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ULTRACENTRIFUGATION AT VARIABLE ANGULAR VELOCITY- DERIVATION OF BASIC EQUATIONS

MATATIAHU GEHATIA

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers," and the research was conducted by Dr. M. T. Gehatia. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The report covers research conducted from January 1964 to November 1964. The manuscript was released by the author in November 1964 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

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ABSTRACT

Equations of sedimentation were derived making assumptions concerning the shapes of macromolecules in solution dependent upon the centrifugal field which can be varied during the experiment. Angular velocity, sedimentation coefficient and diffusion coefficient were considered as general functions of time: $\omega = \omega(t)$; $s^* = s^*(t)$; and $D^* = D^*(t)$, where s and D are the values of these coefficients for $\omega = 0$. Considering the displacement, Δr , of the flowing particles as being very small in comparison with their average radial distance, r , from the center of rotation, the dependency upon the centrifugal field could be seen to be dependent on the angular velocity alone.

Neglecting the influence of the meniscus and the bottom of the ultracentrifugal cell, and further, disregarding dependency on concentration c , such concentration appearing in a sectorial synthetic boundary cell could be expressed by the following formula:

$$c(r; t) = 2c_0 e^{-2B} e^{-\rho^2} \int_{\rho_0}^{\infty} u e^{-u^2} I_0(2\rho u) du,$$

where

c_0 = initial concentration; r_0 = initial boundary;

$$\beta(t) = s^* \omega^2; \quad B(t) = \int_0^t \beta(u) du;$$

$$\alpha = \frac{1}{t} e^{2B(t)} \int_0^t e^{-2B(u)} D(u) du;$$

$$\rho_0 = \frac{r_0 e^B}{(4D\alpha t)^{1/2}}; \quad \rho = \frac{r}{(4D\alpha t)^{1/2}}$$

I_0 = Zero Order Complex Bessel Function.

The gradient of concentration was expressed by the following approximate equation:

$$\frac{\partial c}{\partial r} = \frac{c_0 e^{-2B}}{(4\pi D\alpha t)^{1/2}} \left(\frac{r_0 e^B}{r} \right)^{1/2} \exp \left\{ -\frac{(r_0 e^B - r)^2}{4D\alpha t} \right\}.$$

Since the functions of time, $B(t)$ and $\alpha(t)$, appearing in the formulas are very general and do not need explicit definitions a priori, a principle of analogy was suggested, based upon a formal similarity between these newly derived equations and formulas obtained previously under different assumptions. With the help of this principle, any other formula

of sedimentation, or any method of computation derived previously for any conditions, can be easily transformed into corresponding expressions satisfying the current assumptions, providing such formulas were derived from analogous basic equations only by integration or by partial differential with regard to r .

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INTRODUCTION

Ultracentrifugation as a method of investigation provides information on molecular weight and sizes of polymers. It seems, this technique may also provide information on additional physical properties of macromolecules such as elasticity and intramolecular field of forces. The nonuniformity of centrifugal forces exercises stress on an elongated particle. The following strain may change its shape and may affect the parameters of hydrodynamic friction. If such changes could be recorded with adequate accuracy, measuring the rate of flow, and if the basic theory of such effects would be developed, techniques of ultracentrifugation could lead to the evaluation of elastic intramolecular forces, and could contribute to a better understanding of the elastic properties of high polymers in solid state.

Since a variable angular velocity during the experiment may be considered to be a better experimental routine for the investigation suggested above, an attempt has been made to derive the corresponding equations of sedimentation assuming such velocity is a function of time. In addition, the shapes of the sedimenting molecules, and also their characteristic parameters of flow, were considered as functions of this variable centrifugal field.

The most general differential equation characterizing the Brownian movement in an n -dimensional "centrifugal field" can be derived from the "universal equation of flow" and expressed by the following formula:

$$\frac{\partial c}{\partial t} = \nabla \left[\nabla (D^* c) - s^* \omega^2 \underline{R} c \right], \quad (1)$$

where c = concentration; t = time; ω = angular velocity; $\underline{R}$ = n -dimensional vector representing the distance from the center of rotation; D^* and s^* = corresponding coefficients of diffusion and sedimentation.

The conventional routine maintains a cylindrical centrifugal field with radical symmetry, retains constant ω , and considers s^* and D^* as constants during the run. The corresponding differential equation of flow derived from Equation 1 is usually known as the "Equation of the Ultracentrifuge" (Reference 1):

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left\{ r \left[D \frac{\partial c}{\partial r} - s \omega^2 r c \right] \right\}, \quad (2)$$

where r denotes the distance from the center of rotation. Equation 2 was solved in different ways by Faxen (Reference 2), Archibald (Reference 3), and Gehatia (Reference 4 and 5). Fujita (Reference 6) modified Equation 2 assuming linear dependence of s^* on c , and suggested its approximate solution. In the current work, Equation 2 is modified to satisfy the newly assumed conditions, and is solved accordingly.

It was already mentioned, that if a sedimenting particle changes its shape because of variable centrifugal field, $\omega^2 r$, the parameters s^* and D^* have to be considered as

functions of such a field:

$$s^* = s^*(\omega^2 r); \quad (3-a)$$

$$D^* = D^*(\omega^2 r). \quad (3-b)$$

As a matter of fact the variations of ω^2 during the experiment can be considerable, and their range extends from 0 to ca $3.5 \times 10^7 \text{ sec}^{-2}$. On the other hand, a displacement, Δr , which a dissolved particle can undergo during the experiment is very small in comparison to the value of r . Therefore, the variations of r can have only a very negligible influence on parameters defining s^* and D^* , and one may consider some average distance $\langle r \rangle$ as constant. Thus one can express s^* and D^* as functions of ω only.

Let angular velocity be any function of time:

$$\omega^2 = R(t), \quad (4)$$

hence:

$$s^* = s^*(\omega^2(t)) = s\mathcal{J}(t); \quad (4-a)$$

$$D^* = D^*(\omega^2(t)) = D\mathcal{D}(t); \quad (4-b)$$

where s and D are corresponding values of s^* and D^* for $\omega = 0$.

Equations 4 and 4-a lead to the following expression:

$$s^* \omega^2 = s\mathcal{J}(t) R(t) = \beta(t). \quad (5)$$

Substituting Equations 4-b and 5 into Equation 2, one can obtain a modified equation of flow corresponding to the conditions assumed in the current work.

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left\{ r \left[D\mathcal{D}(t) \frac{\partial c}{\partial r} - \beta(t) r c \right] \right\}. \quad (6)$$

An expression describing distribution of concentrations in the ultracentrifugal cell will be obtained by applying a stochastic method. This same method proved to be successful in the case where the conventional equation was treated, assuming constant ω , s^* and D^* (Reference 4). It will be shown, that this method of calculation does not require explicit expression for $\mathcal{D}(t)$ and $\beta(t)$ a priori, and therefore, it is most general in all cases in which the parameters are only functions of time.

RANDOM WALK OF A SINGLE PARTICLE IN SOLUTION EXPOSED TO ONE DIMENSIONAL CENTRIFUGAL FIELD

Consider a hypothetical, infinitely long one dimensional centrifugal field along x-coordinate. A particle in a viscous medium moves in that field according to Stoke's relationships, and carries out a latent flow which permits one to neglect accelerations caused by constant forces. Its total velocity is a sum of velocity caused by pure sedimentation (v_s) and velocity caused by pure Brownian movement (v_D), each independent of the other. According to the Svedberg theory (Reference 7):

$$v_s = \beta(t)x, \quad (7)$$

where

$$\beta = s\omega^2. \quad (7-a)$$

Hence, the total velocity can be expressed by:

$$\dot{x} = \beta(t)x + v_D. \quad (8)$$

Integration of Equation 8 leads to the following formula:

$$x - x_0 e^{B(t)} = e^{B(t)} \int_0^t e^{-B(u)} v_D du, \quad (9)$$

where

$$B(t) = \int_0^t \beta(u) du, \quad (10)$$

and x_0 is the initial location of the moving particle.

Since the quantity v_D appearing under the integral in Equation 9 is an undefined random variable, this integral cannot be evaluated. Therefore, the following method will be applied. First, the time interval, 0-t, will be divided into N number of equal time intervals τ :

$$t = \sum_{n=1}^N \tau_n = N\tau, \quad (11)$$

where N is a very large, and τ a very small number. Now, the integral under consideration will be replaced by the following summation:

$$x - x_0 e^{B(t)} = e^{B(t)} \sum_{n=1}^N e^{-B(n\tau)} v_{Dn}, \quad (12)$$

where $g_n = v_{D,n} \tau_n$ is a displacement caused by Brownian movement during the time interval τ_n .

In general, g_n does not depend on a field of forces, providing such forces do not change the shape of a particle during the experiment. Thus, such displacement can be treated according to the theory of diffusion (Reference 8). However, in the current work the shape varies with time which is dependent upon a variable field, and the usual way of computation of such a random walk cannot be applied. According to the Einstein theory of diffusion (Reference 9), the second statistical moment of g_n is given by the following relationship:

$$\mu_2(g_n) = \langle g_n^2 \rangle = 2 D^* \tau_n, \quad (13)$$

Substituting Equation 4-b into Equation 13 one can obtain:

$$\langle g_n^2 \rangle = 2 D \mathcal{D}(n\tau) \tau_n \quad (13-a)$$

In the absence of a centrifugal field:

$$g_n(\omega = 0) = \delta_n, \quad (14)$$

where δ_n is a pure normal diffusion, characterized by:

$$\langle \delta_n^2 \rangle = 2 D \tau_n \quad (14-a)$$

Since the factor $\mathcal{D}(n\tau)$ is a systematic function of time, Equations 13 through 14-a are valid, if:

$$g_n = \delta_n \mathcal{D}^{\frac{1}{2}}(n\tau). \quad (15)$$

Therefore, substituting Equation 15 into Equation 12 one will obtain:

$$x - x_0 e^{B(t)} = e^{B(t)} \sum_{n=1}^N e^{-B(n\tau)} \mathcal{D}^{\frac{1}{2}}(n\tau) \delta_n. \quad (16)$$

According to the theory of Brownian movement (Reference 10) the probability, $f(\delta_n)$, that a single event δ_n may occur leads to the following expressions for statistical moments:

$$\mu_0(\delta_n) = \int_{-\infty}^{+\infty} f(\delta_n) d(\delta_n) = 1; \quad (17-a)$$

$$\mu_1(\delta_n) = (1/\mu_0(\delta_n)) \int_{-\infty}^{+\infty} \delta_n f(\delta_n) d\delta_n = 0; \quad (17-b)$$

$$\mu_2(\delta_n) = (1/\mu_0(\delta_n)) \int_{-\infty}^{+\infty} \delta_n^2 f(\delta_n) d\delta_n = \sigma_n^2; \quad (17-c)$$

where σ_n is the standard deviation of δ_n . If all τ_n 's are equal, then σ_n is a constant for any n:

$$\sigma_n = \sigma = \text{const}, \quad n = 1 \dots N. \quad (18)$$

Now, both sides of Equation 16 will be divided by σ . Each term y_n appearing in the new summation can be defined as:

$$y_n = \frac{1}{\sigma} e^{B(t) - B(n\tau)} \mathcal{D}^{\frac{1}{2}}(n\tau) \delta_n, \quad (19)$$

and the total expression becomes:

$$\frac{x - x_0 e^{B(t)}}{\sigma} = \sum_{n=1}^N y_n = Y. \quad (20)$$

Each term y_n of Equation 20 represents a single displacement which occurs during τ_n . In the following the moments of distribution of y_n will be evaluated for any n. From these particular moments one can derive a function of probability that the total resulting displacement Y will occur during the entire interval of time t.

The displacement y_n is a random quantity, given as the product of another random quantity δ_n , which is the pure Brownian displacement, and a following systematic function of time:

$$\frac{1}{\sigma} T(n\tau) = \frac{1}{\sigma} e^{B(t) - B(n\tau)} \mathcal{D}^{\frac{1}{2}}(n\tau). \quad (21)$$

Since the event y_n occurs if the event δ_n occurs simultaneously, the probability $p(y_n)$ of the displacement y_n is identical with the probability of $f(\delta_n)$ of δ_n :

$$f(\delta_n) = p(y_n). \quad (22)$$

Therefore, the statistical moments of any particular distribution of y_n can be obtained from the following calculations:

$$\mu_0(y_n) = \int_{-\infty}^{+\infty} p(y_n) dy_n = \frac{1}{\sigma} T(n\tau) \int_{-\infty}^{+\infty} f(\delta_n) d\delta_n = \frac{1}{\sigma} T(n\tau); \quad (22-a)$$

$$\mu_1(y_n) = (1/\mu_0(y_n)) \int_{-\infty}^{+\infty} y_n p(y_n) dy_n = \frac{1}{\sigma} T(n\tau) \int_{-\infty}^{+\infty} \delta_n f(\delta_n) d\delta_n = 0; \quad (22-b)$$

and:

$$\mu_2(y_n) = (1/\mu_0(y_n)) \int_{-\infty}^{+\infty} y_n^2 p(y_n) dy_n = \frac{1}{\sigma^2} T^2(n\tau) \int_{-\infty}^{+\infty} \delta_n^2 f(\delta_n) d\delta_n = T^2(n\tau). \quad (22-c)$$

Thus, it has been shown $T(n\tau)$ is the standard deviation of y_n .

A new function S_N will be now introduced according to the following definition:

$$S_N^2 = \sum_{n=1}^N T^2(n\tau) = e^{2B(t)} \sum_{n=1}^N e^{-2B(n\tau)} \mathcal{D}(n\tau). \quad (23)$$

Since N is very large, the summation appearing in Equation 23 can be replaced by the integral:

$$S_N^2 = \int_0^N T^2(v\tau) dv = \frac{1}{\tau} \int_0^{N\tau} T^2(u) du = \frac{N}{t} e^{2B(t)} \int_0^t e^{-2B(u)} \mathfrak{D}(u) du. \quad (24)$$

Denoting:

$$\alpha = \frac{1}{t} e^{2B(t)} \int_0^t e^{-2B(u)} \mathfrak{D}(u) du, \quad (25)$$

the introduced function S_N can be defined as:

$$S_N = N^{\frac{1}{2}} \alpha^{\frac{1}{2}}. \quad (26)$$

According to the Central Limit Theorem (Reference 11) the total displacement Y defined by Equation 20 would have Gaussian distribution, if all standard deviations of the particular displacements y_n 's are equal. In the case under consideration each standard deviation of y_n depends upon n . Therefore, this theorem cannot be applied with regard to Y .

However, there exists another Limit Theorem which shows that the Gaussian distribution can be attributed to the function Y/S_N , providing the two following Lindeberg Conditions (Reference 12) are held:

$$\lim_{N \rightarrow \infty} S_N = \infty, \quad (27-a)$$

and:

$$\lim_{N \rightarrow \infty} \frac{T(n\tau)}{S_N} = 0, \quad n = 1 \dots N. \quad (27-b)$$

Therefore, if at any time α is larger than zero:

$$0 < k \leq \alpha, \quad (28-a)$$

and the standard deviation of any y_n is a bounded quantity:

$$T(n\tau) \leq H < \infty, \quad n = 1 \dots N, \quad (28-b)$$

the Lindeberg conditions do exist:

$$\lim_{N \rightarrow \infty} S_N = \lim_{N \rightarrow \infty} (N^{\frac{1}{2}} \alpha^{\frac{1}{2}}) \geq k^{\frac{1}{2}} \lim_{N \rightarrow \infty} N^{\frac{1}{2}} = \infty, \quad (29-a)$$

and:

$$\lim_{N \rightarrow \infty} \frac{T(n\tau)}{S_N} \leq \frac{H}{k^{1/2}} \lim_{N \rightarrow \infty} N^{-\frac{1}{2}} = 0, \quad (29-b)$$

If Equations 28-a and b hold, the Lindeberg conditions are fulfilled, and according to the modified Limit Theorem the Gaussian distribution can be attributed to the function Y/S_N :

$$P\left(\frac{Y}{S_N}\right) d\left(\frac{Y}{S_N}\right) = \frac{1}{(2\pi)^{1/2}} e^{-\frac{Y^2}{2S_N^2}} d\left(\frac{Y}{S_N}\right). \quad (30)$$

By combining Equations 13, 20 and 30 one can show the probability that a single particle located initially at x_0 will be found at time t at x . This may be expressed by the following formula:

$$P(x; x_0; t) = \frac{1}{(4\pi D\alpha t)^{1/2}} e^{-\frac{(x-x_0 e^B)^2}{4D\alpha t}} \quad (31)$$

Consider now a system of identical particles in solution, located initially within an infinitesimal layer dx_0 at x_0 , and having concentration c_0 . If the flow of each particle

is independent of the other, the expression for concentration at any t and any x can be derived from Equation 31:

$$c(x; t) = \frac{c_0 dx_0}{(4\pi D \alpha t)^{1/2}} e^{-\frac{(x-x_0 e^B)^2}{4 D \alpha t}} \quad (32)$$

Assuming the following initial conditions, $c(t=0)=0$ for $x < x_0$, and $c(t=0)=c_0$ for $x \geq x_0$, the corresponding expressions for concentration can be obtained by integrating Equation 32:

$$c(x; t) = \int_{x_0}^{\infty} \frac{c_0}{(4\pi D \alpha t)^{1/2}} e^{-\frac{(x-x_0 e^B)^2}{4 D \alpha t}} dx_0 \quad (33)$$

Hence:

$$c(x; t) = \frac{1}{2} c_0 e^{-B} \left\{ 1 - \operatorname{erf} \left[\frac{x_0 e^B - x}{(4 D \alpha t)^{1/2}} \right] \right\} \quad (34)$$

where:

$$\operatorname{erf}(y) = \frac{2}{\pi^{1/2}} \int_0^y e^{-u^2} du \quad (35)$$

The corresponding differential equation of one dimensional flow along the x -coordinate can be derived from the general equation of flow, Equation 1. The resulting expression is given by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D^* \frac{\partial c}{\partial x} - \beta(t) x c \right] \quad (36)$$

It can be shown, the formulas obtained for concentration, Equations 32 and 33, satisfy the differential Equation 36.

DISTRIBUTION OF CONCENTRATION IN A CENTRIFUGAL FIELD MAINTAINING RADIAL SYMMETRY OF FLOW

The conventional experimental techniques utilize a sectorial cell in which the equations of flow maintain radial symmetry. In the current work a two-dimensional field with such a symmetry is constructed in the following manner: First, two one-dimensional centrifugal fields previously discussed and characterized by corresponding x- and y-coordinates are perpendicularly superimposed. Consider a particle located initially at point $(x_0; y_0)$. It moves in this newly constructed plane under influence of the simultaneously acting centrifugal forces, and in addition, it undergoes Brownian movement. A probability that such a particle may move during a time interval 0-t from the point $(x_0; y_0)$ to another point $(x; y)$ is equal to the product of two independent probabilities: (1) the displacement from x_0 to x , and (2) the displacement from y_0 to y , during the same interval of time. Applying Equation 31 one can obtain:

$$\begin{aligned}
 P(x; x_0; y, y_0; t) dx_0 dy_0 &= P(x; x_0; t) dx_0 P(y; y_0; t) dy_0 \\
 &= \frac{1}{4\pi D\alpha t} \exp \left\{ -\frac{[(x_0 e^B - x)^2 + (y_0 e^B - y)^2]}{4D\alpha t} \right\} dx_0 dy_0, \quad (37)
 \end{aligned}$$

Now assume that a system of particles located initially within an infinitesimal area $ds_0 = dx_0 dy_0$ undergoes random walk in the plane described above. If the movement of each particle can be considered to be independent, and if the initial concentration is c_0 , then the concentration c at time t and any point of the plane $(x; y)$ can be expressed by the following equation:

$$dc = \frac{c_0 ds_0}{4\pi D\alpha t} \exp \left\{ -\frac{[(x_0 e^B - x)^2 + (y_0 e^B - y)^2]}{4D\alpha t} \right\} \quad (38)$$

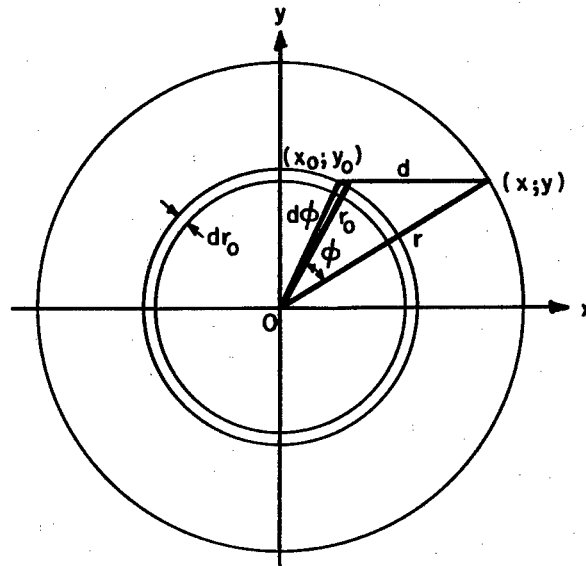


Figure 1. Displacement of a Particle in a Two-Dimensional Centrifugal Field

To transform the theoretically constructed centrifugal field into a real field characterized by radial symmetry, the system of two linear perpendicular coordinates (x, y) must be replaced by a new system of polar coordinates (r, ϕ) . (See Figure 1.) From such a transformation one can derive the following relationship between old and new coordinates:

$$dx_0 dy_0 = ds_0 = r_0 dr_0 d\phi ; \quad (39-a)$$

$$x^2 + y^2 = r^2 ; \quad (39-b)$$

$$xx_0 + yy_0 = rr_0 \cos \phi ; \quad (39-c)$$

where r_0 is the radial distance of (x_0, y_0) .

By substituting Equations 39-a, b and c into Equation 38 one can transform Equation 38 into the corresponding expression for polar coordinates:

$$dc(r; r_0; t) = \frac{c_0 r_0 dr_0}{4\pi D \alpha t} \exp \left\{ \frac{2rr_0 e^B \cos \phi - r^2 - r_0^2 e^{2B}}{4D \alpha t} \right\} . \quad (40)$$

A further generalization of Equation 40 may be obtained by assuming the molecules to be initially enclosed within one infinitesimal ring at distance r_0 from the origin, and that their initial uniform concentration was c_0 . A corresponding expression for c can be found by integrating Equation 40 over all values of ϕ :

$$c = 2 \int_0^\pi dc(r, \phi) d\phi = \frac{2 c_0 r_0 dr_0}{4 \pi D \alpha t} e^{-\frac{(r^2 + r_0^2 e^{2B})}{4 D \alpha t}} \int_0^\pi e^m \cos \phi d\phi, \quad (41)$$

where:

$$m = \frac{2 r r_0 e^B}{4 D \alpha t} \quad (42)$$

Since:

$$\int_0^\pi e^m \cos \phi d\phi = \pi I_0(m), \quad (43)$$

where I_0 is a Zero Order Complex Bessel Function, Equation 41 goes into the following expression:

$$c(r; r_0; t) = \frac{2 c_0 r_0}{4 D \alpha t} e^{-\frac{(r^2 + r_0^2 e^{2B})}{4 D \alpha t}} I_0\left(2 \frac{r r_0 e^B}{4 D \alpha t}\right) dr_0 \quad (44)$$

It can be shown that Equation 44 satisfies the corresponding differential equation of flow, Equation 6.

PRINCIPLE OF FORMAL ANALOGY AND ITS APPLICATION

To derive expressions describing real systems, Equation 44 must be integrated over all values of r_0 within the appropriate limits, according to the experimental conditions.

It is obvious the resulting expressions will need further mathematical treatment and additional transformations to derive formulas according to the different experimental objectives and corresponding methods of computations. However, such additional mathematical treatment can be avoided in many cases by utilizing the following suggested principle.

Since the functions of time $B(t)$ and $\alpha(t)$ appearing in the derived expressions are very general, all corresponding equations derived under any assumptions made for ω , D^* and s^* , can be brought to the same analogous formal expressions, providing the mathematical treatment necessary is carried out only with regard to the r -coordinate, and does not involve any transformations of functions of time with regard to the variable t .

Therefore, any type of expression obtained only by partial differentiation of similar basic equations, or by integration with regard to r , can be expressed by the same formal corresponding equation. After the final expressions have been derived according to the formal analogy, the explicit definitions have to be substituted a posteriori into the appearing functions of time. By help of this method any existing expression for any other case, if evaluated without utilizing variable t , can be transformed into another formula associated with different assumptions for ω , s^* and D^* .

Applying this principle of analogy, one can easily obtain the following expressions, which can be given as examples:

1. According to the initial conditions, let $c(t=0)=0$ for $r < r_0$, and $c(t=0)=c_0$ for $r \geq r_0$.

The corresponding formula for concentration derived previously for constant centrifugal field and constant coefficients of sedimentation and diffusion (Reference 5) can be transformed into the equation describing the current conditions:

$$c(r, t) = 2 c_0 e^{-2B} e^{-\rho^2} \int_{\rho_0}^{\infty} u e^{-u^2} I_0(2\rho u) du, \quad (45)$$

where

$$\rho = \frac{r}{(4D\alpha t)^{1/2}} \quad (46-a)$$

$$\rho_0 = \frac{r_0 e^B}{(4D\alpha t)^{1/2}} \quad (46-b)$$

2. Maintaining these assumptions, one can transform an approximate formula of gradient of concentration derived for constant field and parameters of flow (Reference 5) into a corresponding equation for the general case:

$$\frac{\partial c}{\partial r} = \frac{c_0 e^{-2B}}{(4\pi D\alpha t)^{1/2}} \left(\frac{r_0 e^B}{r} \right)^{\frac{1}{2}} e^{-\frac{(r_0 e^B - r)^2}{4D\alpha t}} \quad (47)$$

3. The well known "Svedberg Method" (Reference 7) leading to the evaluation of sedimentation coefficient under conventional conditions from the shifting of the peak of experimental curve, can be transformed by analogy into a general formula:

$$\ln r_{\max} = \ln r_0 + B(t), \quad (48)$$

where $r_{\max}$ is a radial distance of the maximum gradient and (Reference 4):

$$B(t) = s \int_0^t R(u) \mathcal{J}(u) du. \quad (49)$$

From Equation 48 one can find s and one of the parameters of the function $\mathcal{J}(t)$.

4. Making the following assumptions:

$$s^* = s = \text{const}; \quad (50-a)$$

$$D^* = D = \text{const}; \quad (50-b)$$

$$\omega(t=0) = 0; \quad (50-c)$$

$$\frac{d\omega^2}{dt} = g = \text{const}; \quad (50-d)$$

one can obtain:

$$\beta = sgt; \quad (51-a)$$

$$B = \frac{1}{2} sgt^2; \quad (51-b)$$

and:

$$\ln r_{\max} = \ln r_0 + \frac{1}{2} sgt^2. \quad (51-c)$$

Plotting $\ln r_{\max}$ vs. t^2 one can evaluate s . The corresponding α is given by:

$$\alpha = \frac{1}{t} e^{sgt^2} \int_0^t e^{-sgu^2} du, \quad (52)$$

or:

$$\alpha = \sum_{n=0}^{\infty} \frac{(2sgt^2)^n}{(2n+1)!!} = 1 + \frac{2sgt^2}{1 \times 3} + \frac{(2sgt^2)^2}{1 \times 3 \times 5} + \quad (53)$$

Usually $(2sg t^2) \ll 1$, and the series in Equation 53 converges rapidly.

5. Let:

$$\omega(t=0) = 0; \quad (54-a)$$

$$\omega^2 = gt; \quad g = \text{const}; \quad (54-b)$$

$$s^* = s(1 + k_s \omega^2); \quad (54-c)$$

$$D^* = D(1 + k_D \omega^2); \quad (54-d)$$

where k_s and k_D are constants.

Hence:

$$\beta(t) = s(k_s g^2 t^2 + gt); \quad (55-a)$$

$$B(t) = \frac{1}{2} s g t^2 + \frac{1}{3} s k_s g^2 t^3; \quad (55-b)$$

$$a = \frac{1}{t} e^{s t^2 g (1 + \frac{2}{3} k_s g t)} \int_0^t e^{-s g (u^2 + \frac{2}{3} k_s g u^3)} (1 + k_D g u) du. \quad (55-c)$$

From the generalized "Svedberg Method" one can find s and k_s , by utilizing a plot of the following expression:

$$\frac{\ln r_{\max}}{t^2} - \frac{\ln r_0}{t} = \frac{1}{2} s g + \frac{1}{3} s k_s g^2 t. \quad (56)$$

CONCLUSIONS

The equations derived in the current work and the method suggested may enable one to carry out a mathematical analysis of experimental data in cases of (1) variable angular velocity, and (2) if s^* and D^* depend upon ω . It seems that the parameters defining $s^* = s^*(\omega)$ and $D^* = D^*(\omega)$ are also functions of concentration. Therefore, one can expect to obtain additional important information on the shape of sedimenting particles and the intramolecular field, if the relationships between the concentration and the parameters of shape could be derived from the theory of hydrodynamics. Such theoretical development may also contribute to a better elucidation of problems related to the statistical mechanics of polymers in solution.

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