The derivation of integration-fragmentation equations in the Becker–Döring case

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Abstract. In the present paper the interconnection between the kinetic equations of evolution of particles distinguishing by masses (number of molecules forming them) or by other property was investigated in the Becker–Döring case. From the continuum integration-fragmentation equation we derived a new equation which we call the continuum Becker–Döring equation. From this equation we obtained the Becker–Döring system of equations and the continuum equation of the Fokker–Planck type (or of the Einstein–Kolmogorov type, or of the diffuse approximation). We clarified the form of the obtained equations basing on the physical sense of these conclusions. Due to unity of the kinetic approach the present work may be useful for specialists of various specialties, who studies the evolution of structures with differing properties.

1. Introduction
In the works of L. Boltzmann [1], J. Cl. Maxwell [2] and etc. appears the distribution function by velocities and coordinates. Now there is a multi-parameter description, which is due to the fact that it becomes available for experimental observation. The problem is to write the equations on the distribution function of particles (bodies) by these many parameters.

In the present paper we continue the line of works [3], [4] and others, devoted to mathematical modeling of emerging and growth of hierarchical structures, using the kinetic approach. In [3] a model of creation of nanostructures as a result of growth of nanoparticles in a supersaturated medium with their multistage modification was proposed. The multistage modification was doing in order to give nanoparticles the desired properties. The aggregation of nanoparticles in agglomerates and integration of aggregates with each other was taken into account and it was formulated the discrete and the continuum balance equations for the number of nanoparticles and aggregates, taking into account the possibility of their growth and fragmentation. The continuum equation has been given to the evolutionary equation of the Fokker–Planck type containing frequency functions. They describe the process of self-organization of aggregates by selection of more resistant forms. Moreover, each stage of modification is characterized by its own frequency functions. They subject to independent determination. Frequency functions for all types of impacts used for the creation of nanostructures can form the basis of a methodology of their optimal synthesis.

The Becker–Döring case [5] is the model when the only one molecule attaches or separates. The formation of solids is well described by division into several stages – firstly primary particles emerge and grow, and then the stage of aggregation or the formation of agglomerates of the primary
particles as a result of their collisions with each other comes, and then the formation of aggregates of them occurs, etc. Although all stages go at the same time, but firstly the process of formation of primary particles, then their aggregation, then aggregation of the secondary agglomerates dominates. Therefore, these processes are well modeled by generalizations of the Becker–Döring case that is considered by us.

2. The derivation of the Becker–Döring system of equations and equations of Fokker–Planck type from continuum integration-fragmentation equations

In this section we derive the equation of the Fokker–Planck type [3]-[4], which is called the Einstein–Kolmogorov equation [6] in probability theory, and the Becker–Döring system of equations [5] from the continuum integration-fragmentation equations.

We’ll call a particle consisting of \( n \) molecules as \( n \)-mer. Let \( n \)-mers are defined by the distribution functions by the status parameters: spatial coordinates \( x \) and velocities (or momenta \( p \)) of center of masses, body’s mass \( mn \) (where \( m \) is the mass of one molecule or monomer), characteristics of body shape and etc.

Let consider the Becker–Döring system of equations:

\[
\frac{dN_n}{dt} = \left( \alpha_{n-1}N_{n-1} - \alpha_n N_n \right) + \left( \beta_{n+1}N_{n+1} - \beta_n N_n \right)
\text{when } n \geq 2,
\]

where \( N_n = N_n(t) \) is a number or concentration of \( n \)-mers, \( \alpha_n \) is a frequency function (section) of integration of \( n \)-mer and monomer, and \( \beta_n \) is a frequency of fragmentation \( n \)-mer to monomer and \((n-1)\)-mer. The system of equations (1a) is supplemented by the conservation law of the number of all molecules of substance, which forms crystals, in the system \( N_0 \):

\[
\sum_{i=1}^{\infty} iN_i(t) = N_0 = \text{const}.
\]

Let take now instead \( n \) some property \( x \), and let it changes not necessarily by one, but by some constant value \( c \), then the system of equations (1) can be rewritten in the form

\[
\frac{dN_x}{dt} = \left( \alpha_{x+c}N_{x+c} - \alpha_x N_x \right) + \left( \beta_{x+c}N_{x+c} - \beta_x N_x \right)
\text{при } x = 2c, 3c, \ldots,
\]

\[
\sum_{i=1}^{\infty} icN_{ic}(t) = N_0 = \text{const}.
\]

Instead of the equation (2b) we can write the following equation:

\[
\frac{dN_{2c}}{dt} = -2\left( \alpha_{2c}N_{2c}^2 - \beta_{2c}N_{2c} \right) - \sum_{i=2c}^{\infty} \left( \alpha_{n}N_{n} - \beta_{x+i}N_{x+i} \right),
\]

which is obtained by differentiation of (2b) with accordance to (2a).

Thus, we here begin to investigate more general equations than just the Becker–Döring system of equations: (2), and its generalizations are already applied for the simulation of the aggregation processes. In this very simple discrete model \( c \) is the number of molecules in the particle that attaches and fragmentize from the aggregate with the number of particles equal to \( x \).

The histograms measuring by the experimenters, as a rule, are replaced by continuous functions. So it requires using a continuous description, and we need to write a continuum equation, an approximation of which is the equation of Fokker–Planck type. From discrete distributions and the system of equations (1) we can go to the continuum model by the introduction of continuous distribution function \( \psi(x,t) \), where \( x \in (0, +\infty) \), for which it is fulfilled accordance to the discrete distribution: for example, \( \sum_{j=1}^{M} N_j = \int_{0}^{M} \psi(y,t)dy \) in the case of the system (1) and
\[
\sum_{j=1}^{\infty} N_j \psi(y, t) dy \quad \text{in the case of the system (2), where } M \in \mathbb{N} . \text{ Here } \psi(t, x) dx \text{ is the number of particles having the property } x \text{ from the interval } dx. \text{ For the sake of simplicity of our consideration, we took the right border of the continuous distribution or the maximum value of the property } x, \text{ described by a continuous distribution, equal to } +\infty. \text{ Let now } \alpha(x) \text{ and } \beta(x) \text{ are continuous analogues of } \alpha_c \text{ and } \beta_c. \text{ They are non-negative functions defined for } x > 0.
\]

Let us write the continuum integration-fragmentation equation:

\[
\frac{\partial \psi(t, x)}{\partial t} = \frac{1}{2} \sum_{y} \left[ A(x-y, y) \psi(x-y) \psi(y) - B(x-y, y) \psi(x) \right] dy - \int_{0}^{\infty} \left[ A(x, y) \psi(x) \psi(y) - B(x, y) \psi(x+y) \right] dy.
\]

We’ll search the function \( A(x, y) \) in the form: \( A(x, y) = \alpha(x) \cdot C(y) + \alpha(y) \cdot C(x) \), where \( C(y) \) we’ll find after substitution from the physical meaning of the Becker–Döring system of equations and equation of the Fokker–Planck type, that we obtain from following equation, which is the equivalent form of (4):

\[
\frac{\partial \psi(t, x)}{\partial t} = \frac{\nu^2}{2} \sum_{y} \left[ A(x-y, y) \psi(x-y) \psi(y) - B(x-y, y) \psi(x) \right] dy - \int_{0}^{\infty} \left[ A(x, y) \psi(x) \psi(y) - B(x, y) \psi(x+y) \right] dy,
\]

The terms with \( B \) in (5) are differed from terms with \( A \), and therefore we need the substitution for \( B \) that corrects it, at least because in the equation of the Fokker–Planck type terms with \( \alpha \) and \( \beta \) are the same with accuracy up to signs and multiplicative multipliers: for example, \( N_c, N_c^2 \) (see below).

So, let us consider the substitution

\[
A(x, y) = \alpha(x) \cdot C(y) + \alpha(y) \cdot C(x), \quad \text{supp}(C(y)) = [0, c],
\]

\[
B(x, y) = \beta(x+y) \cdot (D(y) + D(x)), \quad \text{supp}(D(y)) = [0, d].
\]

Here in the condition of the equality \( A(x, y) \) to zero if \( y \not\in [0, c] \) and the equality \( B(x, y) \) to zero when \( y \not\in [0, d] \) we laid that only particles with non-negative property \( y \), not exceeding \( c \) and \( d \), respectively attach to and fragmentizes from the body with property \( x \).

Let us make the substitution (6) in the equation (5), which is considered for \( x \in (x_0, +\infty) \), where \( x_0 \) cannot be less than twice the value of the property attaching or fragmentizing particle, i.e. less than \( \max(c, d) \). Then

\[
\frac{\partial \psi(t, x)}{\partial t} = \int_{0}^{c} \alpha(x-y) \psi(x-y) \psi(y) C(y) dy - \int_{0}^{d} \beta(x+y) \psi(x+y) D(y) dy - \int_{0}^{c} \alpha(x) \psi(x) C(y) dy + \int_{0}^{d} \beta(x+y) \psi(x+y) D(y) dy =
\]
\[
\frac{\partial \psi(t,x)}{\partial t} = \int_0^c \left[ \alpha(x-y)\psi(x-y) - \alpha(x)\psi(x) \right] \psi(y) C(y) dy + \\
+ \int_0^d \left[ \beta(x+y)\psi(x+y) - \beta(x)\psi(x) \right] D(y) dy.
\]

We supplement the equation (7a) by the continuum conservation law of the number of all molecules in the system

\[
\int_0^\infty y \psi(y) dy = N_0 = \text{const},
\]

which is a consequence of equation (5).

The following simple lemma is valid.

**Lemma 1.** Let \( c = d \), \( C(c) = 1 \), \( D(0) = 0 \), \( D(c) = 1 \). Then the substitution of the sum of \( \delta \)-functions: \( \psi(x,t) = \sum_{i=1}^{\infty} N_i (t) \delta(x-ic) \), in (7) under the condition \( \alpha(x) = \alpha_x \) and \( \beta(x) = \beta_x \) for \( x = c, 2c, 3c, \ldots \) gives (2).

**The proof.** If after substituting for each \( x = 2c, 3c, 4c, \ldots \) we integrate the two parts of equation (7a) on the interval that contains only one \( x \), which is a multiple of \( c \), we obtain (2) for \( x = 2c, 3c, 4c, \ldots \). The lemma is proved.

**Definition.** We'll name the equation (7) as the continuous the Becker–Döring equation.

So, here we have confined ourselves by the consideration of the unclosed equation (7), but we have obtained from it the Becker–Döring system of equations in Lemma 1, and we shall get a closed equation of the Fokker–Planck type.

According to (7)

\[
\frac{\partial \psi(t,x)}{\partial t} = \int_0^c \left[ \alpha(x-y)\psi(x-y) - \alpha(x)\psi(x) \right] \psi(y) C(y) dy + \\
+ \int_0^d \left[ \beta(x+y)\psi(x+y) - \beta(x)\psi(x) \right] D(y) dy \approx \\
\approx \int_0^c \left[ \alpha(x) - \frac{d\alpha(x)}{dx} y \left( \frac{\partial \psi(x)}{\partial x} y + \frac{1}{2} \frac{d^2 \psi(x)}{dx^2} y^2 \right) \right] \psi(y) C(y) dy - \\
- \int_0^c \left[ \frac{d\alpha(x)}{dx} y + \frac{1}{2} \frac{d^2 \alpha(x)}{dx^2} y^2 \right] \psi(x) \psi(y) C(y) dy + \\
+ \int_0^d \left[ \beta(x) + \frac{d\beta(x)}{dx} y \left( \frac{\partial \psi(x)}{\partial x} y + \frac{1}{2} \frac{d^2 \psi(x)}{dx^2} y^2 \right) \right] D(y) dy + \\
+ \int_0^d \left[ \frac{d\beta(x)}{dx} y + \frac{1}{2} \frac{d^2 \beta(x)}{dx^2} y^2 \right] \psi(x) \psi(y) D(y) dy \approx \\
\approx - \frac{\partial (\alpha(x)\psi(x))}{\partial x} \int_0^c y \psi(y) C(y) dy + \frac{1}{2} \frac{\partial^2 (\alpha(x)\psi(x))}{\partial x^2} \int_0^c y^2 \psi(y) C(y) dy + \\
+ \frac{\partial (\beta(x)\psi(x))}{\partial x} \int_0^d y D(y) dy + \frac{1}{2} \frac{\partial^2 (\beta(x)\psi(x))}{\partial x^2} \int_0^d y^2 D(y) dy.
\]

We assume that
\[
\int_0^y y \psi(y) C(y) dy = \left\langle c \right\rangle N_{x \in [0,c]}, \quad \int_0^y y^2 \psi(y) C(y) dy = \left\langle c^2 \right\rangle N_{x \in [0,c]},
\]
\[
\int_0^d y D(y) dy = \left\langle d \right\rangle \int_0^d D(y) dy, \quad \int_0^d y^2 D(y) dy = \left\langle d^2 \right\rangle \int_0^d D(y) dy,
\]
where \( N_{x \in [0,c]} \equiv \int_0^y \psi(y) C(y) dy \), if \( y = n \left\langle c \right\rangle \) and \( \left\langle c^2 \right\rangle \) are the average number and the average of the square of the number of molecules in an attaching particle, molecules in which is not more than \( c \), \( \left\langle d \right\rangle \) and \( \left\langle d^2 \right\rangle \) are the average number and the average of the square of the number of molecules in a fragmentizing particle, molecules in which is not more than \( d \). Let \( \int_0^d C(y) dy = \int_0^d D(y) dy = 1 \). The equalities (8), (9) is valid, if \( C(y) \) is the density of the conditional probability that an attaching to an aggregate particle has property equal to \( y \), \( D(y) \) is the density of the probability that an fragmentizing particle has property equal to \( y \). The equation of the Fokker–Planck type takes the form:
\[
\frac{\partial \psi}{\partial t} = - \frac{\partial}{\partial x} \left( \left( \alpha \left\langle c \right\rangle N_{x \in [0,c]} - \beta \left\langle d \right\rangle \right) \psi \right) + \frac{\partial^2}{\partial x^2} \left( \left( \alpha \left\langle c^2 \right\rangle N_{x \in [0,c]} + \beta \left\langle d^2 \right\rangle \right) \psi \right).
\]
(10)

So, from the equation (5) we obtained the equation of the Fokker–Planck type (10) by substitution (6), (8), (9). But this model is not closed, therefore we consider more simple: let us take \( c = d \), \( \left\langle c \right\rangle = 1 \), \( D(x) = \delta(x-c) \), and instead \( \psi \) we substitute \( N_c(t) \delta(x-c) + \psi(x,t) \), where \( \text{supp} \psi(x) = [2c, +\infty) \), \( N_{2c}(t) \equiv \psi(2c,t) \). Then we obtain the equation of the Fokker–Planck type on an unknown function \( \psi = \psi(x,t) \), which has the form:
\[
\frac{\partial \psi}{\partial t} = - \frac{\partial}{\partial x} \left( \left( \alpha \left\langle N_c \right\rangle - \beta \left\langle N_{2c} \right\rangle \right) \psi \right) \left( \alpha \left\langle N_c \right\rangle + \beta \left\langle N_{2c} \right\rangle \right) \psi - \frac{\partial}{\partial x} \left( \left( \alpha \left\langle N_c \right\rangle + \beta \left\langle N_{2c} \right\rangle \right) \psi \right).
\]
(11)

where \( J[N_c(t), \psi(x,t)] \) is the stream of formation of clusters with the property \( x \) at time moment \( t \): \( J[N_c(t), \psi(x,t)] \equiv \left( \left( \alpha \left\langle N_c \right\rangle - \beta \left\langle N_{2c} \right\rangle \right) \psi \right) \left( \alpha \left\langle N_c \right\rangle + \beta \left\langle N_{2c} \right\rangle \right) \psi - \frac{\partial}{\partial x} \left( \left( \alpha \left\langle N_c \right\rangle + \beta \left\langle N_{2c} \right\rangle \right) \psi \right)
\]
(12)

From (11), (12) we obtain analogue of (3):
\[
\frac{d N_c}{dt} = - \int_{2c}^{+\infty} \frac{\partial}{\partial x} J[N_c(t), \psi(x,t)] dx,
\]
where \( N_{2c}(t) \equiv \psi(2c,t) \), if the boundary conditions for (12) have the form:
\[
J[N_c(t), \psi(x,t)] \bigg|_{x=2c} \equiv \left( \left( c \left( \alpha \left\langle N_c \right\rangle - \beta \left\langle N_{2c} \right\rangle \right) \psi - \frac{\partial}{\partial x} \left( \left( \alpha \left\langle N_c \right\rangle + \beta \left\langle N_{2c} \right\rangle \right) \psi \right) \right) \bigg|_{x=2c} = \alpha N_c^2 - \beta N_{2c},
\]
\[ J\left[ N_c(t), \psi(x,t) \right] = \left( c(\alpha N_c - \beta) \psi - c^2 \frac{\partial}{\partial x} \left( (\alpha N_c + \beta) \psi \right) \right)_{x \to \pm \infty} = 0. \]

Now, when we introduce the physical and mathematical sense of quantities \( C(y) \) and \( D(y) \), it is of interest the following proposition, which is worth to compare with Lemma 1.

**Lemma 2.** Let \( c = d \), \( C(x) = \delta(x-c) \), \( D(x) = \delta(x-c) \). Then (7) gives the equation

\[ \frac{\partial \psi(t,x)}{\partial t} = \left[ \alpha(x-c)\psi(x-c) - \alpha(x)\psi(x) \right] \psi(c) + \left[ \beta(x+c)\psi(x+c) - \beta(x)\psi(x) \right] \]

for \( x > c \), which is another form of (2a).

Considering a Taylor series up to second order for the increments of the functions in this equation, and assuming \( \psi(c) = N_c \), we get the equation of the Fokker–Planck type (11). We have taken in (11) \( x \geq 2c \) (instead of \( x > c \)) in order to correctly set the boundary conditions.

3. Conclusion

We wrote a new simple discrete model of the balance of the number of particles, which is some generalization of the Becker–Döring system of equations, and derived it and the continuum the Fokker–Planck equation, corresponding to it, from a continuum equation of integration-fragmentation. These models take into account the possibility of integration and fragmentation of bodies in the case when the agglomerate of particles attaches only aggregates of particles of the previous generation, and the integration of the bodies of one generation is not considered. This situation is described by some generalizations of the Becker–Döring case. Meanwhile we obtained the new continuum Becker–Döring equation (8), the approximation of which is the equation of the Fokker–Planck type. (8) is a unclosed model, but its development seems to be important, because the experimenters obtain histograms approximated by continuum functions, and the diffuse approximation of this equation, which we got clarified on the basis of the physical meaning of this derivation (on the basis of the physico-mathematical sense of functions \( C(y) \) and \( D(y) \)) and which is often used [3]–[4].

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