissolved condensation nucleus, the size of the residue of the nucleus is a function of the number of condensate molecules in the droplet. The deliquescence threshold value of the vapor chemical potential coincides with a maximum in the dependence of the condensate chemical potential in the heterogeneous droplet on the number of condensate molecules in the droplet. In the case of high solubility of the matter of condensation nuclei in the liquid condensate, this maximum turns to be below the equilibrium value of the condensate chemical potential for a flat interface between liquid and vapor phases of pure condensate. Thus the deliquescence threshold value of the vapor chemical potential corresponds to negative vapor supersaturations and can be well observed in undersaturated vapor [5].

Below the deliquescence threshold, the kinetic theory of heterogeneous nucleation [6 - 8] provides a link between thermodynamics and experimental data on nucleation rates and characteristic times. The kinetic theory requires knowledge of the direct (deliquescence) and reversal (efflorescence) activation barriers for the transition of the droplet between the states with partially and completely dissolved nucleus. If we decrease the vapor chemical potential below the deliquescence threshold, the probability of overcoming the direct activation barrier stays significant only at small deviations from the threshold.

We will extend in this paper the description of the deliquescence stage of soluble nuclei in undersaturated vapor by investigation of the dependence of the deliquescence and efflorescence barriers on the vapor undersaturation. First we will study the behaviour of minima and saddle points of the work of droplet formation on soluble condensation nucleus as functions of the nucleus size and vapor chemical potential. As a next step, the values of the direct and reversal activation barriers will be numerically found. For a droplet formed around partially dissolved condensation nucleus, the analysis of coefficients of the quadratic forms of the work of the droplet formation in the vicinities of extrema of the work will be performed. This analysis will allow us to establish and explain the important new fact: exchange of roles of thermodynamically stable and thermodynamically unstable variables in transitions over the deliquescence and efflorescence barriers at values of the vapor chemical potential near the deliquescence threshold and noticeably below it but far from reaching the efflorescence threshold.

## 18.2 Two-dimensional Surface of the Work of Droplet Formation

As was shown in [4], the work  $W(\nu, \nu'_n)$  of droplet formation on a partially dissolved nucleus (determined as a function of the number  $\nu$  of molecules condensed in the droplet out of vapor, the number  $\nu'_n$  of molecules in spherical residue of condensation nucleus, and the chemical potential  $\mu^\beta$  of vapor molecules at absolute temperature  $T$ ) has the following form in the approximation of an ideal solution within the liquid film around the residue of nucleus:

$$\begin{aligned}
 W = & -\nu \left( \mu^\beta - \mu_\infty \right) + k_B T \left( \nu_n - \nu'_n \right) \left( \ln \left( \frac{x}{x_\infty} \right) - 1 \right) + 4\pi R_n'^2 \sigma^{\gamma\alpha} + \\
 & + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n'^2 \sigma^{\gamma\beta} + 4\pi R_n'^2 l K \exp \left[ -\frac{(R - R_n')}{l} \right], \tag{18.1}
 \end{aligned}$$

where  $\mu_\infty$  is the equilibrium value of the condensate chemical potential in the case of flat interface between liquid and vapor phases of pure condensate,  $k_B$  is the Boltzmann constant,  $\nu_n$  is the initial number of molecules within the soluble nucleus,  $x = (\nu_n - \nu'_n)/\nu$  is the relative bulk solute concentration (in the solution with the same chemical potentials of the solvent and solute molecules as in the thin liquid film around the residue of the nucleus),  $x_\infty$  is the solubility of the nucleus matter at equilibrium with a flat interface between solid phase of the nucleus matter and the bulk solution. Indices  $\alpha$ ,  $\beta$  and  $\gamma$  mark the quantities referred to the liquid, vapor and solid phases, correspondingly, while the double indices  $\gamma\beta$ ,  $\gamma\alpha$  and  $\alpha\beta$  mark the quantities referred to the interfaces between the solid particle and vapor, solid particle and liquid film, the film and the vapor, respectively;  $\sigma^{\gamma\beta}$ ,  $\sigma^{\gamma\alpha}$  and  $\sigma^{\alpha\beta}$  are the surface tensions referred to indicated interfaces.  $4\pi R_n^2$ ,  $4\pi R'_n{}^2$  and  $4\pi R^2$  are the areas of spherical surfaces with radii  $R_n$ ,  $R'_n$  and  $R$ . The last term in Eq. (18.1) takes into account the effect of overlapping of the liquid film surface layers at the boundaries with the vapor and the residue of the nucleus. This overlapping is responsible for existence of the disjoining pressure in the film. It is assumed in Eq. (18.1) that the structural component  $\Pi_D$  of the disjoining pressure plays the main role:  $\Pi_D = K \exp [-(R - R'_n)/l]$  [6, 9, 10] where  $K = (\sigma^{\gamma\beta} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta})/l$  and  $l$  are the parameters of the isotherm of structural component of the disjoining pressure.

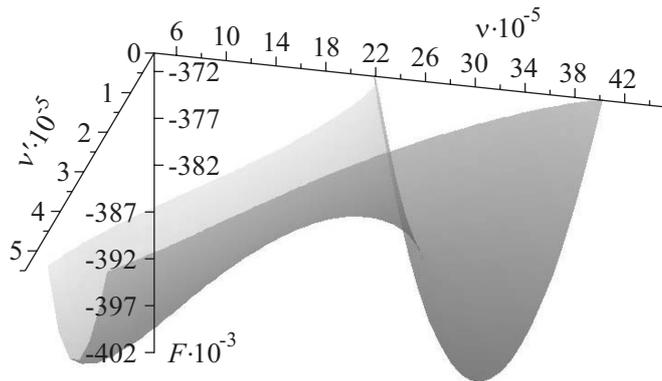


Fig. 18.1 Surface of the work  $F(\nu, \nu'_n)$  of droplet formation at the vapor chemical potential  $b = -0.2$ .

Under the assumption of nonvolatile nucleus matter and negligible adsorption of condensate and dissolved matter of nucleus at the boundaries of the liquid film in the droplet, the number  $\nu$  of condensate molecules in the droplet with partially dissolved nucleus may be related to the droplet volume  $V_R = 4\pi R^3/3$ , to the

volume of the nucleus residue  $V_{R'_n} = 4\pi R_n^3/3$ , to the numbers  $\nu_n = 4\pi R_n^3/3v_n$  and  $\nu'_n = 4\pi R_n^3/3v'_n$  of molecules in the nucleus and its residue ( $v_n$  is the specific molecular volume of the nucleus matter in solid phase) by the relation

$$\nu = [V_R - V_{R'_n} - v_n^\alpha (\nu_n - \nu'_n)] / v^\alpha, \quad (18.2)$$

where  $v^\alpha$  and  $v_n^\alpha$  are the partial molecular volumes in bulk solution for solvent and solute, respectively.

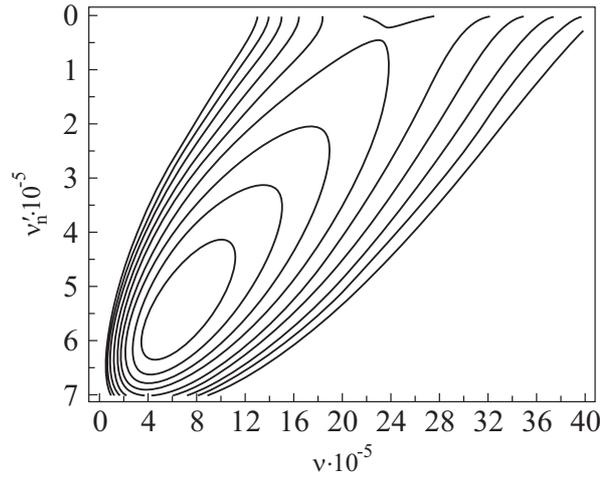


Fig. 18.2 Level lines of the work  $F(\nu, \nu'_n)$  of droplet formation at the vapor chemical potential  $b = -0.25$ .

We will deal below with the dimensionless work of droplet formation  $F \equiv W/k_B T$  and the dimensionless chemical potential of vapor  $b \equiv (\mu^\beta - \mu_\infty) / k_B T$ . The computed surface of the dimensionless work of droplet formation  $F(\nu, \nu'_n)$  is shown in Fig. 18.1 for the value  $b = -0.2$  of the vapor chemical potential. This surface of the work has been computed with Eqs. (18.1) and (18.2) and following numerical values for the parameters:

$$\begin{aligned} R_n &= 15 \cdot 10^{-7} \text{ cm}, & v_n &= 2 \cdot 10^{-23} \text{ cm}^3, \\ v^\alpha &= 3 \cdot 10^{-23} \text{ cm}^3, & v_n^\alpha &= 2.2 \cdot 10^{-23} \text{ cm}^3, \\ T &= 298 \text{ K}, & \sigma^{\alpha\gamma} &= 200 \text{ dyn/cm}, & \sigma^{\alpha\beta} &= 72 \text{ dyn/cm}, \\ x_\infty &= 0.2, & l &= 2 \cdot 10^{-7} \text{ cm}, & K &= 3 \cdot 10^9 \text{ dyn/cm}^2. \end{aligned} \quad (18.3)$$

Profile of the bottom of the surface of work  $F(\nu, \nu'_n)$  of droplet formation in Fig. 18.1 corresponds to a specific (equilibrium) path of transition of the condensing droplet between the states with partially and completely dissolved nucleus that goes through the states where the residue of the nucleus stays in equilibrium with solution in the liquid film. This path is clearly visible in Fig. 18.1 as the valley-line with minimum and maximum. The similar path has no maximum in the case of droplet formation at the value  $b = -0.25$  of the vapor chemical potential. So we used in Fig. 18.2 the lines of level to show the behaviour of the work  $F(\nu, \nu'_n)$  of droplet formation at the value  $b = -0.25$  of the vapor chemical potential. Fig. 18.1 illustrates the situation when the droplet state with completely dissolved nucleus is more stable than the droplet state with partially dissolved nucleus because the minimum of the work  $F(\nu, \nu'_n)$  at the state of complete dissolution of nucleus in droplet is deeper than the minimum at the state with partially dissolved nucleus. Fig. 18.2 illustrates the opposite case when the state with partially dissolved nucleus corresponds to deeper minimum of the work  $F(\nu, \nu'_n)$  than the state with completely dissolved nucleus.

Previously [4], within the framework of the one-dimensional kinetic approach associated with the equilibrium path of droplet transition from the state with partially dissolved nucleus to the state with completely dissolved nucleus, we did not consider heterogeneous nucleation at such notable undersaturations of vapor as in the case corresponding to the value of the vapor chemical potential  $b = -0.25$ . The one-dimensional kinetic approach is applicable in the vicinity of the deliquescence threshold. The deliquescence transition is impossible noticeably below the deliquescence threshold, but the efflorescence transition may take place if we already have a distribution of droplets with completely dissolved nuclei.

Below we will analyze the well and saddle points of the work  $F(\nu, \nu'_n)$  of heterogeneous droplet formation and their two-dimensional neighborhoods in variables  $\nu$  and  $\nu'_n$  at any concentration of undersaturated vapor, keeping in mind not only the kinetics of direct transitions with dissolution of nucleus in droplet but also the development of kinetics of reversal transitions with crystallization of nucleus in droplet of solution.

### 18.3 Well and Saddle Points of the Work of Droplet Formation at Partial Dissolution of the Nucleus

The equations for extreme points of the work  $W(\nu, \nu'_n)$  of droplet formation at partial dissolution of the nucleus serve as conditions of chemical equilibrium within the droplet with respect to the solvent and solute. These conditions lead to

the Gibbs-Kelvin-Kohler and Ostwald-Freudlich equations [4], respectively:

$$\mu^\beta - \mu_\infty = k_B T \frac{\nu_n - \nu'_n(\nu)}{\nu} - \frac{2\sigma^{\alpha\beta} v^\alpha}{R} + \frac{R_n'^2}{R^2} K v^\alpha \exp \left[ -\frac{(R - R'_n)}{l} \right], \quad (18.4)$$

$$k_B T \ln \left( \frac{\nu_n - \nu'_n(\nu)}{\nu x_\infty} \right) = \frac{2v_n}{R'_n(\nu)} \left[ \sigma^{\alpha\gamma} + lK \exp \left( -\frac{R - R'_n(\nu)}{l} \right) \right] \quad (18.5)$$

$$- \frac{2\sigma^{\alpha\beta} (v_n^\alpha - v_n)}{R} + K \exp \left( -\frac{R - R'_n(\nu)}{l} \right) \left[ v_n - \frac{R_n'^2(\nu)}{R^2} (v_n - v_n^\alpha) \right].$$

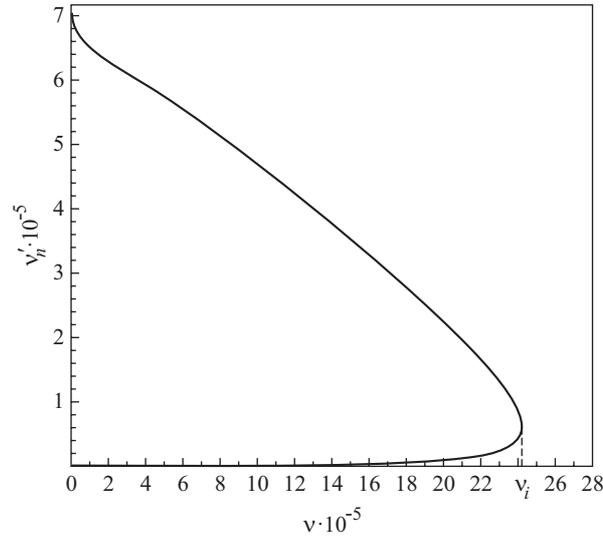


Fig. 18.3 Dependence of equilibrium values of  $\nu'_n$  on  $\nu$ .

The numerical solution of the equation Eq. (18.4) with the help of Eqs. (18.2) and (18.3) allows us to determine an equilibrium path  $\nu'_n(\nu)$  which is depicted in Fig. 18.3. We see that the path  $\nu'_n(\nu)$  has a turning point at  $\nu = \nu_i$ . The solution in a droplet cannot be in equilibrium with the residue of nucleus at  $\nu > \nu_i$ . It means that the nucleus should be completely dissolved in the droplet in equilibrium state at  $\nu > \nu_i$ . Let us notice that  $\nu_i$  depends on the initial number  $\nu_n$  of molecules in the nucleus as the external parameter of the task.

If a value of the number  $\nu$  of condensate molecules in a droplet is not arbitrary but satisfies Eq. (18.4) at a specified value of dimensionless vapor chemical potential

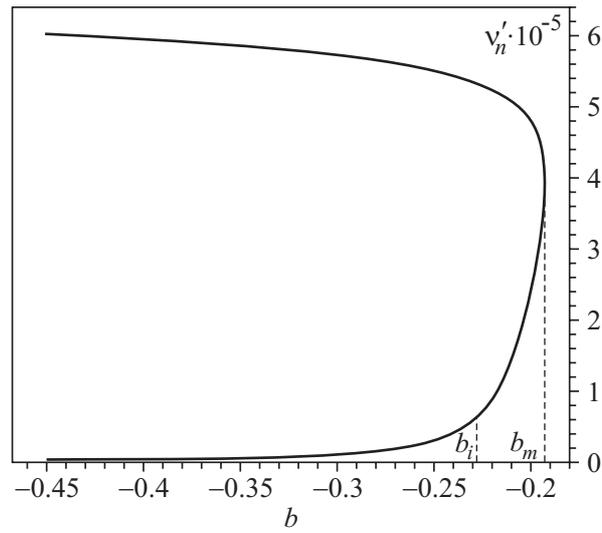


Fig. 18.4 Dependence of equilibrium values of  $\nu'_n$  on dimensionless vapor chemical potential  $b$ .

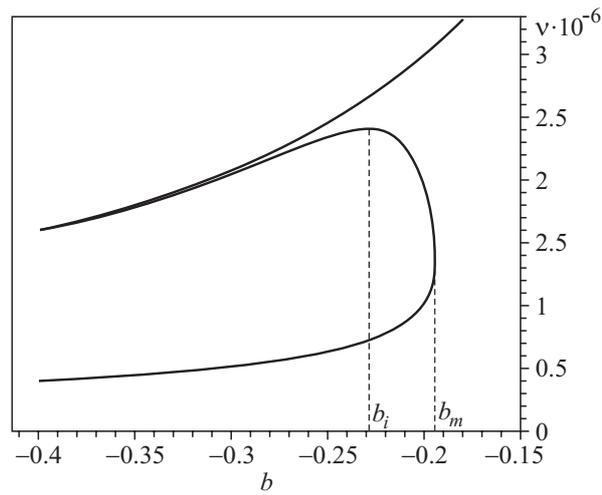


Fig. 18.5 Dependence of equilibrium values of  $\nu$  on dimensionless vapor chemical potential  $b$ .

$b$ , then the points of the path  $\nu'_n(\nu)$  in Fig. 18.3 correspond to different values of  $b$ . In particular, the point  $\nu'_n(\nu_i)$  at  $\nu = \nu_i$  corresponds to the value  $b = b_i$ . The dependences of equilibrium values of  $\nu'_n$  and  $\nu$  on  $b$ , obtained as a result of

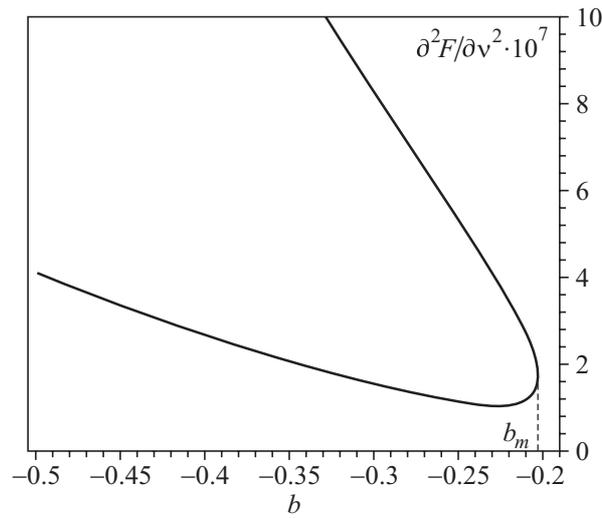


Fig. 18.6 Dependence of the second-order derivative ( $\partial^2 F / \partial \nu^2$ ) on dimensionless vapor chemical potential  $b$  for equilibrium  $\nu'_n = \nu'_n(b)$  and  $\nu = \nu(b)$ .

simultaneous numerical solution of Eqs. (18.4) and (18.5) with use of Eqs. (18.2) and (18.3), are shown in Figs. 18.4 and 18.5. The upper curve for  $\nu(b)$  in Fig. 18.5 corresponds to the droplet state with completely dissolved nucleus and the lower curve (with turning points  $b = b_i$  and  $b = b_m$ ) corresponds to the state with partially dissolved nucleus.

As can be seen from Fig. 18.4 and Fig. 18.5, there are no stable equilibrium values of  $\nu'_n$  and  $\nu$  in the state with partially dissolved nucleus at  $b > b_m$ , but there are stable values of  $\nu$  at the state of full dissolution of the nucleus. Obviously, the value  $b_m$  coincides with the deliquescence threshold value of vapor chemical potential for transition of droplet from the states with partially dissolved nucleus to states with completely dissolved nucleus.

Let us now separate the equilibrium values of  $\nu'_n(b)$  and  $\nu(b)$  in Figs. 18.4 and 18.5 with respect to minimum and saddle points of the work of droplet formation in the state at incomplete dissolved nucleus in the droplet. We will mark quantities taken at the minimum and saddle points with the lower indices  $e$  and  $c$ , respectively.

As is known, the criteria of a minimum of the work  $F(\nu, \nu'_n)$  as a function of two variables can be written as

$$\left. \frac{\partial F}{\partial \nu} \right|_{\nu_e, \nu'_n(\nu_e)} = 0, \quad \left. \frac{\partial F}{\partial \nu'_n} \right|_{\nu_e, \nu'_n(\nu_e)} = 0, \quad (18.6)$$

$$\left. \frac{\partial^2 F}{\partial \nu^2} \right|_{\nu_e, \nu'_n(\nu_e)} > 0, \quad D|_{\nu_e, \nu'_n(\nu_e)} > 0, \quad (18.7)$$

where

$$D \equiv \left( \frac{\partial^2 F}{\partial \nu^2} \right) \left( \frac{\partial^2 F}{\partial \nu'^2_n} \right) - \left( \frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)^2. \quad (18.8)$$

The corresponding criteria of a saddle point of the work  $F(\nu, \nu'_n)$  have the form

$$\left. \frac{\partial F}{\partial \nu} \right|_{\nu_c, \nu'_n(\nu_c)} = 0, \quad \left. \frac{\partial F}{\partial \nu'_n} \right|_{\nu_c, \nu'_n(\nu_c)} = 0, \quad D|_{\nu_c, \nu'_n(\nu_c)} < 0. \quad (18.9)$$

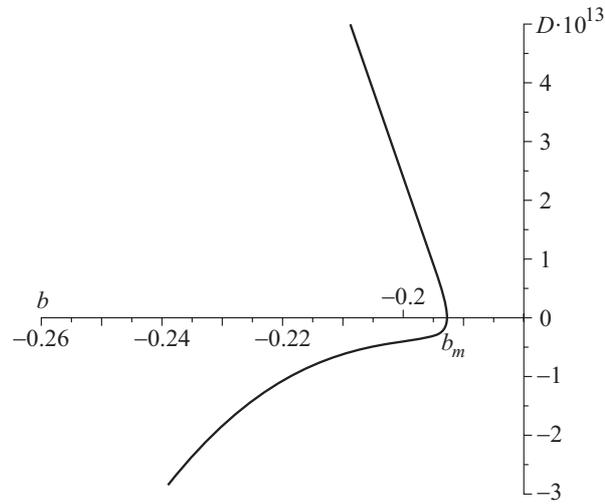


Fig. 18.7 Dependence of  $D$  on dimensionless vapor chemical potential  $b$ .

The behaviour of the quantities  $\partial^2 F / \partial \nu^2$  and  $D$  in their dependences on the vapor chemical potential is shown in Figs. 18.6 and 18.7, respectively. These quantities have been calculated for a droplet with partially dissolved nucleus of condensation with Eqs. (18.1)–(18.3) at equilibrium values of  $\nu'_n = \nu'_n(b)$  and  $\nu = \nu(b)$  (which correspond to the curves in Figs. 18.4 and 18.5) at different values of vapor chemical potential. As follows from Eqs. (18.6) and (18.9), the points  $\nu'_n = \nu'_n(b)$  and  $\nu_c = \nu(b)$  at values  $b$  for which the curve  $D$  in Fig. 18.7 lies below zero, coincide with the saddle points of the work of droplet formation. We have at this  $0 < \nu'_n(\nu_c) < \nu'_n(b_m)$  and  $\nu(b_m) < \nu_c < \nu(b_i)$ . The points  $\nu'_n = \nu'_n(b)$

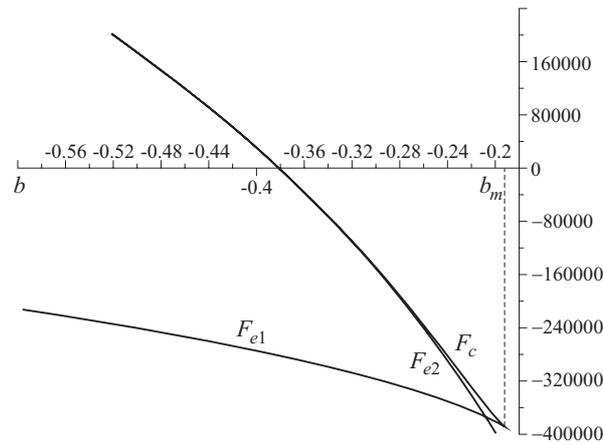


Fig. 18.8 Dependence of minima and saddle point of the work  $F$  of droplet formation on dimensionless vapor chemical potential  $b$ .

and  $\nu_e = \nu(b)$  at values  $b$  for which the curve  $D$  in Fig. 18.7 lies above zero, coincide with the minimum points of the work of droplet formation. We have at this  $\nu'_n(b_m) < \nu'_n(\nu_e) < \nu_n$  and  $0 < \nu_c < \nu(b_m)$ .

The results obtained, together with Eqs. (18.1)–(18.3), allow us to study the behaviour of the values  $F_{e1}$ ,  $F_{e2}$  of the work of droplet formation in the minima points at partial and complete dissolution of nucleus and the behavior of the value  $F_c$  of the work of droplet formation in the saddle point. The corresponding dependences of  $F_{e1}$ ,  $F_{e2}$  and  $F_c$  on the vapor chemical potential are presented in Fig. 18.8. As we can see from Fig. 18.8, the curves of  $F_{e1}$  and  $F_c$  converge at the deliquescence threshold value  $b = b_m$  of vapor chemical potential. The curves of  $F_{e1}$  and  $F_{e2}$  can intersect at some value of the chemical potential. This means that the values of direct  $\Delta F_1 \equiv F_c - F_{e1}$  and reversal  $\Delta F_2 \equiv F_c - F_{e2}$  activation barriers for transition of droplet between states with partially and completely dissolved nucleus become equal at this value.

For clarity sake, the dependences of deliquescence and efflorescence barriers on the vapor chemical potential are shown in Fig. 18.9. It should be noted that transitions between the states of the droplet with partially and completely dissolved nucleus are possible in a real situation only at  $\Delta F_{1,2} \lesssim 100$ . As follows from Fig. 18.9, the activation barrier  $\Delta F_1$  is small at those values of undersaturated vapor chemical potential, at which the activation barrier  $\Delta F_2$  is always very high, and on the contrary, the activation barrier  $\Delta F_2$  is small at those values of vapor chemical potential, at which the activation barrier  $\Delta F_1$  appears to be high. As

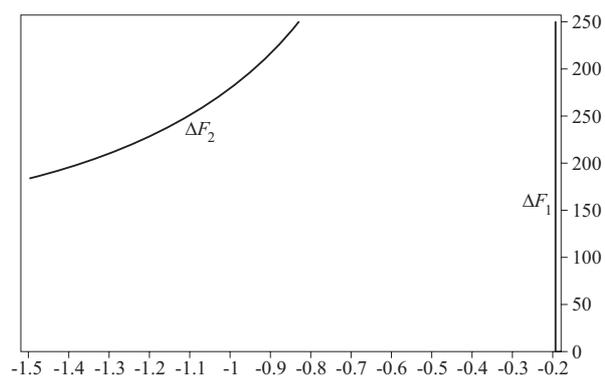


Fig. 18.9 Dependence of values of direct  $\Delta F_1$  and reversal  $\Delta F_2$  activation barriers on dimensionless vapor chemical potential  $b$ .

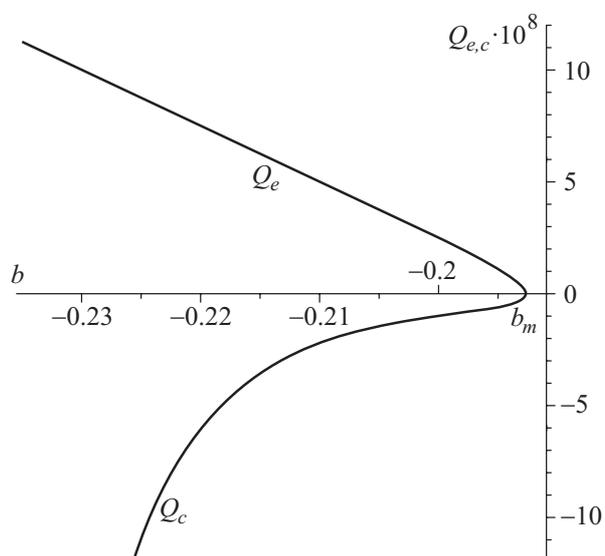


Fig. 18.10 Dependence of coefficients  $Q_e$  and  $Q_c$  on dimensionless vapor chemical potential  $b$ .

can be seen from Fig. 18.9, the range of values of the vapor chemical potential, which is of importance for deliquescence transition, lies in the very narrow vicinity of the deliquescence threshold below  $b = b_m = -0.193$ . The range of values of

the vapor chemical potential, which is of importance for efflorescence transition, lies in the vicinity of the efflorescence threshold at  $b = b_{eff} < -1.5$ .

## 18.4 Stable and Unstable Variables of the Droplet State

In order to describe the overcoming the activation barrier in kinetics of nucleation, one needs to know the behaviour of the work of droplet formation only in rather small neighborhoods of extreme points of the work. In these neighborhoods, the work  $F(\nu, \nu'_n)$  can be approximated by the quadratic form in deviations  $\nu - \nu_{e,c}$  and  $\nu'_n - \nu'_{n_{e,c}}$ :

$$F = F_{e,c} + \frac{1}{2} \left( \frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} (\nu - \nu_{e,c})^2 + \left( \frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} (\nu - \nu_{e,c})(\nu'_n - \nu'_{n_{e,c}}) + \frac{1}{2} \left( \frac{\partial^2 F}{\partial \nu'^2_n} \right)_{e,c} (\nu'_n - \nu'_{n_{e,c}})^2. \quad (18.10)$$

As was already noticed, the bottom indices e and c mark the values referring to the minimum and saddle point of the work at incomplete dissolution of the nucleus, respectively. Thus the quadratic form in Eq. (18.10) refers to both the well and saddle neighborhoods.

The quadratic form in Eq. (18.10) can be reduced to a diagonal form in new variables  $y^{(e,c)}$  and  $z^{(e,c)}$  with the help of linear transformations [11 - 13]:

$$F = F_{e,c} + Q_{e,c} \left( y^{(e,c)} \right)^2 + P_{e,c} \left( z^{(e,c)} \right)^2, \quad (18.11)$$

$$y^{(e,c)} = (\nu - \nu_{e,c}) \cos \varphi_{e,c} + (\nu'_n - \nu'_{n_{e,c}}) \sin \varphi_{e,c}, \quad (18.12)$$

$$z^{(e,c)} = -(\nu - \nu_{e,c}) \sin \varphi_{e,c} + (\nu'_n - \nu'_{n_{e,c}}) \cos \varphi_{e,c}. \quad (18.13)$$

The coefficients  $Q_{e,c}$  and  $P_{e,c}$  in Eq. (18.11) and the parameter  $\varphi_{e,c}$  of the transformations in Eqs. (18.12) and (18.13) are determined with the help of second derivatives of the work  $F(\nu, \nu'_n)$  by [7]:

$$Q_{e,c} = \frac{1}{2} \left[ \left( \frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} \cos^2 \varphi_{e,c} + \left( \frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left( \frac{\partial^2 F}{\partial \nu'^2_n} \right)_{e,c} \sin^2 \varphi_{e,c} \right],$$

$$P_{e,c} = \frac{1}{2} \left[ \left( \frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} \sin^2 \varphi_{e,c} - \left( \frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left( \frac{\partial^2 F}{\partial \nu_n'^2} \right)_{e,c} \cos^2 \varphi_{e,c} \right],$$

$$\operatorname{tg} 2\varphi_{e,c} = \frac{2 \left( \frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c}}{\left( \frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} - \left( \frac{\partial^2 F}{\partial \nu_n'^2} \right)_{e,c}}. \quad (18.14)$$

It is interesting to investigate the dependence of the coefficients  $Q_{e,c}$  and  $P_{e,c}$  on the vapor chemical potential  $b$ . The behaviour of the coefficients  $Q_{e,c}$  and  $P_{e,c}$  near the threshold value  $b = b_m$  of the vapor chemical potential is shown in Figs. 18.10 and 18.11. The curves of  $Q_e$  and  $Q_c$ , as well as curves  $P_e$  and  $P_c$ , merge at the threshold value  $b = b_m$  of the vapor chemical potential.

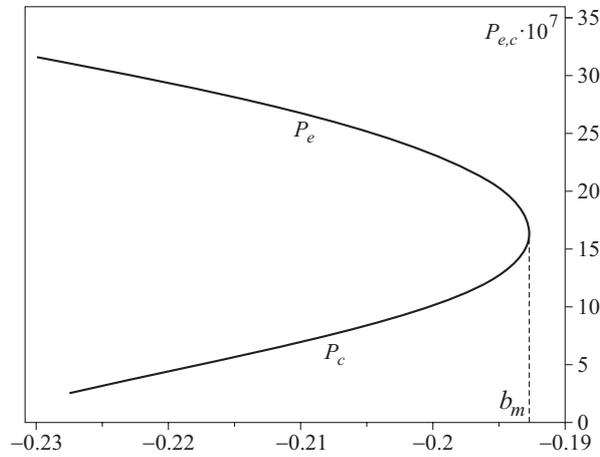


Fig. 18.11 Dependence of coefficients  $P_e$  and  $P_c$  on dimensionless vapor chemical potential  $b$ .

As follows from Fig. 18.10,  $Q_c < 0$  and  $Q_e > 0$ . As follows from Fig. 18.11,  $P_e > 0$  at any  $b \leq b_m$ , whereas  $P_c$  remains positive only at  $b_i < b \leq b_m$ . It was noticed in [11 - 13], that the positive coefficient before a squared variable in the diagonalized form in Eq. (18.11) means, that this variable is stable during phase transformation, i.e. the droplet tends to return to an equilibrium state after deviation of this variable from its equilibrium value. Negative coefficient before a squared variable in the diagonalized form in Eq. (18.11) means, that this variable is unstable during the phase transformation, i.e. the phase transformation occurs with changing this variable. Thus the variable  $y^{(e)}$  is unstable while the variable

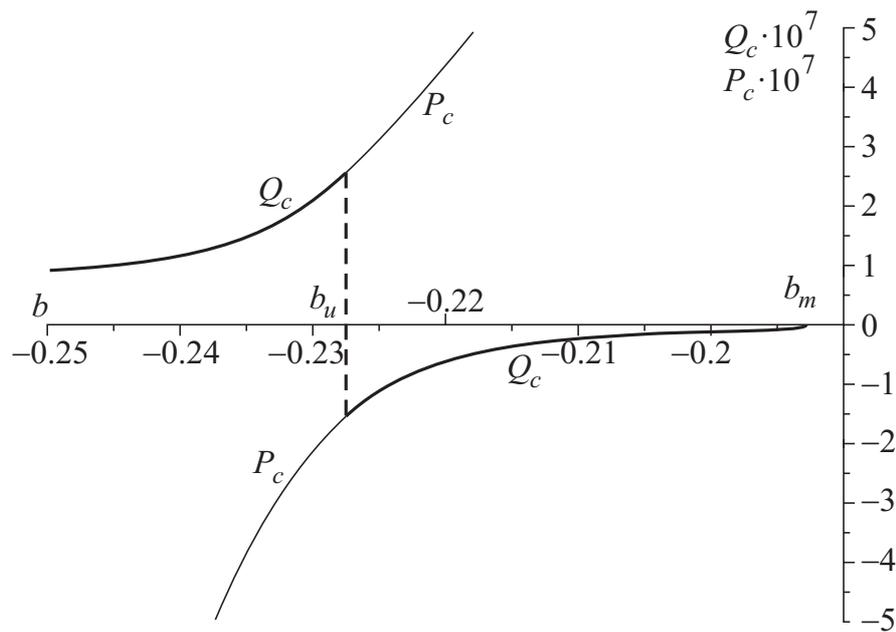


Fig. 18.12 Switching of coefficients  $Q_c$  and  $P_c$  in the neighborhood of the value  $b = b_i$ .

$z^{(c)}$  is stable in transitions over direct and reversal activation barriers slightly below the deliquescence threshold.

Let us see the behaviour of coefficients  $Q_c$  and  $P_c$  in the range of values of vapor chemical potential  $b \leq b_i$  which is noticeably below the deliquescence threshold but can be well above the efflorescence threshold. As follows from Fig. 18.12, there is a jump of coefficients  $Q_c$  and  $P_c$  at the point  $b = b_u$ ,  $b_i \lesssim b_u$ . Both coefficients change their signs with passing  $b = b_u$ , the coefficient  $Q_c$  becomes positive at  $b < b_u$  whereas it was negative at  $b > b_u$ , and the coefficient  $P_c$  becomes negative at  $b < b_u$  whereas it was positive at  $b > b_u$ . Therefore we can say that the variables  $y^{(c)}$  and  $z^{(c)}$  interchange their roles with passing  $b = b_u$ . The variable  $y^{(c)}$  becomes thermodynamically stable and the variable  $z^{(c)}$  turns to be thermodynamically unstable in transitions over the deliquescence and efflorescence activation barriers below  $b = b_u$ . This interchange of the roles of variables corresponds to switching (with decreasing the vapor chemical potential) from the heterogeneous nucleation of droplets on condensation nuclei in the vapor (with slow dissolution of the nucleus in the droplet and fast increasing the droplet size) to fast homogeneous crystallization of nuclei in the existing droplets consisted of supersaturated solution (with slow decreasing the droplet size).

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