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Abstract

Different distribution functions and their moments used in the Theory of coagulation are summarized and analysed. Relations between the moments of these distribution functions are derived and the physical meaning of individual moments is briefly discussed. The time evolution of the moment of order zero (total number concentration) during the coagulation process is analysed for the general kernel of the Smoluchowski equation. On this basis the time evolution of certain physically important quantities related to this moment such as mean particle size, surface and volume as well as surface concentration is described. Equations for the half time of coagulation for the general collision frequency factor are derived.

Verteilungsfunktionen und Momente in der Theorie der Koagulation

Zusammenfassung

Verschiedene Verteilungsfunktionen und ihre Momente, die in der Theorie der Koagulation Anwendung finden, werden zusammengefaßt und analysiert. Die Beziehungen zwischen den Momenten dieser Verteilungsfunktionen werden abgeleitet, und die physikalische Bedeutung von individuellen Momenten wird kurz diskutiert. Die zeitliche Veränderung des Momentes der Ordnung Null (gesamte Anzahlkonzentration) während des Koagulationprozesses wird analysiert für den allgemeinen Kern der Smoluchowski-Gleichung. Auf dieser Grundlage wird die zeitliche Entwicklung bestimmter physikalisch bedeutsamer Größen beschrieben, die in einer Beziehung zu diesem Moment stehen, wie z. B. mittlere Partikelgröße, Oberfläche und Volumen sowie Oberflächenkonzentration. Die Gleichungen für die Halbzeit der Koagulation im Falle des allgemeinen Koagulationkerns werden abgeleitet.

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1. INTRODUCTION

A large number of distribution functions is used at present in the theoretical physics of disperse systems and specifically in the theory of coagulation. These functions have different variables, they may have a dimension or they can be dimensionless. Moreover these functions can be normalized in a different way. The basic kinetic equation describing the coagulation process - Smoluchowski equation - describes the time evolution of the certain, specified distribution function. Consequently the type and character of the distribution function determines the form of the Smoluchowski equation. This form in turn is very important from the mathematical point of view as this equation is complicated non-linear, integro-differential equation. Moreover each of these distribution functions can be - with a certain precision - characterized by a set of its moments. Some of these moments have a physical meaning and can be applied for a simplified description of the investigated process in this case of the process of coagulation. As there is a number of these distribution functions and sets of their moments to find out the interrelations and transformations between these quantities is sometimes not very easy. Consequently one of the aims of our investigation is an attempt to organize and clarify the situation in this field especially from the point of the theory of dimension, theory of similarity and stressing the physical significance of the discussed quantities.

2. DISTRIBUTION FUNCTIONS AND MOMENTS

The basic significance in the theory of disperse systems and specifically in the theory of coagulation has the number-volume distribution function n(v, t) where v is the particle volume, t the time and the quantity n (v, t)dv gives the number of particles in unit volume of the system with volumes in the interval v, v + dv. From this definition it follows that the unit and simultaneously the dimension of this quantity is dim n (v, t) = $1/m^6$. In terms of this function the Smoluchowski equation has the most simple form given by

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta(v-u,u)\, n(v-u,t)\, n(u,t)\, du - n(v,t)\int_0^\infty \beta(v,u)\, n(u,t)\, du \qquad (1)$$

where u is the variable particle volume and β (v, u) collision frequency factor or coagulation constant. The function β (v, u) is the kernel of equation (1) and on dimensional grounds from (1) it follows dim β (v, u) = m^3/s. The moments of the function n (v, t) are defined by

$$M_k(t) = \int_o^\infty v^k n(v,t)\,dv \tag{2}$$

where k is a real number. On dimensional grounds from (2) it follows dim $M_k(t)$ = $m^{3(k-1)}$. Important special cases of (2) are

$$M_o(t) = \int_o^\infty n(v,t)\,dv = N(t) \tag{3}$$

where N (t) is the total number concentration and dim $M_0(t)$ = dim N (t) = $1/m^3$. For the next moment M_1 from equation (1) it follows

$$M_1 = \int_o^\infty v\,n(v,t)\,dv = \Phi = const \tag{4}$$

so that the first moment is time independent. From the physical point of view this quantity represents the volume concentration of the system and as follows from (4) dim M_1 = dim Φ = 1. There are others integer as well as non-integer moments M_k but let us limit to these two.

Next important is the normalised number-volume distribution function f (v, t) defined by

$$f(v,t) = \frac{1}{N(t)}\,n(v,t) \tag{5}$$

From this definition it follows dim f (r, t) = $1/m^3$.

Moments of this function are given by

$$F_k(t) = \int_o^\infty v^k f(v,t)\,dv \tag{6}$$

Again on dimensional grounds from (6) it follows dim $F_k(t)$ = m^{3k}.

Applying (5) from (6) we obtain

$$F_k(t) = \frac{1}{M_o(t)}\,M_k(t) \tag{7}$$

As special cases of (7) we have $F_0 = 1$ and

$$F_1(t) = \frac{1}{M_o(t)} M_1 = \frac{\Phi}{N(t)} = \bar{v}(t) \tag{8}$$

where $\bar{v}$ (t) is the mean volume of particles in time t. This moment is important not only because of its physical significance but also because its zero-time value is frequently used for construction of distribution functions with dimensionless variables. From (8) it follows

$$\bar{v}_o = \bar{v}(t=0) = \frac{\Phi}{N(t=0)} = \frac{\Phi}{N_o} = F_1(t=0) \tag{9}$$

where, of course, N (t = 0) = N_0 is the initial total number concentration.

Next important is the normalized volume distribution function given by

$$j(v,t) = \frac{1}{\Phi} v \,.\, n(v,t) \tag{10}$$

From this definition it follows dim j(v, t) = $1/m^3$.

Moments of this function are

$$J_k(t) = \int_o^\infty v^k j(v,t)\, dv \tag{11}$$

so that dim J_k (t) = m^{3k}.

Applying (10) from (11) it follows

$$J_k(t) = \frac{1}{M_1} M_{k+1}(t) \tag{12}$$

with special cases $J_0 = 1$ and $J_1 = M_2/M_1$, so that dim $J_1 = m^3$.

All these distributions n (v, t), f (v, t) and j (v, t) have the same variables. However very important are distributions with different variables first of all number size distribution function n (r, t) where r is the particle radius. As n (v, t) dv = n (r, t) dr and $v = 4\pi r^3/3$ we have

$$n(r,t) = 4\,\pi\, r^2 n(v,t) \tag{13}$$

From (13) it follows dim n(r, t) = $1/m^4$. The moments of this function are

$$Q_k(t) = \int_o^\infty r^k n(r,t)\, dr \tag{14}$$

so that dim Q_k (t) = m^{k-3}. Applying (13) from (14) it follows

$$Q_{3k}(t) = \left(\frac{3}{4\pi}\right)^k M_k(t) \tag{15}$$

As special cases of (15) we have $Q_0(t)$ = N(t) and Q_3 = 3 $\Phi/4\pi$.

Next important is the normalised number-size distribution f(r, t) given by

$$f(r,t) = \frac{n(r,t)}{N} \tag{16}$$

so that dim f(r, t) = 1/m. The moments of this function are

$$R_k(t) = \int_o^\infty r^k f(r,t)\, dr \tag{17}$$

so that dim R_k (t) = m^k. Applying (16) from (17) it follows

$$R_{3k}(t) = \left(\frac{3}{4\pi}\right)^k \cdot \frac{1}{M_o(t)} \cdot M_k(t) \tag{18}$$

with special cases $R_0 = 1$ and $R_3 = 3\Phi/4\pi N$.

Further generalisation of the distribution functions is one dimensionless variable x = $v/\bar{v}_0$ of these functions. As n (x,t) dx = n(v,t) dv we obtain

$$n(x,t) = \overline{v}_o\, n(v,t) = \frac{\Phi}{N_o}\, n(v,t) \tag{19}$$

where equation (9) was applied. From (19) it follows dim n(x,t) = $1/m^3$. The moments of this function are given by

$$S_k(t) = \int_o^\infty x^k n(x,t)\, dx \tag{20}$$

so that dim $S_k(t) = m^{-3}$ for arbitrary k. Applying (19) from (20) it follows

$$S_k(t) = \frac{N_o^k}{M_1^k} \cdot M_k(t) \tag{21}$$

with special cases $S_0(t) = N(t)$ and $S_1 = N_0$.

Consequently n(x, t) is a dimensional function of one dimensionless variable.

Further generalisation is a dimensionless function of one dimensionless variable. Such properties has the normalized distribution f (x, t) given by

$$f(x,t) = \frac{n(x,t)}{N} \tag{22}$$

so that really dim f (x, t) = 1. Its moments are

$$T_k(t) = \int_o^\infty x^k f(x,t)\, dx \tag{23}$$

so that dim $T_k(t)$ = 1 for arbitrary k and all these moments are dimensionless. Applying (22) from (23) we have

$$T_k(t) = \frac{N_o^k}{M_o(t) \cdot M_1} \cdot M_k(t) \tag{24}$$

with special cases $T_0 = 1$ and $T_1(t) = N_0/N(t)$.
Using (5) and (22) one can easily prove that the function f(x, t) is related to f(v, t) by $f(x, t) = \bar{v}_0 f(v, t)$ in agreement with (19).
Next important dimensionless function of one dimensionless variable is the function

$$h(x,t) = \frac{\Phi}{N_o^2}\, n(v,t) = \frac{\bar{v}_o}{N_o}\, n(v,t) \tag{25}$$

From this definition it follows that really dim h(x, t) = 1 and the moments of this function are

$$H_k(t) = \int_o^\infty x^k h(x,t)\, dx \tag{26}$$

so that dim $H_k(t)$ = 1 for arbitrary k. Applying (25) from (26) it follows

$$H_k(t) = \frac{N_o^{k-1}}{M_1^k} \; M_k(t) \tag{27}$$

with important special case

$$H_o(t) = \frac{N(t)}{N_o} \tag{28}$$

so that $H_0(t = 0) = \underline{1}$ and $H_1 = \underline{1}$.

The most general case of dimensionless distribution with both dimensionless variables is given by

$$z(x,\tau) = \frac{\bar{v}_o}{N_o} \, n(v,t) = \frac{\Phi}{N_o^2} \, n(v,t) \tag{29}$$

where again $x = v/\bar{v}_0$ and dimensionless time τ is given by

$$\tau = 1 - \frac{N(t)}{N_o} \tag{30}$$

so that the values of τ are in the intervall $0 \leqq \tau \leqq \underline{1}$. The quantity τ is called age of the spectrum or age of the distribution Martynov and Bakanov (1961) and Voloshchuk and Sedunov (1975). Defining the moments of this function in a standard way we have

$$Z_k(\tau) = \int_o^\infty x^k \, z(x,\tau) \, dx \tag{31}$$

so that dim $Z_k(\tau) = 1$ for arbitrary k. Applying (29) from (31) it follows

$$Z_k(\tau) = \frac{N_o^{k-1}}{M_1^k} \, . \, M_k(t) \tag{32}$$

with special case $Z_0 = N_{(t)}/N_0 = H_0$. Combining this expression with (30) we obtain

$$Z_o + \iota = 1 \tag{33}$$

Hence the age of the distribution can be expressed by the zero-moment of the functionz(x, τ) using the simple relation (33). As $0 \leqq \tau \leqq \underline{1}$ from (33) immediately follows $0 \leqq Z_0 \leqq \underline{1}$ in agreement with physical interpratation of Z_0. Finally from (32) we have $Z_1 = \underline{1}$.

Summarizing all the discussed moments F_k, J_k, Q_k, R_k, S_k, T_k, H_k and Z_k have been related to basic moments M_k so that the interrelations can be easily derived.

3. TIME EVOLUTION OF THE MOMENT OF ZERO ORDER

As follows from the definition of individual moments and from the foregoing analysis some of these moments are constant, time independent quantities (e.g. the moment M_1 expressing the law of mass conservation) and some of them evolute in time (e.g. the moment M_0). This time evolution in general depends on the form of the collision frequency factor β (v, u) appearing as a kernel in the Smoluchowski equation (1). Probably the most general case which can be treated analytically is given by

$$\beta(x,y) = \beta_o + \beta_1(x+y) + \beta_2 x \cdot y \tag{34}$$

where again $x = v/\bar{v}_{0.}$, $y = u/\bar{v}_{0.}$, are the dimensionless particles volumes, β_0, β_1 and β_2 are constants satisfying the condition $\dim\beta = \dim\beta_0 = \dim\beta_1 = \dim\beta_2 = m^3/s$. Starting from equation (1) one can derive a setof ordinary differential equations describing the time evolution of individual moments. For the moment of zero order and general kernel (34) the corresponding differrential equation becomes

$$\frac{dH_o(t)}{dt} = -\frac{1}{2} N_o \left\{ \beta_o H_o^2(t) + 2\beta_1 H_o(t) + \beta_2 \right\} \tag{35}$$

The moment $H_0(t) = Z_0(t)$ is used because of its physical meaning - see (28) - and because of mathematical simplicity. Perhaps the first who solved the analogy to equation (35) was Drake (1972). Using his original solution and the theory of dimension, his results can be further developed in the following way:

case 1: $\beta_0 \cdot \beta_2 = \beta_1^2$

Then the solution of (35) can be expressed by

$$H_o(t) = \frac{N(t)}{N_o} = \frac{2 - N_o(\beta_1 + \beta_2)t}{2 + N_o(\beta_o + \beta_1)t} \tag{36}$$

case 2:

$$a = (\beta_o\beta_1 - \beta_1^2)^{1/2} > 0$$

Then the solution can be expressed by

$$H_o(t) = \frac{a - (\beta_1 + \beta_2)\, tg\left(\frac{1}{2} N_o a t\right)}{a + (\beta_o + \beta_1)\, tg\left(\frac{1}{2} N_o a t\right)} \tag{37}$$

case 3:

$$b = (\beta_1^2 - \beta_o\beta_2)^{1/2} > 0$$

Then the solution is

$$H_o(t) = \frac{b\left(1 + e^{-N_o bt}\right) - (\beta_1 + \beta_2)\left(1 - e^{-N_o bt}\right)}{b\left(1 + e^{-N_o bt}\right) + (\beta_o + \beta_1)\left(1 - e^{-N_o bt}\right)} \tag{38}$$

All solutions (36), (37) and (38) satisfy the condition $H_0(t = 0) = \underline{1}$ in agreement with (28). Important special cases are as follows:

a) $\beta_1 = \beta_2 = 0$

Then evidently case 1 applies and from (36) we obtain the classical equation

$$N(t) = \frac{N_o}{1 + \frac{1}{2} N_o \beta_o t} \tag{39}$$

derived already by Smoluchowski (1936).

b) $\beta_0 = \beta_2 = 0$

Then again case 3 applies, quantity b reduces to $b = \beta_1$ and solution (38) reduces to

$$N(t) = N_o \cdot e^{-N_o \beta_1 t} \tag{40}$$

c) $\beta_0 = \beta_1 = 0$

Then again case 1 applies and from (36) we obtain

$$N(t) = N_o\left(1 - \frac{1}{2} N_o\beta_2 t\right) \tag{41}$$

As follows from (41) and already pointed out by Voloshchuk and Sedunov (1975) the coagulation process in this case can end in the finite time t_c given by

$$t_c = \frac{2}{N_o\beta_2} \tag{42}$$

However the equation for t_c derived.by Voloshchuk and Sedunov (1975) is incorrect. The same applies to (35), (their equation 6.2.13 and subsequent special solutions (6.2.14) and (6.2.15)). All these equations are dimensionally incorrect.

4. TIME EVOLUTION OF PHYSICAL QUANTITIES RELATED TO THE MOMENT OF ZERO ORDER

The knowledge of the time evolution of the moment of order zero (total number concentation) enables the simplified description of the time change of certain physically important quantities during the coagulation process.

The time evolution of the mean particle volume $\bar{v} = \bar{v}(t)$ given by (8) and using (28) can be expressed

$$\bar{v}(t) = \frac{\Phi}{N(t)} = \frac{\Phi}{N_o H_o(t)} \tag{43}$$

where $H_0(t)$ is given according to 3 possible cases by egs. (36), (37) and (38). Important special cases are again

a) $\beta_1 = \beta_2 = 0$ with $H_0(t)$ given by (39) so that (43) reduces to

$$\bar{v}(t) = \frac{\Phi}{N_o}\left(1 + \frac{1}{2} N_o \beta_o t\right) \tag{44}$$

which corresponds to the classical Smoluchowski solution (39). Consequently in this case the mean particle volume increases linearly with time.

b) $\beta_0 = \beta_2 = 0$. Then (40) applies and (43) becomes

$$\bar{v}(t) = \frac{\Phi}{N_o} e^{N_o \beta_1 t} \tag{45}$$

Hence in this case the mean particle volume increases exponentially.

c) $\beta_0 = \beta_1 = 0$. Then (41) applies and (43) becomes

$$\bar{v}(t) = \frac{\Phi}{N_o\left(1 - \frac{1}{2} N_o \beta_2 t\right)} \tag{46}$$

so that in the finite time $t = t_c$ is $\bar{v} \to \infty$. In the similar way we can express and discuss the time evolution of the particle size $\bar{r}(t)$ which is

$$\bar{r}(t) = \left(\frac{3}{4\pi}\right)^{1/3} \cdot \frac{\Phi^{1/3}}{N_o^{1/3} \cdot H_o^{1/3}(t)} \tag{47}$$

and increases with time as $H_0(t)$ is a decreasing function. The particle mean surface $\bar{s}(t)$ becomes

$$\bar{s}(t) = 4\pi r^2 = (36\pi)^{1/3} \frac{\Phi^{2/3}}{N_o^{2/3} \cdot H_o^{2/3}(t)} \tag{48}$$

and is also increasing with time. Finally the surface concentration $S = \bar{s}(t) \cdot N(t)$ becomes

$$S = (36\pi)^{1/3} \Phi^{2/3} N_o^{1/3} H_o^{1/3}(t) = (36\pi)^{1/3} \frac{2/3}{v(t)} \cdot N(t) \tag{49}$$

which is decreasing function of time. Hence the time evolution of the total number concentration with mean particle volume and the simplified description of the time evolution of the mean particle size, mean particle surface and surface concentration during the coagulation process characterized by the general kernel (34) can be expressed in closed analytical form.

5. HALF TIME OF COAGULATION

This is a useful characteristics describing the rate of the coagulation process and defined simply as atime im which the initial total concentration decreases to one half of its initial value so that $N(t = t_h) = No/2$. For $t = t_h$ from (30) it follows $\tau = 1/2$ and from (33) $Z_0 = 1/2$. Solutions (36), (37) and (38) enable to calculate this quantity for the general kernel (34).

Case 1:

Solving equation (36) for $H_0(t = t_h) = 1/2$ we obtain

$$t_h = \frac{1}{N_o\left(\frac{1}{2}\beta_o + \frac{2}{3}\beta_1 + \beta_2\right)} \tag{50}$$

Case 2:

Solving (37) for $H_0(t = t_h) = 1/2$ we obtain

$$t_h = \frac{2}{N_o\left(\beta_o\beta_2 - \beta_1^2\right)^{1/2}} \cdot arctg \frac{\left(\beta_o\beta_2 - \beta_1^2\right)^{1/2}}{\beta_o + 3\beta_1 + 2\beta_2} \tag{51}$$

Case 3:

Solving (38) for $H_0(t = t_h) = 1/2$ we obtain

$$t_h = \frac{1}{N_o\left(\beta_1^2 - \beta_o\beta_2\right)^{1/2}} \cdot ln \frac{\beta_o + 3\beta_1 + 2\beta_2 + \left(\beta_1^2 - \beta_o\beta_2\right)^{1/2}}{\beta_o + 3\beta_1 + 2\beta_2 - \left(\beta_1^2 - \beta_o\beta_2\right)^{1/2}} \tag{52}$$

Important special cases are correspondingly

a) $\beta_1 = \beta_2 = 0$

Case 1 applies and from (50) we have

$$t_h = \frac{1}{\frac{1}{2} N_o\beta_o} \tag{53}$$

b) $\beta_0 = \beta_2 = 0$

Case 3 applies and (52) reduces to

$$t_h = \frac{1}{N_o\beta_1} ln\, 2 \tag{54}$$

c) $\beta_0 = \beta_1 = 0$

Case 1 again applies and (50) reduces to

$$t_h = \frac{1}{N_o\beta_2} \tag{55}$$

comparing (42) and (55) we obtain

$$t_h = \frac{1}{2} t_c \tag{56}$$

in confirming the simple fact the coagulation half time in this case is one half of the coagulation life time.

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