A MATHEMATICAL STUDY OF THE PARTICLE SIZE DISTRIBUTION OF COAGULATING DISPERSE SYSTEMS

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1966

(Submitted May 10, 1966)

ACKNOWLEDGMENT

I wish to express my deepest gratitude to my adviser, Professor S. K. Friedlander, who introduced me to the field of disperse systems. His constant and inspiring guidance has been invaluable.

The financial support from the California Institute of Technology in the form of Tuition Scholarships, Graduate Research and Teaching Assistantships, and a Woodrow Wilson Summer Fellowship is deeply appreciated.

ABSTRACT

The behavior of the particle size distribution of coagulating dispersions is studied theoretically. If the collision frequency factor is a homogeneous function of particle volume, the partial integro-differential equation describing the coagulation kinetics can be transformed into an ordinary integro-differential equation by a similarity transformation originally proposed by Friedlander. The solution to the resulting equation, called the self-preserving spectrum, is determined for three different collision mechanisms: (1) constant collision frequency factor, (2) Brownian motion, and (3) simultaneous Brownian motion and shear flow, in which the shear rate decreases with time in a particular way. The results of this study indicate that the shape of the self-preserving spectrum is greatly influenced by the collision mechanism.

If a slip correction for the particle drag is taken into consideration, the coagulation equation for Brownian motion cannot be reduced to an ordinary integro-differential equation. However, the coagulation equation can be written in terms of a reduced size spectrum. By assuming that the reduced size spectrum varies slowly with time, a family of "quasi-self-preserving" spectra are obtained for various values of a parameter Λ , which is a function of the mean free path of the fluid, the total volume concentration and the total number concentration of particles.

The self-preserving hypothesis concerning the particle size distribution is proved to be true for the case of constant collision frequency factor. For Brownian coagulation, arguments are presented to support the hypothesis.

In the cases which are worked out, it is assumed that the particles are uncharged and spherical in shape and that their density is conserved in the coagulation process.

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I. INTRODUCTION

Disperse systems, consisting of solid or liquid particles suspended in a fluid, play a significant role in nature and industry. Cloud, a suspension of water drops in atmosphere, is a major factor affecting climate. The atomization of liquid fuels and the pulverization of solid fuels, are common industrial operations which generate disperse systems. Many chemical materials are handled in the form of emulsions during manufacture. Some disperse systems are undesirable, such as dusts formed during mechanical processing of rocks and smoke evolved during the combustion of fuel.

The physical properties of a particle or drop depend on its size. The rate of evaporation of a spherical drop, for example, is proportional to its radius. The fraction of light scattered by a particle larger than the wavelength of light is proportional to the square of its radius. The sedimentation velocity of a particle with radius much larger than the mean free path of the suspending medium is also proportional to the square of its radius. In general, disperse systems consist of particles of many different sizes and knowledge of the size distribution is necessary to understand the behavior of the system as a whole (1). A better understanding of the particle size distribution of disperse systems has application in the processing of emulsions, gas cleaning, water treatment, and the study of cloud physics and air pollution.

Particles in a disperse system move in response to external forces such as gravitational and electrical fields, hydrodynamic drag and fluctuating forces resulting from the thermal motion of the ambient fluid. Relative movement of particles can bring them into contact; when they collide and stick, the process is called coagulation. As a result of coagulation, diffusion and sedimentation, the particle size distribution of a disperse system changes continually.

The basic theory of coagulation produced by Brownian motion and by laminar shear flow was developed almost 50 years ago by Smoluchowski (2). However, no general analytical solution has been obtained to the integro-differential equation of coagulation. Previous mathematical studies of the coagulation equation can be roughly divided into two groups. The first includes those in which the Smoluchowski theory was tested for the initial stage of coagulation. The agreement between theory and experiments is satisfactory. The second group includes those concerned with the particle size distributions of aged disperse systems. Their results indicate that the particle size distribution of an aged coagulating system approaches a universal asymptotic form called the self-preserving particle size distribution. It is hypothesized but not yet proven that the shape of the self-preserving distribution is independent of the initial distribution, although it does depend on the mechanism of coagulation. If the self-preserving hypothesis can be firmly established, the tedious job of the determination of particle size distribution can be reduced to the determination of only a few parameters for aged systems. In view of the abundance of aged disperse systems in nature and industry, the self-preserving hypothesis should have many practical applications. Previous studies in this field were mainly concerned with testing the self-preserving hypothesis by experiments and by numerical solutions of coagulation equation. This work is concerned with the theoretical foundation of this hypothesis and the solutions to the equations for the self-preserving spectra for various collision mechanisms. The asymptotic behavior of the coagulation equation is studied for a simplified coagulation model and for Brownian coagulation. In the simplified coagulation model, the collision frequency between particles is assumed to be independent of particle size. Self-preserving particle size distributions are determined for the simplified coagulation model, for Brownian coagulation, and for coagulation caused by simultaneous Brownian motion and shear flow. In the cases which are worked out, it is assumed that the particles are uncharged and spherical in shape and that their density is conserved in the coagulation process.

II. THEORY OF COAGULATION

In this Chapter, the theory of coagulation originally developed by Smoluchowski is briefly summarized. A short review on the previous works devoted to the study of the coagulation equation is given.

A. Particle Size Distributions.

The particle size distribution of a coagulating system can be described by either a discrete or a continuous model. In the discrete model, the number concentration $n_i(t)$ represents the number of particles with volume v_i in a unit volume of the system at time t. In the continuous model, the number concentration of particles in the size range from v to $v+dv$ at time t is represented by $n(v,t)\,dv$.

Two useful parameters associated with a disperse system are the total number of particles per unit volume of the system N, and the total volume of particles per unit volume of the system ϕ. These two quantities can be evaluated from the following relations:
in the discrete model:

$$N(t) = \sum_{i=1}^{\infty} n_i(t)$$

$$\phi = \sum_{i=1}^{\infty} v_i n_i(t)$$

in the continuous model:

$$N(t) = \int_0^{\infty} n(v,t)\,dv \qquad (1)$$

$$\phi = \int_0^{\infty} v\,n(v,t)\,dv \qquad (2)$$

Particle size distributions are best visualized by plotting the number distribution function $n(v,t)$ versus the volume v using the time t as parameter. The total number concentration $N(t)$ is represented by the area under the distribution curve, and the total volume concentration ϕ is represented by the first moment of the curve. In a coagulating system isolated from its surroundings, both $n(v,t)$ and $N(t)$ are functions of time t. The total volume concentration is invariant with respect to time if the density of particles is assumed to remain the same throughout the coagulation process.

B. Coagulation Equations.

If collisions of three or more particles are neglected, the collision frequency f_{ij} between particles of volume v_i and v_j is proportional to the product of their number concentrations:

$$f_{ij} = \beta(v_i, v_j)\, n_i(t)\, n_j(t)$$

in which $\beta(v_i, v_j)$ is the collision frequency factor. In general, the collision frequency factor is a function of the physical properties of the medium and the colliding particles. However, it will be written as $\beta(v_i, v_j)$, since particle size is the main variable to be considered in this study.

The collision frequency factor is determined by the mechanism for producing relative motion of the particles. For Brownian motion of spherical particles, Smoluchowski (2) showed that

$$\beta(v_i, v_j) = 4\pi\,(D_i + D_j)(r_i + r_j)$$

in which D_i is the diffusion coefficient for particles with radius r_i . If particle radii are larger by at least an order of magnitude than the mean free path of the medium, the Stokes-Einstein relation for the diffusion coefficient (3) can be used. $\beta(v_i, v_j)$ for Brownian motion can then be expressed as

$$\beta(v_i, v_j) = \frac{2kT}{3\mu}\left(v_i^{1/3} + v_j^{1/3}\right)\left(\frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}}\right) \qquad (3)$$

in which k is Boltzmann's constant, T the absolute temperature, and μ the viscosity of the medium. When the particle radii are of the same order of magnitude as the mean free path of the medium λ , a slip ("Cunningham") correction (4) for Stokes' friction formula can be used to account for the increased mobility of particles. $\beta(v_i, v_j)$ for Brownian motion of such small particles is then given by

$$\beta(v_i, v_j) = \frac{2kT}{3\mu}\left(v_i^{1/3} + v_j^{1/3}\right)\left(\frac{1}{v_i^{1/3}} + \frac{A_i\lambda}{v_i^{2/3}} + \frac{1}{v_j^{1/3}} + \frac{A_j\lambda}{v_j^{2/3}}\right) \qquad (4)$$

$$A_i = 1.257 + 0.4\,\exp\left(-1.1\,r_i/\lambda\right)$$

The limitations on this approximation have been discussed by Fuchs (1).

For spherical particles in laminar shear flow, Smoluchowski (2) showed that

$$\beta(v_i, v_j) = \frac{G}{\pi} \left(v_i^{1/3} + v_j^{1/3} \right)^3 \tag{5}$$

in which G is the shear rate. In deriving this expression, particles are assumed to have no effect upon the flow field.

The collision of drops in turbulent flow has been studied by Levich (5), and subsequently by Saffman and Turner (6). For drops much smaller than the small eddies of the turbulence, the collision frequency factor depends only on the dimensions of the drops, the rate of energy dissipation per unit mass ϵ, and the kinematic viscosity of the medium ν. The expression derived by Saffman and Turner is

$$\beta(v_i, v_j) = \left(\frac{3\epsilon}{10\pi\nu}\right)^{1/2} \left(v_i^{1/3} + v_j^{1/3} \right)^3 = 0.31 \left(\frac{\epsilon}{\nu}\right)^{1/2} \left(v_i^{1/3} + v_j^{1/3} \right)^3 \tag{6}$$

which is valid for v_i/v_j between one and eight.

If particles adhere to each other at every collision and the density of particles is conserved in the process of coagulation, the rate of change of the number concentration of particles is given by

$$\frac{dn_i(t)}{dt} = \frac{1}{2} \sum_{\substack{j=1 \\ j+k=i}}^{j=i-1} \beta(v_j, v_k) n_j(t) n_k(t) - \sum_{j=1}^{\infty} \beta(v_i, v_j) n_i(t) n_j(t) \tag{7}$$

$$i = 1, 2, \cdots$$

in which the volume v_j is related to the smallest volume v_1 by the relation $v_j = j v_1$. The first term on the right of Eq. (7) represents the number of particles with volume v_i formed by coagulation of smaller particles; the second term represents the number of particles with volume v_i lost by coagulation with other particles.

Eq. (7) is the coagulation equation written in terms of the discrete size distribution. The corresponding equation for the continuous distribution is

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^{v} \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v}, t)\, n(v-\tilde{v}, t)\, d\tilde{v} - \int_0^{\infty} \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v}, t)\, d\tilde{v} \tag{8}$$

The expression for the rate of change of the total number concentration of particles can be readily obtained by integrating both sides of Eq. (8) with respect to v from 0 to ∞ :

$$\frac{dN(t)}{dt} = -\frac{1}{2}\int_0^{\infty}\int_0^{\infty} \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, dv\, d\tilde{v} \tag{9}$$

By multiplying both sides of Eq. (8) by v and integrating with respect to v from 0 to ∞ it can be shown that the total volume concentration of particles ϕ is invariant with respect to time.

Analytical solutions to the coagulation equation have been found for the following simplified collision frequency factors:

(1) $\beta(v, \tilde{v})$ = constant (independent of v and $\tilde{v}$)(2,7,8)

(2) $\beta(v, \tilde{v})$ = constant $\times (v + \tilde{v})$ (9)

(3) $\beta(v, \tilde{v})$ = constant $\times\ v\,\tilde{v}$ (10,11,12,13)

The solution to Eq. (7) with constant $\beta(v, \tilde{v})$ for an initially monodisperse system is

$$n_i(t) = \frac{n_1(0)\left[\dfrac{4kT\,n_1(0)\,t}{3\mu}\right]^{i-1}}{\left[1 + \dfrac{4kT\,n_1(0)\,t}{3\mu}\right]^{i+1}} \qquad i = 1, 2, \cdots \tag{10}$$

in which $n_1(0)$ is the initial concentration of particles with volume v_1 . The total number concentration of particles in this case is given by

$$N(t) = \frac{1}{\dfrac{1}{N(0)} + \dfrac{4kTt}{3\mu}} \tag{11}$$

This set of solutions is of particular interest, since it is a good approximation for the initial stage of coagulation of a nearly monodisperse system, and therefore can be used to test the results of coagulation experiments. Eq. (10) has been experimentally tested by Turkevich (14) and Higuchi et al (15). Eq. (11) has been experimentally tested by Zsigmondy (16), Kruyt and van Arkel (17), and Tuorila (18). The agreement between theory and experiments was satisfactory for the early stages of coagulation.

The effect of polydispersity on coagulation has been studied by Junge (19) and Zebel (20) by solving numerically the coagulation equation for Brownian motion with the Cunningham slip correction. This approach gives results for particular initial distributions, but little information on the general behavior of polydisperse systems. Martynov and Bakanov (21) suggested that the coagulation equation can be solved by a method of series decomposition. They asserted that the method permits a general study of the initial stage of coagulation. However, their method is in fact not always applicable. The applicability of this method in solving the kinetic equation for Brownian coagulation is discussed in Appendix I.

The question of the particle size distribution for an aged coagulating disperse system was first discussed by Schumann (7). For the coagulation equation with constant $\beta(v, \tilde{v})$, Schumann found a particular solution, $n(v,t) = \frac{[N(t)]^2}{\phi} \exp\left(-\frac{N(t)v}{\phi}\right)$, corresponding to the initial distribution of the same form. He also found that the size spectrum for an initially monodisperse system asymptotically approaches the same exponential form as $t \to \infty$. Based on these results, he suggested that the exponential form might be the asymptotic solution for any initial distribution but was unable to give a rigorous proof.

For Brownian coagulation, Todes (22) argued that the size distribution becomes very diffuse after a sufficiently long time, so that the individual peculiarities in the initial distribution become smoothed out and the size spectrum tends to a limiting form independent of the initial distributions. Todes found that, if $\beta(v, \tilde{v})$ is a homogeneous function of its arguments, the coagulation equation can be transformed into an ordinary integro-differential equation by the similarity transformation $n(v,t) = \frac{A}{t^2} h(v^*)$, in which $v^* = \frac{Bv}{t}$, A and B are constants. However, the function $n(v,t)$ given by this transformation does not behave properly as $t \to 0$. In order for the total volume concentration to remain finite, the function $h(v^*)$ must vanish faster than $1/(v^*)^2$ as $v^* \to \infty$. Therefore, as $t \to 0$, the function $n(v,t) = \frac{A}{t^2} h(\frac{Bv}{t})$ vanishes everywhere except at $v = 0$.

A similarity theory for the size spectrum of coagulating disperse systems was developed independently by Friedlander (23,24,25) to account for similarities in the shapes of atmospheric aerosol spectra observed experimentally. One of the similarity transformations used by Friedlander is

$$n(v,t) = g(t)\,\psi(\eta) \tag{12}$$

$$\eta = \frac{v}{v^+(t)}$$

in which $g(t)$ and $v^+(t)$ are functions of time. By substituting Eq. (12) into Eqs. (1) and (2), it was found that $g(t)$ and $v^+(t)$ can be expressed as functions of $N(t)$ and ϕ :

$$g(t) = \frac{[N(t)]^2}{\phi} \cdot \frac{\int_0^\infty \eta\,\psi(\eta)\,d\eta}{\left[\int_0^\infty \psi(\eta)\,d\eta\right]^2}$$

$$v^{+}(t) = \frac{N(t)}{\phi} \frac{\int_0^\infty \eta \psi(\eta) d\eta}{\int_0^\infty \psi(\eta) d\eta}$$

in which the two integrals $\int_0^\infty \eta \psi(\eta) d\eta$ and $\int_0^\infty \psi(\eta) d\eta$ are dimensionless constants. The following two normalization conditions can be imposed on $\psi(\eta)$ and η :

$$\int_0^\infty \psi(\eta) d\eta = 1 \tag{13}$$

$$\int_0^\infty \eta \psi(\eta) d\eta = 1 \tag{14}$$

The similarity transformation represented by Eq. (12) then becomes:

$$n(v,t) = \frac{[N(t)]^2}{\phi} \psi(\eta) \qquad \eta = \frac{N(t) v}{\phi} \tag{15}$$

The kinetic equation for Brownian coagulation can be reduced to an ordinary integro-differential equation by the transformation given in Eq. (15). If the solution to the resulting ordinary integro-differential equation exists, it represents a particular solution to the coagulation equation. This particular solution does not depend on time explicity, and is therefore called the self-preserving size spectrum. If the particle size distribution of a disperse system is initially in the self-preserving form, the shape of its size spectrum will be preserved throughout the coagulation process.

The experiments of Swift and Friedlander (26) showed that the size distributions of coagulating hydrosols approached a self-preserving form. Subsequently, Hidy (27) solved the discrete version of the kinetic equation of Brownian coagulation by a numerical method. His results indicated that essentially the same self-preserving form was approached by an initially monodisperse sol and a sol initially in four peaked distribution, if the Cunningham slip correction was not taken into consideration. Thus the experimental results of Swift and Friedlander, and the numerical calculations of Hidy support the self-preserving hypothesis which can be stated as follows:

> "The particle size spectra of coagulating dispersions approach a form independent of the initial distribution after a sufficiently long time. This holds true for certain classes of particle collision mechanisms."

III. TRANSFORMATIONS OF THE COAGULATION EQUATION

In this chapter, the equation obtained by applying the similarity transformation given in Eq. (15) to the coagulation equation is presented. A general transformation is introduced for the purpose of studying the asymptotic solution of the coagulation equation.

A. The Self-preserving Similarity Transformation.

If the collision frequency factor $\beta(v,\tilde{v})$ is a homogeneous function of its arguments, the coagulation equation given in Eq. (8) can be reduced to an ordinary integro-differential equation by the similarity transformation. Substituting Eq. (15) into Eqs. (8) and (9) and then combining the resulting equations gives

$$\left[\int_0^\infty\int_0^\infty \beta(\eta,\tilde{\eta})\,\psi(\eta)\,\psi(\tilde{\eta})\,d\eta\, d\tilde{\eta}\right]\left(\eta\frac{d\psi}{d\eta}+2\psi\right)$$
$$+\int_0^\eta \beta(\tilde{\eta},\eta-\tilde{\eta})\,\psi(\tilde{\eta})\,\psi(\eta-\tilde{\eta})\,d\tilde{\eta} \;-\; 2\int_0^\infty \beta(\eta,\tilde{\eta})\,\psi(\eta)\,\psi(\tilde{\eta})\,d\tilde{\eta}=0 \quad (16)$$

The solution to this equation, if it exists, is a particular solution to the coagulation equation and is called the self-preserving spectrum.

The function $\beta(v,\tilde{v})$ given in Eq. (3) for Brownian motion is a homogeneous function of degree zero. Substituting Eq. (3) into Eq. (16) gives after some simplifications:

$$(1+\mu^*_{1/3}\mu^*_{-1/3})\eta\frac{d\psi}{d\eta} + (2\mu^*_{1/3}\mu^*_{-1/3} - \mu^*_{-1/3}\eta^{1/3} - \mu^*_{1/3}\eta^{-1/3})\psi(\eta)$$

$$+ \int_0^\eta \psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\left[1+\left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right]d\tilde{\eta} = 0 \qquad (17)$$

in which $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ are two constants given by

$$\mu^*_{1/3} = \int_0^\infty \eta^{1/3}\psi(\eta)\,d\eta \qquad (18)$$

$$\mu^*_{-1/3} = \int_0^\infty \eta^{-1/3}\psi(\eta)\,d\eta \qquad (19)$$

Eq. (17) is equivalent to one originally derived by Swift and Friedlander (26). This equation will be studied in detail in Chapter V.

The functions $\beta(v,\tilde{v})$ for laminar and turbulent shear flow, given in Eqs. (5) and (6) respectively, are homogeneous functions of degree one. Substituting these two different expressions for $\beta(v,\tilde{v})$ into Eq. (16) gives the same ordinary integro-differential equation:

$$(2+6\mu^*_{1/3}\mu^*_{2/3})\eta\frac{d\psi}{d\eta}$$

$$+ (2+12\mu^*_{1/3}\mu^*_{2/3} - 2\eta - 6\mu^*_{2/3}\eta^{1/3} - 6\mu^*_{1/3}\eta^{2/3})\psi(\eta)$$

$$+ \eta\int_0^\eta \psi(\tilde{\eta})\psi(\eta-\tilde{\eta})d\tilde{\eta} + 6\int_0^\eta \psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\tilde{\eta}^{2/3}(\eta-\tilde{\eta})^{1/3}d\tilde{\eta} = 0 \qquad (20)$$

in which $\mu^*_\nu = \int_0^\infty \eta^\nu \psi(\eta)d\eta$, $\nu = \frac{1}{3}, \frac{2}{3}$. Eq. (20) is equivalent to one originally derived by Swift and Friedlander (26). This equation, however, does not seem to have a solution with finite value at $\eta = 0$. This can be seen by observing that if $\psi(\eta)$ is finite at the origin, Eq. (20) can be approximated by the following equation for small values of η:

$$(2+6\mu^*_{1/3}\,\mu^*_{2/3})\,\eta\frac{d\psi}{d\eta} + (2+12\mu^*_{1/3}\,\mu^*_{2/3})\,\psi(\eta)=0$$

The general solution to this first order ordinary differential equation is

$$\psi(\eta) = \text{constant} \times \eta^{-\frac{1+6\mu^*_{1/3}\mu^*_{2/3}}{1+3\mu^*_{1/3}\mu^*_{2/3}}}$$

which indicates that $\psi(\eta)\to\infty$ as $\eta\to 0$.

Small particles suspended in a shear flow are also subject to fluctuations in the ambient fluid and exhibit Brownian motion. The coagulation equation with the form of $\beta(v,\tilde{v})$ given by Eqs. (5) and (6) cannot describe the complete physical situation. It is necessary to consider the effect of both shear flow and molecular collisions. This problem will be studied in Chapter VI.

B. A General Transformation.

In order to study the asymptotic behavior of the coagulation equation, the following transformation is introduced:

$$n(v,t) = \frac{[N(t)]^2}{\phi} \Phi(\eta,\tau) \tag{21}$$

$$\eta = \frac{N(t)\,v}{\phi}$$

$$\tau = \left[\frac{N(t)}{N(0)}\right]^2 \qquad 0 \leq \tau \leq 1$$

The Jacobian of this transformation is

$$\frac{\partial(\eta,\tau)}{\partial(v,t)} = \frac{2}{\phi}\left[\frac{N(t)}{N(0)}\right]^2 \frac{dN}{dt}$$

which differs from zero everywhere and hence assures that the transformation is a general one. By suppressing the dependence on τ, the function $\Phi(\eta,\tau)$ reduces to the self-preserving form $\psi(\eta)$ given in Eq. (15), which is a degenerate transformation. $\Phi(\eta,\tau)$ has the following two normalization conditions

$$\int_0^\infty \Phi(\eta,\tau)\,d\eta = 1 \tag{22}$$

$$\int_0^\infty \eta\Phi(\eta,\tau)\,d\eta = 1 \tag{23}$$

These two relationships can be readily obtained from Eqs. (1)(2) and (21).

If the collision frequency factor is a homogeneous function of its arguments, substituting Eq. (21) into Eqs. (8) and (9) and then combining the resulting equations gives:

$$\left[\int_0^\infty\int_0^\infty \beta(\eta,\tilde{\eta})\,\Phi(\eta,\tau)\,\Phi(\tilde{\eta},\tau)\,d\eta\,d\tilde{\eta}\right]\left[\eta\frac{\partial\Phi(\eta,\tau)}{\partial\eta} + 2\Phi(\eta,\tau) + 2\tau\frac{\partial\Phi(\eta,\tau)}{\partial\tau}\right]$$
$$+\int_0^\eta \beta(\tilde{\eta},\eta-\tilde{\eta})\,\Phi(\tilde{\eta},\tau)\,\Phi(\eta-\tilde{\eta},\tau)\,d\tilde{\eta} - 2\int_0^\infty \beta(\eta,\tilde{\eta})\,\Phi(\eta,\tau)\,\Phi(\tilde{\eta},\tau)\,d\tilde{\eta} = 0 \qquad (24)$$

Eq. (24) is the coagulation equation written in terms of the reduced size spectrum function $\Phi(\eta,\tau)$ and the reduced volume η. In the next two chapters, Eq. (24) will be used to study the asymptotic behavior of the size distributions for a simplified coagulation model with constant collision frequency factor and for the more realistic case of Brownian coagulation.

IV. A SIMPLIFIED COAGULATION MODEL

The collision frequency factor for Brownian motion given in Eq. (3) is a homogeneous function of degree zero. The coagulation equation for Brownian motion therefore can be written in terms of the reduced spectrum function $\Phi(\eta,\tau)$. However, an analytical solution of this equation does not seem possible. The simplest form of $\beta(v,\tilde{v})$ with zero degree of homogeneity is $\beta(v,\tilde{v})$ = constant (independent of v and $\tilde{v}$). Since the collision frequency factor for Brownian motion can be approximated by $\beta(v,\tilde{v})$ = constant if the range of particle size is not too wide, it seems worthwhile to study the asymptotic solution to the transformed coagulation equation with constant $\beta(v,\tilde{v})$. The manner in which the reduced size spectrum function $\Phi(\eta,\tau)$ approaches the self-preserving form can be seen clearly for the case of constant $\beta(v,\tilde{v})$, since analytical solutions to the transformed coagulation equation can be found for certain initial distributions. The study of the case of constant $\beta(v,\tilde{v})$ should shed light on Brownian coagulation. The mathematics involved in this study also has some interest in its own right.

In this chapter, the self-preserving size spectrum for the simplified coagulation model is determined, and the transformed coagulation equation with constant $\beta(v,\tilde{v})$ is solved for systems initially possessing a particular class of gamma distributions. It is shown that the function $\Phi(\eta,\tau)$ for this class of initial distributions asymptotically approaches the self-preserving form. Finally, the method of moments is employed to show that the size spectrum of a system with an arbitrary initial distribution approaches the self-preserving form asymptotically.

A. <u>The Self-preserving Size Spectrum</u>.

If $\beta(v,\tilde{v})$ is constant, the equation for the self-preserving size spectrum represented by Eq. (16) reduces to

$$\eta \frac{d\psi}{d\eta} + \int_0^\eta \psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\,d\tilde{\eta} = 0$$

Taking the Laplace transform of this equation gives

$$-p\frac{d}{dp}\bar{\psi}(p) - \bar{\psi}(p) + \left[\bar{\psi}(p)\right]^2 = 0 \qquad (25)$$

in which $\bar{\psi}(p)$ is the Laplace transform of $\psi(\eta)$ defined as

$$\bar{\psi}(\eta) = \int_0^\infty e^{-p\eta}\psi(\eta)\,d\eta$$

Solving Eq. (25) for $\bar{\psi}(p)$ gives

$$\bar{\psi}(p) = \frac{1}{1+p}$$

The inverse transform of $\bar{\psi}(p)$ gives the self-preseving size spectrum for the case of constant $\beta(v,\tilde{v})$ *

$$\psi(\eta) = e^{-\eta}$$

It can be readily shown that this form of $\psi(\eta)$ satisfies the two normalization conditions given in Eqs. (13) and (14). The particle size distribution corresponding to this form of the self-preserving spectrum is $n(v,t) = \frac{[N(t)]^2}{\phi} \exp\left(-\frac{N(t)v}{\phi}\right)$, which has a non-zero value at $v=0$. Such a distribution is not unrealistic, as can readily be seen by writing it in terms of $n(r,t)\,dr$, which is the number concentration of particles having radii between r and $r+dr$.

$n(r,t)$ is related to $n(v,t)$ by $n(r,t) = 4\pi r^2\, n(v,t)$.

Therefore the function $n(r,t)$ corresponding to $\psi(\eta) = e^{-\eta}$ is

$$n(r,t) = \frac{4\pi r^2 [N(t)]^2}{\phi} \exp\left(-\frac{4\pi r^3 N(t)}{3\phi}\right)$$, which vanishes at $r=0$

A solution equivalent to $\psi(\eta) = e^{-\eta}$ was obtained by Schumann (7) by a different approach.

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* This is one of the few self-preserving size spectra which can be expressed in closed form. Two other self-preserving size spectra written in closed form will be given in Appendix II.

B. Particle Size Spectra for Systems Initially Possessing a Particular Class of Gamma Distribution

If $\beta(v,\tilde{v})$ is a constant, the transformed coagulation equation represented by Eq. (24) reduces to

$$2\tau\frac{\partial\Phi(\eta,\tau)}{\partial\tau}+\eta\frac{\partial\Phi(\eta,\tau)}{\partial\eta}+\int_0^{\eta}\Phi(\tilde{\eta},\tau)\Phi(\eta-\tilde{\eta},\tau)\,d\tilde{\eta}=0 \tag{26}$$

This equation is to be solved with the initial condition

$$\Phi(\eta,1)=\Phi_0(\eta)$$

Taking the Laplace transform of Eq. (26) gives

$$2\tau\frac{\partial\bar{\Phi}(p,\tau)}{\partial\tau}-p\frac{\partial\bar{\Phi}(p,\tau)}{\partial p}-\bar{\Phi}(p,\tau)+\left[\bar{\Phi}(p,\tau)\right]^2=0 \tag{27}$$

in which $\bar{\Phi}(p,\tau)$ is the Laplace transform of $\Phi(\eta,\tau)$:

$$\bar{\Phi}(p,\tau)=\int_0^{\infty}e^{-p\eta}\,\Phi(\eta,\tau)\,d\eta$$

If the Laplace transform of the initial distribution is represented by $\bar{\Phi}_0(p)$, the solution to Eq. (27) is found to be

$$\bar{\Phi}(p,\tau) = \frac{\sqrt{\tau}\;\bar{\Phi}_0(p\sqrt{\tau})}{\sqrt{\tau}\;\bar{\Phi}_0(p\sqrt{\tau}) - \bar{\Phi}_0(p\sqrt{\tau}) + 1}$$

Formally, the solution to Eq. (26) is

$$\Phi(\eta,\tau) = \frac{\sqrt{\tau}}{2\pi i}\int_{c-i\infty}^{c+i\infty} \frac{e^{p\eta}\;\bar{\Phi}_0(p\sqrt{\tau})\,dp}{\sqrt{\tau}\;\bar{\Phi}_0(p\sqrt{\tau}) - \bar{\Phi}_0(p\sqrt{\tau}) + 1} \qquad (28)$$

in which i is the imaginary unit and c is a constant greater than the greatest real part of the singular points of $\bar{\Phi}(p,\tau)$

The inversion integral given in Eq. (28) can be worked out if the initial distribution is of a particular class of gamma distributions* represented by

$$\Phi_0(\eta) = \frac{n^n}{\Gamma(n)}\,\eta^{n-1}\,e^{-n\eta} \qquad (29)$$

---

* The gamma distribution is given by (28)

$$p(x_1) = \frac{q^s}{\Gamma(s)}\,x_1^{s-1}\,e^{-q x_1} \qquad \text{for} \quad x_1 \geq 0$$

$$= 0 \qquad \text{for} \quad x_1 < 0$$

in which $q > 0$, $s > 0$.

in which n is any positive integer. Substituting the Laplace transform of $\Phi_0(\eta)$ given in Eq. (29) into Eq. (28) and carrying out the integration yields

$$\Phi(\eta,\tau) = (1-\sqrt{\tau})^{(1-n)/n} \sum_{k=1}^{n} \exp\left(\frac{2k\pi i}{n} + p_k \eta\right) \tag{30}$$

in which $p_k = \frac{n}{\sqrt{\tau}}\left[(1-\sqrt{\tau})^{1/n} \exp(2k\pi i/n) - 1\right]$

This is the solution to the transformed coagulation equation for the initial condition given in Eq. (29). It is shown in Appendix II that this solution satisfies the two normalization conditions represented by Eqs. (22) and (23).

By using Euler's formula, Eq. (30) can be rewritten as

$$\Phi(\eta,\tau) = \frac{e^{-n\eta/\sqrt{\tau}}}{(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \exp\left(\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\cos\frac{2k\pi}{n}\right) \cos\left[\frac{2k\pi}{n} + \frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\sin\frac{2k\pi}{n}\right] \tag{31}$$

which is a better form for computing $\Phi(\eta,\tau)$. The details of the algebra involved in the derivation of Eq. (31) are presented in Appendix IV.

A solution equivalent to Eq. (30) but expressed in terms of $n(v,t)$ and v was obtained by Melzak (8) by a different method.

The behavior of $\Phi(\eta,\tau)$ as $t \to \infty$ can be found by letting $\tau \to 0$ in Eq. (30). The result is

$$\lim_{\tau \to 0} \Phi(\eta,\tau) = e^{-\eta}$$

which is identical with the self-preserving spectrum $\psi(\eta) = e^{-\eta}$. This shows that the size distributions for systems initially possessing the particular class of gamma distribution represented by Eq. (29) approach the self-preserving form asymptotically. To visualize how the function $\Phi(\eta,\tau)$ approaches $e^{-\eta}$, Eq. (31) with $n = 2$ was used to compute the function $\Phi(\eta,\tau)$ for several values of τ. The results are shown in Fig. 1. It can be seen that the upper end $(\eta > 0.1)$ essentially becomes self-preserving at $\tau = 0.001$.

C. The Asymptotic Behavior of Size Spectra of Systems with Arbitrary Initial Distributions.

Although an analytical solution to the transformed coagulation equation represented by Eq. (26) does not seem possible for an arbitrary initial distribution, the asymptotic solution for long times can be found by the method of moments. Under certain conditions, a distribution is uniquely determined by its moments (29). To show that the size spectrum of a system with an arbitrary initial distribution approaches the self-preserving form $e^{-\eta}$ asymptotically, it suffices to show that the moments of the size distribution of this system asymptotically approach the moments of $e^{-\eta}$. To facilitate the discussion, the following change of variable is introduced:

$$\tau = e^{-2\theta}$$

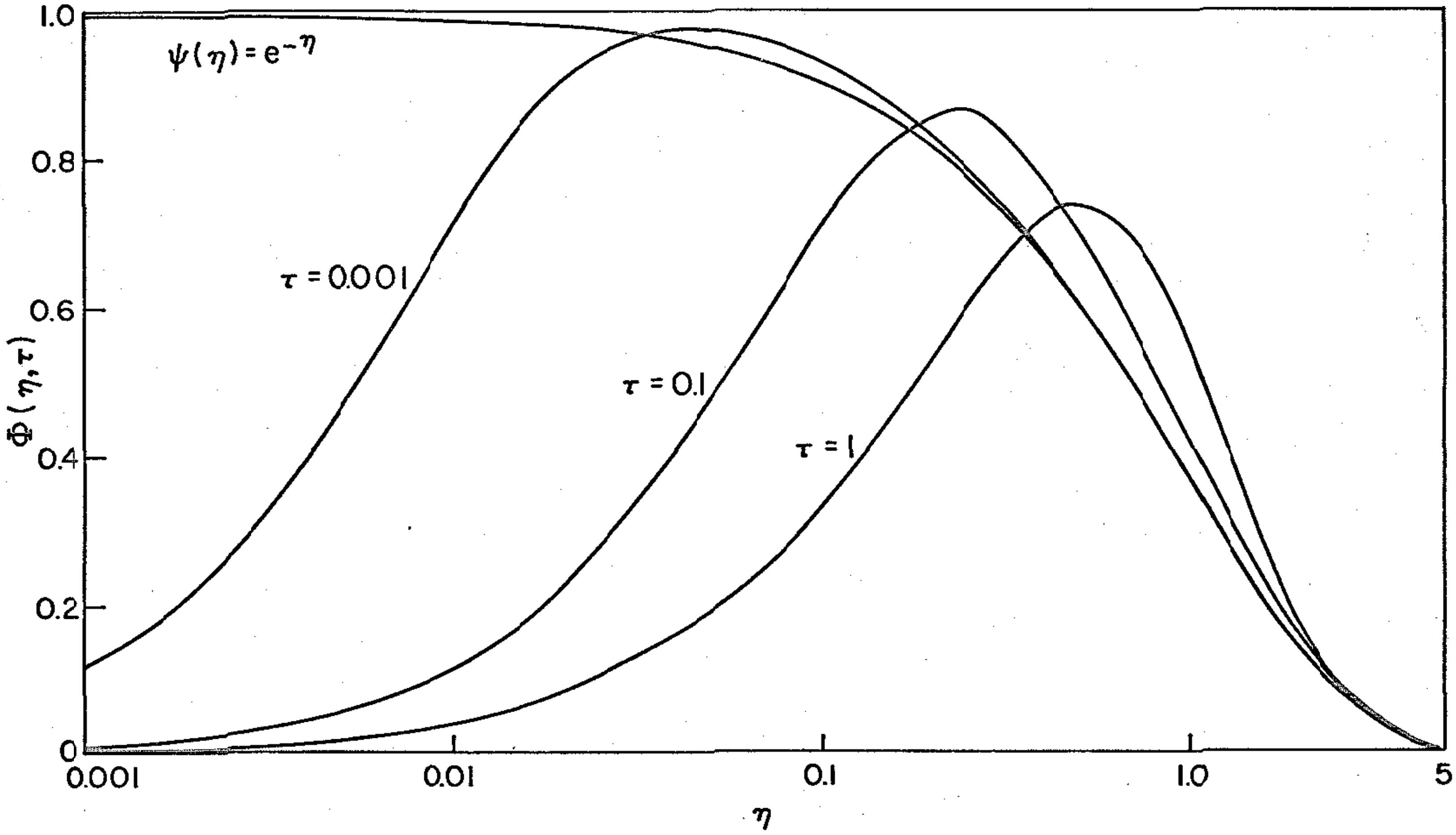

Fig. 1. The reduced spectrum function $\Phi(\eta, \tau)$ for the case of constant $\beta(v, \bar{v})$ with the initial distribution $\Phi(\eta, 1) = 4\eta e^{-2\eta}$.

θ vanishes at $\tau = 1$ (or equivalently at t = o) and approaches infinity as $\tau \rightarrow o$ (or equivalently at $t \rightarrow \infty$). The transformed coagulation equation represented by Eq. (26) becomes after change of variable:

$$\frac{\partial \Phi(\eta,\theta)}{\partial \theta} = \eta \frac{\partial \Phi(\eta,\theta)}{\partial \eta} + \int_0^{\eta} \Phi(\tilde{\eta},\theta)\Phi(\eta-\tilde{\eta},\theta)\, d\tilde{\eta} \qquad (32)$$

The n-th moment of the reduced spectrum function $\Phi(\eta,\theta)$ is defined as

$$\mu_n = \int_0^{\infty} \eta^n \Phi(\eta,\theta)\, d\eta$$

in which n is any positive interger. Multiplying both sides of Eq. (32) by η^n and integrating with respect to η from o to ∞ gives the following equation

$$\frac{d\mu_n}{d\theta} = -(n+1)\mu_n + \sum_{i=0}^{n} \binom{n}{i} \mu_i \mu_{n-i} \qquad n = 1, 2, \cdots \qquad (33)$$

in which $\binom{n}{i}$ are the binomial coefficients.

Eq. (33) is a system of first order ordinary differential equation for μ_n , n = 1, 2,... These equations can be solved one by one, starting from n = 1. The solutions to the first three equations are:

$$\mu_1(\theta) = 1$$

$$\mu_2(\theta) = 2! + [\mu_2(0) - 2!]\, e^{-\theta}$$

$$\mu_3(\theta) = 3! + 3!\,[\mu_2(0) - 2!]\, e^{-\theta} + \left\{ [\mu_3(0) - 3!] - 3!\,[\mu_2(0) - 2!] \right\} e^{-2\theta}$$

in which $\mu_n(0)$ represents the initial value of $\mu_n(\theta)$. It can be seen from these three solutions that

$$\lim_{\theta \to \infty} \mu_n(\theta) = n! \qquad \text{for} \quad n = 1, 2, 3 \tag{34}$$

A general solution for μ_n is not obvious, but it can be shown that Eq. (34) is true for all moments. (See Appendix V). It is also easy to prove that the n-th moment of the self-preserving spectrum $e^{-\eta}$ is $n!$. Thus the asymptotic value of the n-th moment of the reduced size spectrum function of a system with arbitrary initial distribution is equal to the n-th moment of the self-preserving spectrum. Since the distribution $e^{-\eta}$ is uniquely determined by its moments (see Appendix VI), it can be concluded that the size spectrum of a system approaches the self-preserving form asymptotically no matter what the initial distribution might be.

V. BROWNIAN COAGULATION

In this chapter, the self-preserving size spectrum is determined for Brownian coagulation of particles having radii larger by at least an order of magnitude than the mean free path of the medium. Because of the complexity of the collision frequency factor, an analytical solution for the whole spectrum does not seem possible. Approximate solutions are derived in closed form for the upper and the lower end of the spectrum, and a numerical solution is given for the whole spectrum.

The asymptotic behavior of the reduced spectrum function $\Phi(\eta,\tau)$ is studied by the method of moments. The system of ordinary differential equations for the moments of $\Phi(\eta,\tau)$ is too complicated to be attacked in the same manner as in the case of constant $\beta(v,\tilde{v})$. Nevertheless, the values of the moments of $\Phi(\eta,\tau)$ seem to approach the moments of the self-preserving spectrum asymptotically.

The inclusion of the Cunningham slip correction for Stokes' friction formula destroys the homogeneity of the collision frequency factor $\beta(v,\tilde{v})$, and therefore makes the similarity transformation inapplicable. The idea of quasi-self-preservation, according to which the reduced spectrum function varies slowly with time, is introduced to solve this problem. By neglecting the τ-derivative term, the transformed coagulation equation can be solved as an ordinary integro-differential equation containing a time-dependent parameter. The solution to this simplified equation for each value of the parameter is called a quasi-self-preserving size spectrum. Approximate analytical solutions are derived for the upper and the lower ends of these spectra, and numerical solutions for the whole spectrum are given for several values of the time-dependent parameter.

A. The Self-preserving Size Spectrum for Brownian Coagulation (in the Absence of a Slip Correction).

The equation for the self-preserving size spectrum for Brownian coagulation of particles in a stationary medium is given by Eq. (17), viz.

$$(1+\mu^*_{1/3}\mu^*_{-1/3})\eta\frac{d\psi}{d\eta} + (2\mu^*_{1/3}\mu^*_{-1/3} - \mu^*_{-1/3}\eta^{1/3} - \mu^*_{1/3}\eta^{-1/3})\psi(\eta)$$
$$+\int_0^\eta \psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\left[1+\left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right]d\tilde{\eta} = 0 \tag{17}$$

in which $\mu^*_{1/3}$ amd $\mu^*_{-1/3}$ are two undetermined constants given by Eqs. (18) and (19):

$$\mu^*_{1/3} = \int_0^\infty \eta^{1/3}\psi(\eta)\,d\eta \tag{18}$$

$$\mu^*_{-1/3} = \int_0^\infty \eta^{-1/3}\psi(\eta)\,d\eta \tag{19}$$

The integral term in Eq. (17) comes from the convolution integral in the original coagulation equation (Eq. (8)), and therefore represents the gain of particles by coagulation of smaller particles. A part of the second term in Eq. (17) comes from the second integral term in Eq. (8). The second term in Eq. (17) therefore partly represents the loss of particles due to coagulation.

The two undetermined constants in Eq. (17) can be reduced to one by the following transformation:

$$\psi(\eta) = \frac{(1+\mu^*_{1/3}\,\mu^*_{-1/3})^4}{(\mu^*_{1/3})^3}\,\chi(\xi) \qquad (35)$$

$$\eta = \frac{(\mu^*_{1/3})^3}{(1+\mu^*_{1/3}\,\mu^*_{-1/3})^3}\,\xi \qquad (36)$$

Substitution of these two equations into Eq. (17) yields:

$$\xi\frac{d\chi(\xi)}{d\xi} + \left[2\alpha - \alpha(1-\alpha)\,\xi^{1/3} - \xi^{-1/3}\right]\chi(\xi)$$

$$+ \int_0^{\xi}\chi(\tilde{\xi})\,\chi(\xi-\tilde{\xi})\left[1+\left(\frac{\xi-\tilde{\xi}}{\tilde{\xi}}\right)^{1/3}\right]d\xi = 0$$

(37)

which contains only one constant α given by

$$\alpha = \frac{\mu^*_{1/3}\,\mu^*_{-1/3}}{1+\mu^*_{1/3}\,\mu^*_{-1/3}} \qquad (38)$$

In terms of $\chi(\xi)$, the two normalization conditions (Eqs. (13) and (14)) and the two defining equations for $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ (Eqs. (18) and (19)) become

$$\int_0^\infty \chi(\xi)\, d\xi = 1 - \alpha \tag{39}$$

$$\int_0^\infty \xi \chi(\xi) d\xi = \frac{1}{(\mu^*_{1/3})^3 (1-\alpha)^2} \tag{40}$$

$$\int_0^\infty \xi^{1/3} \chi(\xi) d\xi = 1 \tag{41}$$

$$\int_0^\infty \xi^{-1/3} \chi(\xi)\, d\xi = \alpha(1-\alpha) \tag{42}$$

Eq. (37) is an ordinary integro-differential equation for $\chi(\xi)$, to be solved with the constraints given in Eqs. (39) through (42). Although an analytical solution does not seem possible, approximate solutions can be derived for the lower end and the upper end of the spectrum.

For the lower end of the spectrum, the integral term in Eq. (37) can be neglected since the product of $\chi(\xi)$ is much smaller than $\frac{d\chi(\xi)}{d\xi}$ and $\chi(\xi)$ itself as $\xi \to 0$. (This assumption can be checked later). Eq. (37) then becomes a first order ordinary differential equation:

$$\xi \frac{d\chi(\xi)}{d\xi} + \left[2\alpha - \alpha(1-\alpha)\xi^{1/3} - \xi^{-1/3}\right]\chi(\xi) = 0$$

The general solution to this equation is

$$\chi(\xi) = \frac{C_1}{\xi^{2\alpha}} \exp\left[3\alpha(1-\alpha)\xi^{1/3} - 3\xi^{-1/3}\right] \qquad (43)$$

in which C_1 is an integration constant to be determined by the constraints on $\chi(\xi)$. Substitution of this form for $\chi(\xi)$ into Eq. (37) confirms the assumption that the integral term is negligible for small ξ. This can be explained by the fact that the gain of particles by coagulation of smaller particles is not important in the lower end of the spectrum.

For the upper end of the spectrum, the second term in Eq. (37) is negligible if it is assumed that $\chi(\xi)$ and $\frac{d\chi(\xi)}{d\xi}$ are of the same order of magnitude. Neglecting the second term in Eq. (37) gives

$$\xi \frac{d\chi(\xi)}{d\xi} + \int_0^{\xi} \chi(\tilde{\xi})\chi(\xi-\tilde{\xi})\left[1 + \left(\frac{\xi-\tilde{\xi}}{\tilde{\xi}}\right)^{1/3}\right]d\tilde{\xi} = 0$$

(44)

A solution to this equation is

$$\chi(\xi) = \frac{C_2\, e^{-C_2 \xi}}{1 + B(\frac{2}{3}, \frac{4}{3})} \tag{45}$$

in which B is the beta function, and C_2 is a constant to be determined by the constraints on $\chi(\xi)$. In obtaining this solution, the integral term in Eq. (44) is evaluated by using Eq. (45) for $\chi(\xi)$ throughout the whole range of integration. This is not exact since the lower end of the spectrum cannot be described by Eq. (45). However, when the upper limit of the integral is large, it can be shown that the value of the integral term evaluated in this way differs only by a small percentage from that evaluated by using the exact form for $\chi(\xi)$ at the lower end of the spectrum. Substitution of Eq. (45) into Eq. (37) shows that the second term is indeed much smaller than the other terms. This can be partly explained by the fact that the loss of particles by coagulation is not important in the upper end of the spectrum.

The evaluation of the constants C_1, C_2 and α in Eqs. (43) and (45) requires information on the whole spectrum. Since no simple approximate expression is available for the central part of the spectrum, these constants were evaluated by numerical solution of Eq. (37), using the IBM 7094 computer at the California Institute of Technology. Eq. (37) can be solved as a first order ordinary differential equation by any standard finite difference method. To facilitate numerical computation, Eq. (37) was transformed into the following form

$$\frac{dY(x)}{dx} = \left[\alpha(1-\alpha)e^{x/3} + e^{-x/3} - 2\alpha\right] Y(x)$$

$$- \int_{-\infty}^{x} Y(\tilde{x})Y(\ln(e^{x} - e^{\tilde{x}}))\left[1 + \left(\frac{e^{x}-e^{\tilde{x}}}{e^{\tilde{x}}}\right)^{1/3}\right] e^{\tilde{x}}\, d\tilde{x} \tag{46}$$

by the changes of variables $\xi = e^{x}$ and $Y(x) = \chi(\xi)$. The advantage of this transformation is that $Y(x)$ looks approximately like a normal distribution, whereas $\chi(\xi)$ is a highly skew distribution. The range of the argument of $Y(x)$ spans from $-\infty$ to ∞. The numerical calculation was carried out only for the range between $x = -4.4$ and $x = 5.4$, since the values of $Y(x)$ outside this range are negligibly small. The Adams extrapolation formula (30) truncated after the fourth difference term was used to compute $Y(x)$ at an interval $\Delta x = 0.1$. The integral term in Eq. (46) was transformed into the form

$$\frac{3e^{x}}{2} \int_{0}^{\infty} Y(x - \tfrac{3}{2}z)Y(x + \ln(1 - e^{-3Z/2}))\left[e^{-Z/2} + (1 - e^{-3Z/2})^{1/3}\right] e^{-Z}\, dZ$$

by the change of variable $z = \frac{2}{3}(x - \tilde{x})$. The value of this integral was computed by the 32-point Gaussian-Laguerre quadrature formula (31). The starting values for $Y(x)$ were calculated from the approximate solution for small η given in Eq. (43). Since Eqs. (43) and (46) contain two undetermined constants C_1 and α, the numerical calculation described above involves a trial-and-error procedure. Values for C_1 and α were first assumed for computing $Y(x)$ and then checked by Eqs. (39), (41) and (42). The integrals in Eqs. (39) through (42) were also evaluated by Gaussian-Laguerre quadrature formula. It was found that the assumed values of $C_1 = 0.2788$ and $\alpha = 0.53$ gave a satisfactory result.

$$\int_0^\infty \chi(\xi)\,d\xi = 0.4674 \qquad \text{compared with} \qquad 1-\alpha = 0.4700$$

$$\int_0^\infty \xi^{1/3}\chi(\xi)\,d\xi = 1.0001 \qquad \text{compared with} \qquad 1$$

$$\int_0^\infty \xi^{-1/3}\chi(\xi)\,d\xi = 0.2491 \qquad \text{compared with} \qquad \alpha(1-\alpha) = 0.2491$$

The value of the constant $\mu^*_{1/3}$ was computed by Eq. (40) and found to be 0.9046. The constant $\mu^*_{-1/3}$ was found to be 1.2480 by Eq. (38). The values of these two constants were then used to calculate $\psi(\eta)$ by Eq. (35). The results thus obtained are given in Table 1, and compared with Hidy's limiting solution for the discrete spectrum (27) in Fig. 2. The agreement between these two curves is fair.

It is interesting to note that the self-preserving size spectrum does not depend on the physical properties of the medium. The particle

Table 1. Self-preserving particle size distribution for Brownian coagulation obtained from Eq. (17) by finite-difference method.

η	$\psi(\eta)$
0.0010	0.0030
0.0019	0.0165
0.0035	0.0593
0.0052	0.1154
0.0070	0.1750
0.0104	0.2764
0.0190	0.4593
0.0345	0.6409
0.0515	0.7394
0.0695	0.7943
0.1037	0.8373
0.1400	0.8451
0.2089	0.8215
0.3444	0.7371
0.5138	0.6279
0.6935	0.5256
1.0346	0.3729
1.8852	0.1572
3.4351	0.0317
5.1246	0.0050

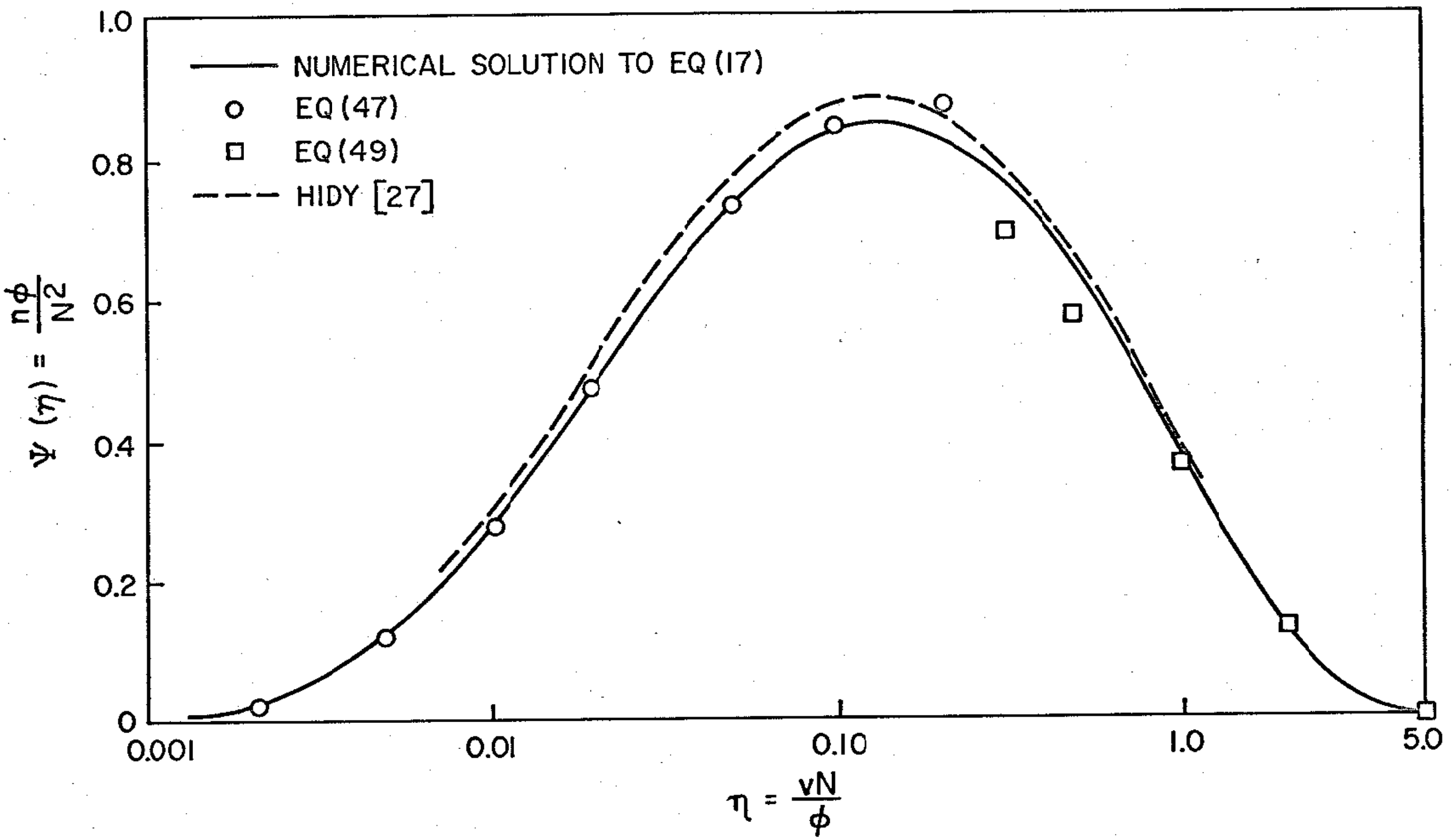

Fig. 2. Self-preserving particle size distribution for Brownian coagulation. The form is very approximately lognormal. The result obtained by solution of the ordinary integro-differential equation for the continuous spectrum is compared with Hidy's limiting solution for the discrete spectrum.

size distribution of a self-preserving system is uniquely determined by its total number concentration N and total volume concentration ϕ, and is independent of the viscosity and the temperature of the medium.

Substituting $C_1 = 0.2788$ and $\alpha = 0.53$ into Eq. (43) and transforming $\chi(\xi)$ and ξ back into $\psi(\eta)$ and η gives the following approximate expression for the lower end of the spectrum:

$$\psi(\eta) = \frac{0.5086}{\eta^{1.06}} \exp\left(1.758\,\eta^{1/3} - 1.275\,\eta^{-1/3}\right) \tag{47}$$

The approximate expression for the upper end of the spectrum given in Eq. (45) can be rewritten in terms of $\psi(\eta)$ and η:

$$\psi(\eta) = \frac{(1+\mu^*_{1/3}\mu^*_{-1/3})\, C_3\, e^{-C_3\eta}}{1 + B\left(\frac{2}{3}, \frac{4}{3}\right)} \tag{48}$$

in which $C_3 = C_2 \left(\dfrac{1+\mu^*_{1/3}\mu^*_{-1/3}}{\mu^*_{1/3}} \right)^3$

The values of C_3 can be estimated by fitting this expression to the upper end of the spectrum obtained numerically. It was found that Eq. (48) with $C_3 = 0.95$ fits the upper end of the spectrum fairly well. Inserting numerical values for $\mu^*_{1/3}, \mu^*_{-1/3}$ and C_3 into Eq. (48) gives the approximate expression for the upper end of the spectrum:

$$\psi(\eta) = 0.915\, e^{-0.95\eta} \tag{49}$$

Values for $\psi(\eta)$ computed by Eqs. (47) and (49) are plotted in Fig. 2 for comparison with the numerical solution. The agreement between these two results is satisfactory for $\eta < 0.1$ and $\eta > 1.0$.

The self-preserving spectrum for the case of constant $\beta(v, \tilde{v})$ and that for Brownian coagulation are compared in Fig. 3. It can be seen that the upper ends of the two self-preserving spectra almost coincide with each other.

The self-preserving spectrum for Brownian coagulation has a maximum value 0.8452 at $\eta = 0.136$. Since it looks approximately like a log-normal distribution, a log-normal distribution with its peak coincided with that of Brownian self-preserving spectrum is also shown in Fig. 3 for comparison. The log-normal distribution is represented by

$$\psi_{LN}(\eta) = \frac{0.292}{\eta} \exp\left[-0.268\,(\ln\eta + 0.1327)^2\right]$$

which has been normalized to satisfy the condition

$$\int_0^\infty \psi_{LN}(\eta)\, d\eta = 1$$

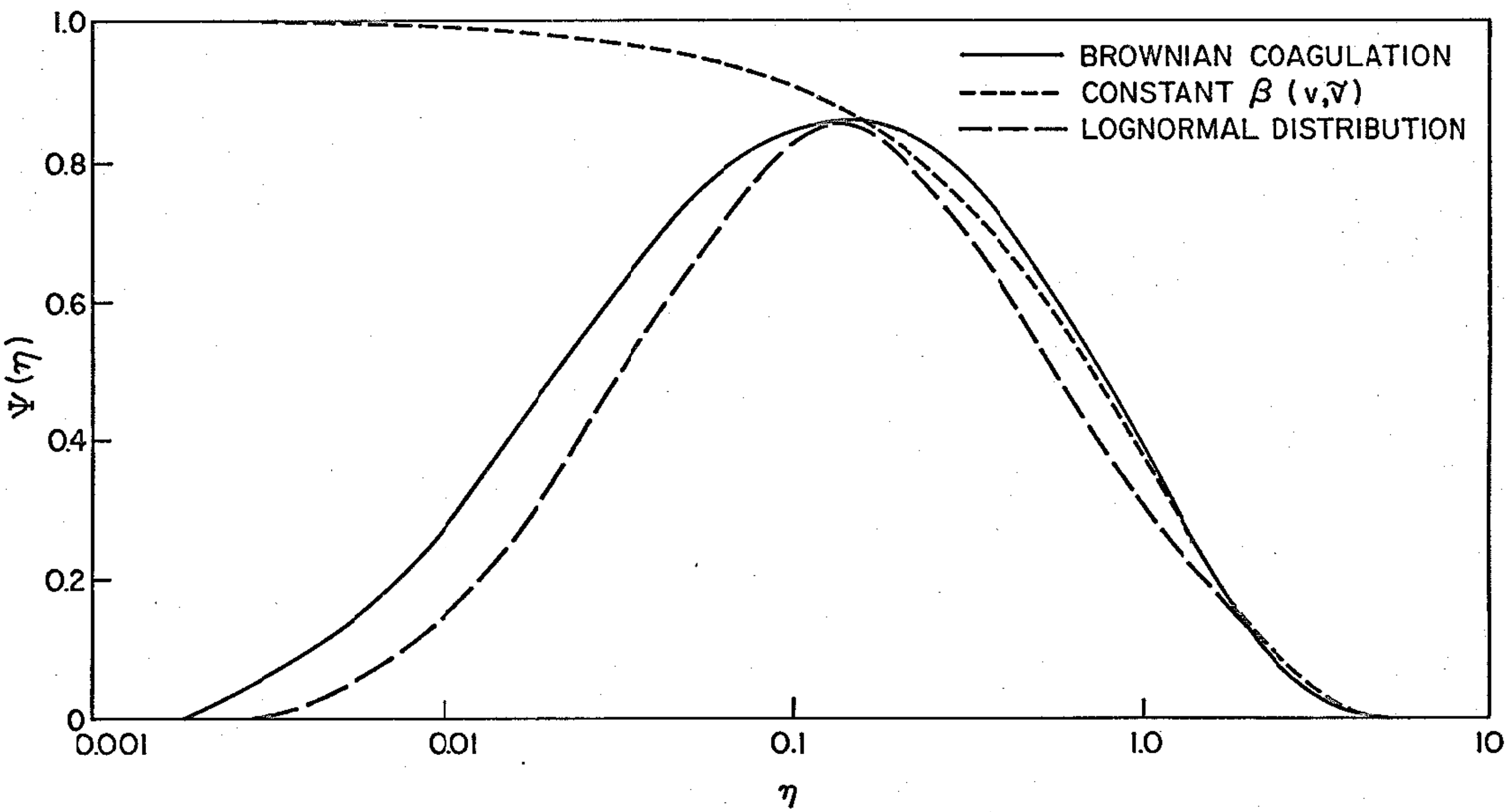

Fig. 3. Comparison of a lognormal distribution with the self-preserving size spectra for the case of constant $\beta(v, \tilde{v})$ and for Brownian coagulation

B. Concerning the Unimodality of the Self-preserving Spectrum for Brownian Coagulation.

Some arguments can be given to support the result of the numerical calculation that the self-preserving distribution is unimodal. Since $\psi(\eta)$ is non-negative and its first derivative vanishes at a maximum, it can be seen from Eq. (17) that maxima can occur only when the coefficient of $\psi(\eta)$ in the second term is negative. The coefficient of $\psi(\eta)$ has negative value when $\eta < (\mu^*_{1/3})^3 \left(1 - \sqrt{1 - \frac{1}{\mu^*_{1/3}\mu^*_{-1/3}}}\right)^3$ or $\eta > (\mu^*_{1/3})^3 \left(1 + \sqrt{1 - \frac{1}{\mu^*_{1/3}\mu^*_{-1/3}}}\right)^3$. It can be shown by Schwarz' inequality that $\mu^*_{1/3}\,\mu^*_{-1/3} \geq 1$. Since $\psi(\eta)$ satisfies the two normalization conditions given in Eqs. (13) and (14), it seems reasonable to assume that $\mu^*_{1/3}\,\mu^*_{-1/3}$ has a value near 1.1 and $\mu^*_{1/3}$ has a value near 0.9. With these numerical values for $\mu^*_{1/3}$ and $\mu^*_{1/3}\,\mu^*_{-1/3}$, the coefficient of $\psi(\eta)$ is negative when $\eta < 0.25$ or $\eta > 1.6$. If any maximum occurs in the lower end $(\eta < 0.25)$, it must lie very close to $\eta = 0.25$, since the integral term in Eq. (17) is negligibly small and hence cannot compensate for the relatively high negative value of the second term for very small η. The integral term continues to increase after $\psi(\eta)$ reaches its first peak, while the second term is vanishing when η is approaching the value 0.25. The increasing positive value of the integral term must now be counterbalanced by the increasing negative value of the first term containing the derivative $\frac{d\psi}{d\eta}$. Therefore, there should be no maximum between the first maximum and $\eta = 0.25$. Thus if there is a second maximum, it must occur in the upper end ($\eta > 1.6$). In the upper end, it seems not unreasonable to assume that $\psi(\eta)$ can at most be the same order of magnitude as $\frac{d\psi}{d\eta}$. The second term in Eq. (17) therefore can be neglected. The first term must always be negative to compensate for the positive integral term. This implies that there is no maximum in the upper end.

The above arguments indicate that there can be at most one maximum which occurs near $\eta = 0.25$. Since the Brownian self-preserving spectrum vanishes at both ends, there should be at least one maximum in the spectrum. These arguments indicate that the self-preserving size distribution is unimodal. The position of the maximum is predicted to occur in the range $\eta < 0.25$, which is in agreement with the numerical solution (the peak occurs at $\eta = 0.136$).

C. Checking the Numerical Solution by the Relationships Among the Moments of $\psi(\eta)$.

The accuracy of the numerical solution to Eq. (17) can be checked using certain relationships among the moments of the self-preserving size spectrum. For this purpose, the definition of the moment is generalized to include nonintegral moments. If ν is a real number, the ν-th moment of the function $\psi(\eta)$ is defined as

$$\mu_\nu^* = \int_0^\infty \eta^\nu \psi(\eta)\, d\eta \qquad (50)$$

The values of the moments can be obtained by numerical integration using values of $\psi(\eta)$ given in Table 1.

Multiplying both sides of Eq. (17) by η^n (n = integer) and integrating with respect to η from 0 to ∞ gives the following relationships among the moments of $\psi(\eta)$:

$$\mu^*_n = \frac{\sum_{i=1}^{n-1} \binom{n}{i} \left(\mu^*_i \mu^*_{n-i} + \mu^*_{i+1/3} \mu^*_{n-i-1/3} \right)}{(n-1)\left(1 + \mu^*_{1/3} \mu^*_{-1/3}\right)} \qquad (51)$$

$$n = 2, 3, \cdots$$

in which $\binom{n}{i}$ are the binomial coefficients. Eq. (51) can be used to compute the values of integral moments from the lower moments evaluated by Eq. (50). The values of the integral moments calculated from Eq. (51) can be compared with those from Eq. (50). Table 2 shows that the agreement between the values of μ^*_n , n = 2,3,4,5, obtained in these two different ways is satisfactory. In evaluating μ^*_i from Eq. (50), the integral was divided into two parts. The first part, covering the range of η from 0 to 1.05, was evaluated by Simpson's rule, using the value of $\psi(\eta)$ given in Table 1. The approximate expression for the upper end of the spectrum given in Eq. (49) was used in calculating the second part of the integral covering the range of η from 1.05 to infinity.

D. Some Physical Properties of Self-preserving Systems.

For the case of constant $\beta(v, \tilde{v})$, the time rate of change of the total number concentration of particles given in Eq. (9)

Table 2. Comparison of the integral moments of the self-preserving spectrum for Brownian coagulation evaluated by Eq. (50) and Eq. (51) respectively.

	From Eq. (50)	From Eq. (51)
μ_2^*	2.014	2.029
μ_3^*	6.100	6.087
μ_4^*	24.77	24.54
μ_5^*	125.9	124.3

reduces to

$$\frac{dN}{dt} = -\frac{4kT}{3\mu} N^2 \qquad \left[\text{for } \beta(v,\tilde{v}) = \frac{8kT}{3\mu}\right] \tag{52}$$

which indicates that the decrease of N is second order with a rate constant $K_c = 4kT/3\mu$. Solving Eq. (52) for N yields:

$$N(t) = \frac{1}{\frac{1}{N(0)} + \frac{4kT}{3\mu}t}$$

For Brownian coagulation, Eq. (9) can be integrated to give

$$\frac{dN}{dt} = -\frac{2kT}{3\mu}\left(N^2 + m_{1/3}\, m_{-1/3}\right) \tag{53}$$

in which $m_{1/3}$ and $m_{-1/3}$ are functions of time given by

$$m_{1/3} = \int_0^\infty v^{1/3} n(v, t)\, dv$$

$$m_{-1/3} = \int_0^\infty v^{-1/3} n(v, t)\, dv$$

Since it is not possible to express $m_{1/3}$ and $m_{-1/3}$ explicitly as functions of N when the form of $n(v, t)$ is undetermined, an explicit solution for N cannot be obtained from Eq. (53).

If the particle size distribution is self-preserving, the right side of Eq. (9) can be written in terms of $\psi(\eta)$ and then integrated to yield

$$\frac{dN}{dt} = -\frac{2kT}{3\mu}\left(1+\mu^*_{1/3}\,\mu^*_{-1/3}\right)N^2 \tag{54}$$

in which $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ are respectively the one third and negative one third moments of $\psi(\eta)$. Eq. (54) was originally derived by Swift and Friedlander (26). Since $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ are constants, Eq. (54) indicates that the decrease of N is second order with a rate constant $K_{SB} = \frac{2kT}{3\mu}\left(1+\mu^*_{1/3}\mu^*_{-1/3}\right)$. The ratio of the rate constant for a self-preserving system to that for a homogeneous system (equivalent to the case of constant $\beta(v,\tilde{v})$) is

$$\frac{K_{SB}}{K_c} = \frac{1+\mu^*_{1/3}\,\mu^*_{-1/3}}{2} \tag{55}$$

Inserting the numerical values for $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ into Eq. (55) gives $\frac{K_{SB}}{K_c} = 1.065$. The experimental value of this ratio determined by Swift and Friedlander for oil-in-water emulsions is 1.162 (26).

Eq. (54) can be solved to give the expression for N of a self-preserving system:

$$N(t) = \frac{1}{\frac{1}{N(0)} + K_{SB}\, t} \tag{56}$$

Dividing ϕ by N(t) given in Eq. (56) yields the expression for the average volume of particles in a self-preserving system:

$$\overline{v(t)} = \overline{v(0)} + K_{SB}\, \phi\, t$$

which shows that $\overline{v(t)}$ is a linear function of time.

The total surface area of particles in a unit volume of the system is given by

$$A_S(t) = (36\pi)^{1/3} \int_0^\infty v^{2/3} n(v,t)\, dv \tag{57}$$

If the size spectrum is self-preserving, Eq. (57) becomes:

$$\begin{aligned} A_S(t) &= (36\pi)^{1/3} \mu^*_{2/3}\, \phi^{2/3} N^{1/3} \\ &= 4.4 \quad \phi^{2/3} N^{1/3} \end{aligned} \tag{58}$$

$A_S(t)$ can be expressed as a function of time by substituting the expression for N(t) given in Eq. (56) into Eq. (58)

$$A_s(t) = \frac{(36\pi)^{1/3}\,\mu^*_{2/3}\,\phi^{2/3}}{\left[\frac{1}{N(0)} + K_{SB}t\right]^{1/3}}$$

$$= \frac{4.4\ \phi^{2/3}}{\left[\frac{1}{N(0)} + K_{SB}t\right]^{1/3}}$$

If the density of particles is ρ_p, the total mass of particles with volume larger than v in a unit volume of the system is given by

$$M(v,t) = \rho_p \int_v^\infty v\,n(v,t)\,dv \qquad (59)$$

For a self-preserving system, Eq. (59) becomes

$$M(v,t) = \rho_p\,\phi \int_{\frac{Nv}{\phi}}^\infty \eta\,\psi(\eta)\,d\eta \qquad (60)$$

The approximate expression for the upper end of the self-preserving size spectrum given in Eq. (49) can be substituted into Eq. (60) to obtain

$$M(v,t) = 1.014\,\rho_p\,(\phi + 0.95\,Nv)\,e^{-\frac{0.95\,Nv}{\phi}}$$

which is the total mass of particles with volume larger than v in a unit volume of the system. The equation is valid only for $v > \overline{v(t)}$

Differentiating the above expression for $M(v,t)$ with respect to time yields the rate of transfer of mass into the upper end of the size spectrum

$$\frac{\partial M(v,t)}{\partial t} = 0.915\, K_{SB}\, \rho_P\, v^2 N^3\, e^{-\frac{0.95 N v}{\Phi}} \qquad (v > \overline{v(t)})$$

E. Asymptotic Behavior of Particle Size Distributions for Brownian Coagulation

1. Approximate Solutions for the Lower and the Upper Ends of the Reduced Size Spectrum.

The analytical results obtained in Chapter IV show that the self-preserving hypothesis holds for the case of constant $\beta(v,\tilde{v})$. The collision frequency factor for Brownian coagulation is too complicated to permit the problem to be attacked in the same way as in the case of constant $\beta(v,\tilde{v})$. Nevertheless, some arguments can be given to support the self-preserving hypothesis for Brownian coagulation.

Substituting the expression of $\beta(v,\tilde{v})$ given in Eq. (3) into Eq. (24) yields the transformed kinetic equation for Brownian coagulation:

$$(1+\mu_{1/3}\mu_{-1/3})\eta\frac{\partial\Phi}{\partial\eta} + 2(1+\mu_{1/3}\mu_{-1/3})\tau\frac{\partial\Phi}{\partial\tau} + (2\mu_{1/3}\mu_{-1/3} - \mu_{-1/3}\eta^{1/3} - \mu_{1/3}\eta^{-1/3})\Phi(\eta,\tau)$$
$$+ \int_0^{\eta}\left[1+\left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right]\Phi(\tilde{\eta},\tau)\,\Phi(\eta-\tilde{\eta},\tau)\,d\tilde{\eta} = 0 \qquad (61)$$

in which $\mu_{1/3}$ and $\mu_{-1/3}$ are functions of time given by

$$\mu_{1/3} = \int_0^{\infty}\eta^{1/3}\,\Phi(\eta,\tau)\,d\eta \qquad (62)$$

$$\mu_{-1/3} = \int_0^{\infty}\eta^{-1/3}\,\Phi(\eta,\tau)\,d\eta \qquad (63)$$

An analytical solution to Eq. (61) does not seem possible. However, the general solution to the equation obtained by neglecting the integral term in Eq. (61) is

$$\Phi(\eta,\tau) = f(\eta/\tau^{1/2})\,\exp\left\{\frac{\tau^{1/6}}{2\eta^{1/3}}\int\frac{\mu_{1/3}\,d\tau}{(1+\mu_{1/3}\mu_{-1/3})\tau^{7/6}} + \frac{\eta^{1/3}}{2\tau^{1/6}}\int\frac{\mu_{-1/3}\,d\tau}{(1+\mu_{1/3}\mu_{-1/3})\tau^{5/6}}\right.$$
$$\left. - \int\frac{\mu_{1/3}\mu_{-1/3}\,d\tau}{(1+\mu_{1/3}\mu_{-1/3})\tau}\right\} \qquad (64)$$

in which $f(\eta/\tau^{1/2})$ is an arbitrary function of $\eta/\tau^{1/2}$ to be determined by the initial distribution and the constraints on $\Phi(\eta,\tau)$.

It can also be shown that a particular solution to the equation obtained by neglecting the third term in Eq. (61) is

$$\bar{\Phi}(\eta,\tau) = C \exp\left\{ - \frac{C'[1+B(\frac{2}{3},\frac{4}{3})]\eta}{2\sqrt{\tau}} \int \frac{d\tau}{(1+\mu_{1/3}\mu_{-1/3})\sqrt{\tau}} \right\} \qquad (65)$$

in which B is the beta function and C is a constant to be determined by the constraints on $\Phi(\eta,\tau)$.

Eqs. (64) and (65) are not sufficient to determine the whole spectrum, since they are approximate solutions for the lower end and the upper end only. However, it is interesting to note that, if $\mu_{1/3}$ and $\mu_{-1/3}$ are assumed to vary slowly with time, Eqs. (64) and (65) approach asymptotically the approximate expressions for the lower end and the upper end of the self-preserving spectrum given in Eqs. (47) and (49) respectively.

2. Relationships Among the Moments of the Reduced Size Spectrum.

Some arguments based on the moments of the distribution can be given to support the conjecture that the self-preserving spectrum is also the asymptotic spectrum approached at the later stages of Brownian coagulation. To facilitate the discussion, the following change of variable is introduced:

$$\theta_1 = \frac{1}{2} \int_{\tau}^{1} \frac{d\tau}{(1+\mu_{1/3}\mu_{-1/3})\tau}$$

θ_1 vanishes at $\tau = 1$ (or equivalently at $t = 0$) and approaches infinity as $\tau \rightarrow 0$ (or equivalently as $t \rightarrow \infty$), if $\mu_{1/3}$ and $\mu_{-1/3}$ are assumed to remain finite for $0 \leq \tau \leq 1$. Eq. (61) becomes after change of variable:

$$\frac{\partial \Phi(\eta,\theta_1)}{\partial \theta_1} = (1+\mu_{1/3}\mu_{-1/3})\eta\frac{\partial \Phi}{\partial \eta} + (2\mu_{1/3}\mu_{-1/3} - \mu_{-1/3}\eta^{1/3} - \mu_{1/3}\eta^{-1/3})\Phi(\eta,\theta_1)$$
$$+ \int_0^{\eta} \left[1 + \left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right] \Phi(\tilde{\eta},\theta_1)\Phi(\eta-\tilde{\eta},\theta_1)\, d\tilde{\eta} \qquad (66)$$

This is another form of the kinetic equation for Brownian coagulation. The definition of the moment is generalized to include the nonintegral moments. If ν is any real number, the ν-th moment of the reduced size distribution $\Phi(\eta, \theta_1)$ is defined as:

$$\mu_{\nu} = \int_0^{\infty} \eta^{\nu} \Phi(\eta, \theta_1)\, d\eta$$

An expression for the time rate of change of the n-th moment (n = integer) of $\Phi(\eta, \theta_1)$ can be derived by multiplying both sides of Eq. (66) by η^n and integrating with respect to η from 0 to ∞ :

$$\frac{d\mu_n}{d\theta_1} = -(n-1)(1+\mu_{1/3}\mu_{-1/3})\mu_n + \sum_{i=1}^{i=n-1} \binom{n}{i} (\mu_i\mu_{n-i} + \mu_{n-i-1/3}\mu_{i+1/3})$$

$$n = 2, 3, \cdots \qquad (67)$$

in which $\binom{n}{i}$ are the binomial coefficients. Eq. (67) is a system of first order ordinary differential equations for μ_n , n=2,3,4,... . These equations are not sufficient to solve for μ_n since they contain the nonintegral moments $\mu_{n\pm 1/3}$, n = 0,1,..., whose time rate of change cannot be calculated from Eq. (66). Nevertheless, the asymptotic behavior of the moments can be examined at least approximately by introducing a family of time dependent functions $a_{i,j}(\theta_1)$ defined as:

$$a_{ij}(\theta_1) = \frac{\mu_{i+1/3}\,\mu_{j-1/3}}{\mu_i\,\mu_j}$$

Replacing $\mu_{i+1/3}\,\mu_{j-1/3}$ by $a_{ij}(\theta_1)\mu_i\mu_j$ in Eq. (67) yields

$$\frac{d\mu_n}{d\theta_1} + (n-1)(1+a_{0,0})\mu_n = \sum_{i=1}^{n-1} \binom{n}{i} (1+a_{i,n-i})\mu_i\,\mu_{n-i}$$

$$n = 2, 3, \cdots \qquad (68)$$

The exact solution to Eq. (68) with n = 2 is

$$\mu_2 = C\, e^{-\int (1+a_{0,0})\,d\theta_1} + 2\, e^{-\int (1+a_{0,0})\,d\theta_1} \int (1+a_{1,1})\, e^{\int (1+a_{0,0})\,d\theta_1}\, d\theta_1 \tag{69}$$

in which the integration constant C is determined by the initial distribution. The integration in the right side of Eq. (69) cannot be carried out, since the forms of the functions $a_{i,j}(\theta_1)$ are unknown. However, it seems not unreasonable to assume that the

$a_{i,j}(\theta_1)$ vary slowly with θ_1 and approach certain constant values $a^*_{i,j}$ when θ_1 becomes sufficiently large. With this assumption, it can be shown from Eq. (69) that

$$\lim_{\theta_1 \to \infty} \mu_2 = \frac{2(1+a^*_{1,1})}{1+a^*_{0,0}}$$

or written in terms of μ_ν

$$\lim_{\theta_1 \to \infty} \mu_2 = \lim_{\theta_1 \to \infty} \frac{2(1+\mu_{2/3}\mu_{4/3})}{1+\mu_{1/3}\mu_{-1/3}} \tag{70}$$

Eq. (70) is identical to Eq. (51) with n = 2, which is the relationship among the moments of the self-preserving spectrum. Relationships for the asymptotic values of higher moments of $\Phi(\eta, \theta_1)$ can be obtained by the same arguments, and shown to be identical to those given in Eq. (51).

To prove by the method of moments that the self-preserving size spectrum is the asymptotic solution to the coagulation equation, it is necessary to show that (1) the moments of the reduced size spectrum $\Phi(\eta, \tau)$ approach those of the self-preserving spectrum asymptotically, and that (2) this sequence of moments determines a unique distribution. The above analysis merely suggests (but does not prove) that the relationships among the moments of the reduced size spectrum of a system with an arbitrary initial distribution asymptotically approach the relationships among moments of the self-preserving spectrum. It remains to be shown that the infinite number of relationships given in Eq. (51) determine a unique distribution. Thus the proof of the self-preserving hypothesis for Brownian coagulation is incomplete.

F. Particle Size Distributions for Brownian Coagulation with the Cunningham Slip Correction.

1. Quasi-self-preserving Size Spectra

If the particle radii are of the same order of magnitude as the mean free path of the medium, the Cunningham slip correction for Stokes' friction formula may be used to account for the increased particle mobility. The inclusion of a slip correction destroys the homogeneity of the collision frequency factor and makes the similarity transformation represented by Eq. (15) inapplicable. However, the coagulation equation with the slip correction can still be transformed by the general transformation given in Eq. (21). To simplify the analysis, the exponential term in the Cunningham slip correction will be neglected. The collision frequency factor of Eq. (4) can then be written as

$$\beta(v_i, v_j) = \frac{2kT}{3\mu}\left(v_i^{1/3} + v_j^{1/3}\right)\left(\frac{1}{v_i^{1/3}} + \frac{1.257\lambda}{v_i^{2/3}} + \frac{1}{v_j^{1/3}} + \frac{1.257\lambda}{v_j^{2/3}}\right)$$

The error introduced in $\beta(v_i, v_j)$ by neglecting the exponential term is at most 24.2% as can be seen from the expression for A_i given in Eq. (4). Substituting Eq. (21) into Eqs. (8) and (9) with this form of $\beta(v_i, v_j)$ and combining the resulting equations yields

$$\left[1 + \mu_{1/3}\mu_{-1/3} + \Lambda(\mu_{-1/3} + \mu_{1/3}\mu_{-2/3})\right]\left(2\tau\frac{\partial\Phi}{\partial\tau} + \eta\frac{\partial\Phi}{\partial\eta}\right)$$
$$+ \left[2\mu_{1/3}\mu_{-1/3} + \Lambda(\mu_{-1/3} + 2\mu_{1/3}\mu_{-2/3}) - (\mu_{-1/3} + \Lambda\mu_{-2/3})\eta^{1/3} - (\mu_{1/3} + \Lambda)\eta^{-1/3}\right.$$
$$\left. - \mu_{1/3}\Lambda\eta^{-2/3}\right]\Phi(\eta, \tau) + \int_0^{\eta}\left[1 + \left(\frac{\eta - \tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right]\left(1 + \frac{\Lambda}{\tilde{\eta}^{1/3}}\right)\Phi(\tilde{\eta}, \tau)\Phi(\eta - \tilde{\eta}, \tau)\,d\tilde{\eta} = 0 \qquad (71)$$

in which $\mu_{1/3}$, $\mu_{-1/3}$, $\mu_{-2/3}$ and Λ are functions of τ given by

$$\mu_\nu = \int_0^\infty \eta^\nu \Phi(\eta,\tau)\,d\eta \qquad \nu = \tfrac{1}{3}, -\tfrac{1}{3}, -\tfrac{2}{3}$$

$$\Lambda = 1.257\,\lambda \left(\frac{4\pi N}{3\phi}\right)^{1/3} = 1.257\,N_0^{1/3}\left(\frac{4\pi}{3\phi}\right)^{1/3}\lambda\tau^{1/6} \qquad (72)$$

Eq. (71) is a partial integro-differential equation for the reduced spectrum function $\Phi(\eta,\tau)$ and is to be solved with the initial condition $\Phi(\eta,1)$. Although a general solution does not seem possible, particular solutions similar to the self-preserving solution can be found. By suppressing the τ-derivative term, Eq. (71) can be solved as an ordinary integro-differential equation for each fixed value of Λ:

$$\begin{aligned}
&\left[1 + \mu^*_{1/3}\mu^*_{-1/3} + \Lambda\left(\mu^*_{-1/3} + \mu^*_{1/3}\mu^*_{-2/3}\right)\right]\eta\,\frac{\partial\Phi(\eta,\Lambda)}{\partial\eta}\\
&+\left[2\mu^*_{1/3}\mu^*_{-1/3} + \Lambda\left(\mu^*_{-1/3} + 2\mu^*_{1/3}\mu^*_{-2/3}\right) - \left(\mu^*_{-1/3} + \Lambda\mu^*_{-2/3}\right)\eta^{1/3}\right.\\
&\left.-\left(\mu^*_{1/3} + \Lambda\right)\eta^{-1/3} - \mu^*_{-1/3}\,\Lambda\,\eta^{-2/3}\right]\Phi(\eta,\Lambda)\\
&+\int_0^\eta \left[1 + \left(\frac{\eta-\tilde\eta}{\tilde\eta}\right)^{1/3}\right]\left(1 + \frac{\Lambda}{\tilde\eta^{1/3}}\right)\Phi(\tilde\eta,\Lambda)\,\Phi(\eta-\tilde\eta,\Lambda)\,d\tilde\eta = 0
\end{aligned}$$

(73)

in which the spectrum function is written as $\Phi(\eta, \Lambda)$ to indicate its dependence on Λ . The moments μ_ν^* are defined as

$$\mu_\nu^* = \int_0^\infty \eta^\nu \Phi(\eta, \Lambda)\, d\eta \qquad \nu = \tfrac{1}{3}, -\tfrac{1}{3}, -\tfrac{2}{3} \qquad (74)$$

The assumption that the τ-derivative term is negligible can be checked by comparing $\eta \left(\frac{\partial\Phi}{\partial\eta}\right)_\Lambda$ with $2\tau\left(\frac{\partial\Phi}{\partial\tau}\right)_\eta = 2\tau\left(\frac{\partial\Phi}{\partial\Lambda}\right)_\eta \frac{d\Lambda}{d\tau}$, in which both $\left(\frac{\partial\Phi}{\partial\eta}\right)_\Lambda$ and $\left(\frac{\partial\Phi}{\partial\Lambda}\right)_\eta$ can be evaluated from the solutions obtained for different values of Λ . The validity of the assumption depends on the value of the term $\frac{d\Lambda}{d\tau}$. If Λ changes sufficiently slowly with time to make the approximation valid, the solutions can be called "quasi-self-preserving" spectra, indicating their slow variation with time. If the mean free path λ increases with time as $N^{-1/3}$, the derivative $\frac{d\Lambda}{d\tau}$ vanishes and the solutions are exact. These exact solutions are the self-preserving spectra for different values of Λ .

For each assumed value of Λ , Eq. (73) can be solved in the same way as Eq. (37). Approximate solutions in closed form can be found for the lower end and the upper end of the quasi-self-preserving spectrum by the same approach used in obtaining Eqs. (43) and (45). The results are:

for the lower end:

$$\Phi(\eta,\Lambda) = \frac{C_4 \exp\left\{ \dfrac{3(\mu^*_{-1/3} + \Lambda \mu^*_{-2/3})\eta^{1/3} - 3(\mu^*_{1/3}+\Lambda)\eta^{-1/3} - 1.5\mu^*_{1/3}\Lambda\eta^{-2/3}}{1+\mu^*_{1/3}\mu^*_{-1/3} + \Lambda(\mu^*_{-1/3} + \mu^*_{1/3}\mu^*_{-2/3})} \right\}}{\eta^{\dfrac{2\mu^*_{1/3}\mu^*_{-1/3} + \Lambda(\mu^*_{-1/3} + 2\mu^*_{1/3}\mu^*_{-2/3})}{1+\mu^*_{1/3}\mu^*_{-1/3} + \Lambda(\mu^*_{-1/3} + \mu^*_{1/3}\mu^*_{-2/3})}}}$$

and for the upper end:

$$\Phi(\eta,\Lambda) = \frac{C_5}{1+B(\frac{2}{3},\frac{4}{3})}\left[1+\mu^*_{1/3}\mu^*_{-1/3} + \Lambda(\mu^*_{-1/3} + \mu^*_{1/3}\mu^*_{-2/3})\right] e^{-C_5\eta}$$

The constants C_4, C_5 and μ^*_ν, ν = 1/3, -1/3, -2/3, are to be determined by the integral constraints on $\Phi(\eta,\Lambda)$ given in Eqs. (13), (14) and (74). This can be achieved by solving Eq. (73) numerically by the same method used in solving Eq. (37). Since there are four undetermined constants C_4, $\mu^*_{1/3}$, $\mu^*_{-1/3}$ and $\mu^*_{-2/3}$, the computing time used in the trial and error procedure is greatly increased. It is more convenient to start from $\Lambda = 0$ and gradually increase its value. Eq. (73) with $\Lambda = 0$ is identical to Eq. (17), which is the equation for the self-preserving size spectrum of Brownian coagulation without the slip correction. For small values of Λ, the spectrum lies very close to the curve with $\Lambda = 0$, and the moments should not differ much from those for the $\Lambda = 0$ spectrum.

Fig. 4 shows the quasi-self-preserving size spectra for Λ = 0, 0.05, 0.275, and 0.495, obtained by the numerical method described above. The numerical values for these spectra are presented

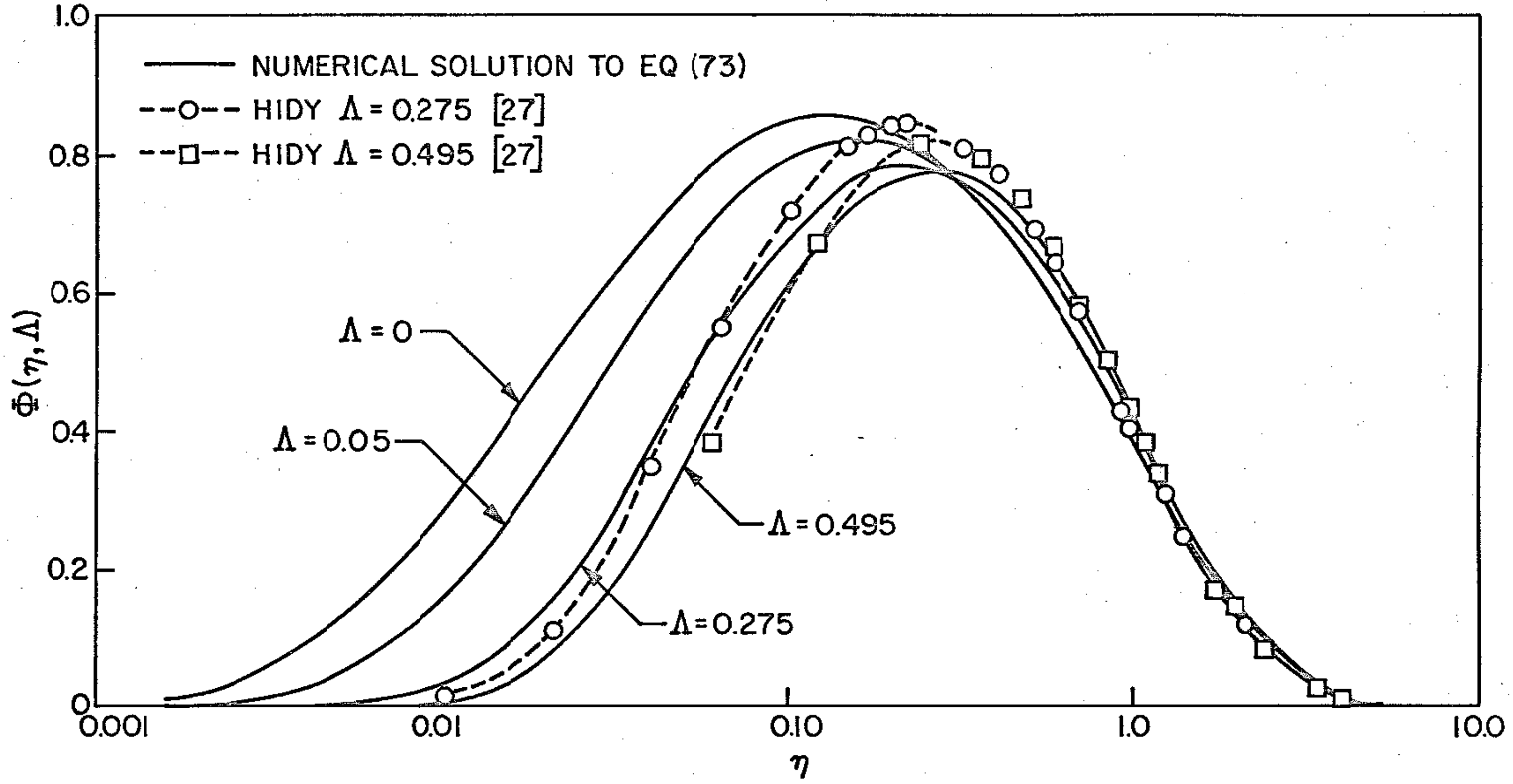

Fig. 4. Quasi-self-preserving size spectra for Brownian coagulation with the Cunningham slip correction

in Table 3. The assumed and the calculated values of the moments of $\Phi(\eta, \Lambda)$ are also shown in the table to indicate the accuracy of the numerical solutions.

2. Systems with Constant Mean Free Path.

If the mean free path of the fluid remains constant throughout the coagulation process, the parameter Λ can be expressed as $\Lambda = \Lambda(0)\,\tau^{1/6}$ in which $\Lambda(0)$ is the value of Λ at t = 0. The quantity $2\tau\left(\frac{\partial \Phi}{\partial \tau}\right)_\eta$ is then given by

$$2\tau\left(\frac{\partial \Phi}{\partial \tau}\right)_\eta = 2\tau\left(\frac{\partial \Phi}{\partial \Lambda}\right)_\eta \frac{d\Lambda}{d\tau} = \frac{\Lambda}{3}\left(\frac{\partial \Phi}{\partial \Lambda}\right)_\eta$$

The derivatives $\left(\frac{\partial \Phi}{\partial \Lambda}\right)_\eta$ and $\left(\frac{\partial \Phi}{\partial \eta}\right)_\Lambda$ can be estimated from Fig. 4. At Λ = 0.05 and η = 0.02, they are found to be

$$\left(\frac{\partial \Phi}{\partial \Lambda}\right)_\eta \sim 2$$

$$\left(\frac{\partial \Phi}{\partial \eta}\right)_\Lambda \sim 16$$

The ratio of $2\tau\left(\frac{\partial \Phi}{\partial \tau}\right)_\eta$ to $\eta\left(\frac{\partial \Phi}{\partial \eta}\right)_\tau$ is about 1/9.6, which confirms the assumption that the τ-derivative term in Eq. (71) is negligible in the lower end. The assumption can also be substantiated for the upper end.

Two distribution curves taken from Hidy's numerical solutions (27) are shown in Fig. 4 for comparison. Hidy's two curves represent the spectra at t = $\frac{45\mu}{kT\,N(0)}$ and t = $\frac{6\mu}{kT\,N(0)}$ respectively,

Table 3. Quasi-self-preserving size distribution for Brownian coagulation with the Cunningham slip correction, obtained from Eq. (73) by a finite difference method

$\Lambda = 0.05$

η	$\Phi(\eta,\Lambda)$
0.0018	0.0025
0.0030	0.0133
0.0050	0.0466
0.0082	0.1198
0.0136	0.2402
0.0224	0.3959
0.0369	0.5588
0.0608	0.6973
0.1003	0.7872
0.1653	0.8152
0.2725	0.7760
0.4493	0.6698
0.7408	0.5061
1.2214	0.3122
2.0138	0.1391
3.3201	0.0359
5.4740	0.0034

Table 3. (Cont'd.)

$\Lambda = 0.275$

η	$\Phi(\eta,\Lambda)$
0.0050	0.0025
0.0082	0.0164
0.0136	0.0643
0.0224	0.1690
0.0369	0.3291
0.0608	0.5112
0.1003	0.6687
0.1653	0.7637
0.2725	0.7753
0.4493	0.6968
0.7408	0.5372
1.2214	0.3307
2.0138	0.1424
3.3201	0.0336
5.4740	0.0024

Table 3. (Cont'd.)

$\Lambda = 0.495$	η	$\Phi(\eta,\Lambda)$
	0.0091	0.0066
	0.0150	0.0360
	0.0247	0.1184
	0.0408	0.2680
	0.0672	0.4589
	0.1108	0.6381
	0.1827	0.7552
	0.3012	0.7784
	0.4966	0.6964
	0.8187	0.5207
	1.3499	0.2986
	2.2255	0.1114
	3.6693	0.0194
	6.0497	0.0002

Table 3. (Cont'd.)

Λ	Moments	Assumed	Computed
0.05	$\mu^*_{1/3}$	0.9044	0.9087
	$\mu^*_{-1/3}$	1.2300	1.2201
	$\mu^*_{-2/3}$	1.8000	1.7623
	μ^*_0	1.(required value)	0.9891
	μ^*_1	1.(required value)	1.0185
	$C_4 = 0.5060$		
0.275	$\mu^*_{1/3}$	0.9170	0.9197
	$\mu^*_{-1/3}$	1.1930	1.1853
	$\mu^*_{-2/3}$	1.6100	1.6083
	μ^*_0	1.(required value)	0.9903
	μ^*_1	1.(required value)	1.0203
	$C_4 = 0.5600$		
0.495	$\mu^*_{1/3}$	0.9200	0.9222
	$\mu^*_{-1/3}$	1.1830	1.1780
	$\mu^*_{-2/3}$	1.5250	1.5562
	μ^*_0	1.(required value)	0.9934
	μ^*_1	1.(required value	1.0026
	$C_4 = 0.6100$		

of an initially monodisperse system with $\lambda/r_1 = 1$. The values of Λ for these two spectra are 0.275 and 0.495 respectively. The agreement between Hidy's results and the numerical solutions to Eq. (73) is fair.

Since the slip correction is most important for the smallest particles, the upper ends of the quasi-self-preserving spectra should lie close to the distribution for $\Lambda = 0$. This is confirmed by the results shown in Fig. 4.

The lower end of the quasi-self-preserving spectrum lies closer to the self-preserving spectrum for small values of Λ, or equivalently for long times. This is to be expected since Eq. (73) gradually reduces to Eq. (17) as Λ decreases. This is also in agreement with the physical picture that the slip correction becomes less important as particles grow larger. The conclusion of Hidy that the self-preserving size distribution varies with the ratio λ/r_1 appears to be incorrect.

For a system started from an arbitrary distribution, the size spectrum will differ from the quasi-self-preserving spectra in the early stages of coagulation. From the similarity between Eqs. (61) and (71), it can be expected that the size spectrum will become quasi-self-preserving as coagulation proceeds; and as it approaches the final self-preserving form ($\Lambda = 0$), it will pass through the family of quasi-self-preserving spectra near $\Lambda = 0$.

VI. COAGULATION BY BROWNIAN MOTION AND SIMULTANEOUS SHEAR FLOW

Equations for the collision frequency among particles have been worked out for Brownian motion and laminar shear considered as separate mechanisms. No theory exists for the case of the two effects occurring simultaneously. A detailed analysis of this phenomenon is beyond the scope of this study. For the purpose of this analysis, it will be assumed that the collision rate for small particles in a shear field is simply the sum of the collision rate for Brownian motion and that for shear flow. Since Brownian motion and shear flow are separately of controlling importance in different ranges of particle size (25), the assumption of additivity of the collision rates may not lead to appreciable error.

The homogeneity of the function $\beta(v,\tilde{v})$ is destroyed when $\beta(v,\tilde{v})$ for Brownian motion is added to that for shear flow. However, if the shear rate varies with time in a particular way, it is found that the coagulation equation has a self-preserving solution. The shape of the self-preserving spectrum depends on the value of a parameter $\mathcal{P}$, which in turn depends on the total volume concentration of particles and the ratio of the initial shear rate to the initial total number concentration. In this chapter, an approximate solution in closed form is derived for the lower end of the spectrum. Numerical solutions are obtained for the whole spectrum for several values of $\mathcal{P}$. The applicability of these results to coagulation in an isotropic turbulence is discussed.

A. The Self-preserving Size Spectrum for Coagulation by Brownian Motion and Simultaneous Laminar Shear Flow.

Assuming additivity, the collision frequency factor for Brownian motion and simultaneous laminar shear flow is given by:

$$\beta(v,\tilde{v}) = \frac{2kT}{3\mu}\,(v^{1/3}+\tilde{v}^{1/3})\left(\frac{1}{v^{1/3}}+\frac{1}{\tilde{v}^{1/3}}\right)+\frac{G}{\pi}(v^{1/3}+\tilde{v}^{1/3})^3$$

Substituting the similarity transformation represented by Eq. (15) into Eqs. (8) and (9) with this form of $\beta(v,\tilde{v})$ and then combining the resulting equations yields:

$$\begin{aligned}&(1+\mu^*_{1/3}\mu^*_{-1/3}+P+3P\mu^*_{1/3}\mu^*_{2/3})\,\eta\frac{d\psi}{d\eta}\\&+\left[2\mu^*_{1/3}\mu^*_{-1/3}+P+6P\mu^*_{1/3}\mu^*_{2/3}-\mu^*_{1/3}\eta^{-1/3}-(\mu^*_{-1/3}+3P\mu^*_{2/3})\eta^{1/3}-3P\mu^*_{1/3}\eta^{2/3}-P\eta\right]\psi\\&+\int_0^{\eta}\left[1+\left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}+\frac{P\eta}{2}+3P\tilde{\eta}^{2/3}(\eta-\tilde{\eta})^{1/3}\right]\psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\,d\tilde{\eta}=0\end{aligned}\tag{75}$$

in which P is given by

$$P = \frac{3\mu G\phi}{2\pi kTN}$$

and μ^*_ν is the ν -th moments of $\psi(\eta)$ defined as

$$\mu_\nu^* = \int_0^\infty \eta^\nu \psi(\eta)\, d\eta \tag{76}$$

$$\nu = \tfrac{1}{3},\ \tfrac{2}{3},\ -\tfrac{1}{3}$$

If the laminar shear rate G varies with time in such a way that the ratio G/N remains unchanged throughout the coagulation process, the parameter $\mathcal{P}$ is constant and Eq. (75) is then explicitly independent of time. Eq. (75) with time-independent parameter $\mathcal{P}$ is similar to the equation for the self-preserving size distribution for pure Brownian coagulation given in Eq.(17). For each value of $\mathcal{P}$, Eq. (75) can be solved in the same way as Eq. (17). The solution so obtained is a particular solution to the coagulation equation for Brownian motion and simultaneous laminar shear flow with constant G/N. The form of the solution depends on the value of $\mathcal{P}$. For a system started from a self-preserving distribution, the reduced size spectrum remains unchanged throughout the process of coagulation. The time rate of change of the total number concentration of such a self-preserving system is:

$$\frac{dN}{dt} = -K_{SBS}\, N^2 \tag{77}$$

in which the rate constant K_{SBS} is a function of $\mathcal{P}$:

$$K_{SBS} = \frac{kT}{3\mu} \int_0^\infty\!\!\int_0^\infty \left[\left(\frac{1}{\eta^{1/3}} + \frac{1}{\tilde{\eta}^{1/3}}\right)\left(\eta^{1/3} + \tilde{\eta}^{1/3}\right) + \mathcal{P}\left(\eta^{1/3} + \tilde{\eta}^{1/3}\right)^3\right] \psi(\eta)\psi(\tilde{\eta})\, d\eta\, d\tilde{\eta}$$

Eq. (77) can be readily obtained by substituting Eq. (15) into Eq. (9). Integrating the rate equation for N gives:

$$\frac{1}{N(t)} - \frac{1}{N(0)} = K_{SBS}\, t$$

The laminar shear rate G can now be expressed as a function of time:

$$G = \gamma N = \frac{\gamma}{K_{SBS}\, t + \frac{1}{N(0)}} = \frac{G(0)}{1 + K_{SBS} N(0)\, t} \qquad (78)$$

in which γ is the proportionality constant and G(0) is the value of G at t = 0. Thus, for the system to be self-preserving, the shear rate must be varied with time as specified by Eq. (78).

The three undetermined constants, $\mu^*_{-1/3}$, $\mu^*_{1/3}$ and $\mu^*_{2/3}$, in Eq. (75) can be reduced to two by combining $\mu^*_{-1/3}$ and $3P\mu^*_{2/3}$. By letting Q represent the sum of $\mu^*_{-1/3}$ and $3P\mu^*_{2/3}$, Eq. (75) becomes:

$$(1+P+\mu^*_{1/3}Q)\,\eta\frac{d\psi}{d\eta} + (P + 2\mu^*_{1/3}Q - \mu^*_{1/3}\eta^{-1/3} - Q\eta^{1/3} - 3P\mu^*_{1/3}\eta^{2/3} - P\eta)\,\psi$$
$$+ \int_0^{\eta}\left[1 + \left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3} + \frac{P\eta}{2} + 3P\tilde{\eta}^{2/3}(\eta-\tilde{\eta})^{1/3}\right]\psi(\tilde{\eta})\,\psi(\eta-\tilde{\eta})\,d\tilde{\eta} = 0$$

(79)

An approximate solution to the lower end of the spectrum can be obtained by neglecting the integral term in Eq. (79). The general solution to the resulting first order ordinary differential equation is

$$\psi(\eta) = C_6 \, \eta^{-\frac{P + 2\mu^*_{1/3} Q}{1 + P + \mu^*_{1/3} Q}} \exp\left(\frac{3Q\eta^{1/3} + 4.5\mu^*_{1/3} P \eta^{2/3} + P\eta - 3\mu^*_{1/3} \eta^{-1/3}}{1 + P + \mu^*_{1/3} Q} \right) \tag{80}$$

in which C_6 is an integration constant to be determined by the constraints on $\psi(\eta)$.

Both the coefficient of $\psi(\eta)$ and the kernel of the integral in Eq. (79) contain the independent variable η up to the first degree. This makes the equation significantly different from that for pure Brownian coagulation. As a result, an approximate solution could not be found for large values of η.

Eq. (79) can be solved numerically by the same approach used in solving Eq. (37). The approximate solution for the lower end of the spectrum given in Eq. (80) was used to compute the starting values of $\psi(\eta)$. Since there are three undetermined constants, Q, $\mu^*_{1/3}$ and C_6, the computing time for the trial and error procedure is much greater than in the case of pure Brownian coagulation. Eq. (79) with $P = 0$ is identical with the equation for the self-preserving size spectrum of Brownian coagulation. For small values of P, the constants Q, $\mu^*_{1/3}$ and C_6 do not differ much from those for Brownian coagulation and therefore are easy to guess.

For this reason, the calculation was made by setting $P = 0$ and gradually increasing its value.

The values of $\psi(\eta)$ thus obtained for $P = 0.01$, 0.1 and 0.3 are presented in Table 4 and Fig. 5. The self-preserving size spectrum for Brownian coagulation is also shown in Fig. 5 for comparison. The computed and the assumed values of the undetermined constants are included in Table 4 to indicate the accuracy of the numerical solution.

Fig. 5 shows that the spectra are quite close to each other for $\eta > 0.5$, but differ greatly for $\eta < 0.1$. The shift in the position of the maximum is noticeable.

If the laminar shear rate is maintained constant, the parameter P will vary with time. In view of the similarity between Eq. (75) and Eq. (73), it might be expected that the effect of constant shear rate on the size distribution could be treated in the same way as the effect of the slip correction for constant mean free path. There is, however, an important difference between these two cases: the parameter P for constant shear rate increases with time whereas the parameter Δ for constant mean free path decreases. Fig. 5 shows that as P increases, the size spectrum changes drastically. Thus the quasi-self-preserving hypothesis is not applicable to the case of constant shear rate.

Table 4. **Self-preserving particle size distributions and their moments for coagulation by Brownian motion with simultaneous shear flow, obtained from Eq. (75) by a finite difference method.**

$P = 0.01$

η	$\psi(\eta)$
0.0010	0.0041
0.0017	0.0164
0.0027	0.0497
0.0045	0.1183
0.0074	0.2304
0.0123	0.3800
0.0202	0.5456
0.0334	0.6991
0.0550	0.8151
0.0907	0.8776
0.1496	0.8794
0.2466	0.8198
0.4066	0.7014
0.6703	0.5335
1.1052	0.3393
1.8221	0.1621
3.0042	0.0482
4.9530	0.0061

Table 4. (Cont'd.)

$P = 0.1$

η	$\psi(\eta)$
0.0005	0.0044
0.0010	0.0319
0.0020	0.1322
0.0037	0.3136
0.0067	0.5728
0.0123	0.8492
0.0224	1.0665
0.0408	1.1743
0.0743	1.1623
0.1353	1.0490
0.2466	0.8630
0.4493	0.6352
0.8187	0.3991
1.4918	0.1955
2.7183	0.0631
4.9530	0.0097
7.3891	0.0012

Table 4. (Cont'd.)

$P = 0.3$

η	$\psi(\eta)$
0.00012	0.0039
0.00022	0.0302
0.00041	0.1408
0.00074	0.4378
0.00136	0.9795
0.00248	1.6786
0.00452	2.3225
0.00823	2.7085
0.0150	2.7564
0.0273	2.5143
0.0498	2.0942
0.0907	1.6097
0.1653	1.1448
0.3012	0.7492
0.5488	0.4451
1.0000	0.2343
1.8221	0.1046
3.3201	0.0366
7.3891	0.0046

Table 4. (Cont'd.)

P	Moments	Assumed	Computed
0.01	$\mu^*_{1/3}$	0.8950	0.8983
	$\mu^*_{-1/3}+3P\mu^*_{2/3}$	1.2950	1.2917
	μ^*_0	1.(required value)	0.9949
	μ^*_1	1.(required value)	0.9913
	$C_6 = 0.4720$		
0.1	$\mu^*_{1/3}$	0.8850	.8720
	$\mu^*_{-1/3}+3P\mu^*_{2/3}$	1.6040	1.6142
	μ^*_0	1.(required value)	0.9933
	μ^*_1	1.(required value)	0.9842
	$C_6 = 0.3050$		
0.3	$\mu^*_{1/3}$	0.8120	0.8200
	$\mu^*_{-1/3}+3P\mu^*_{2/3}$	2.3250	2.3814
	μ^*_0	1.(required value)	1.0016
	μ^*_1	1.(required value)	1.0126
	$C_6 = 0.1620$		

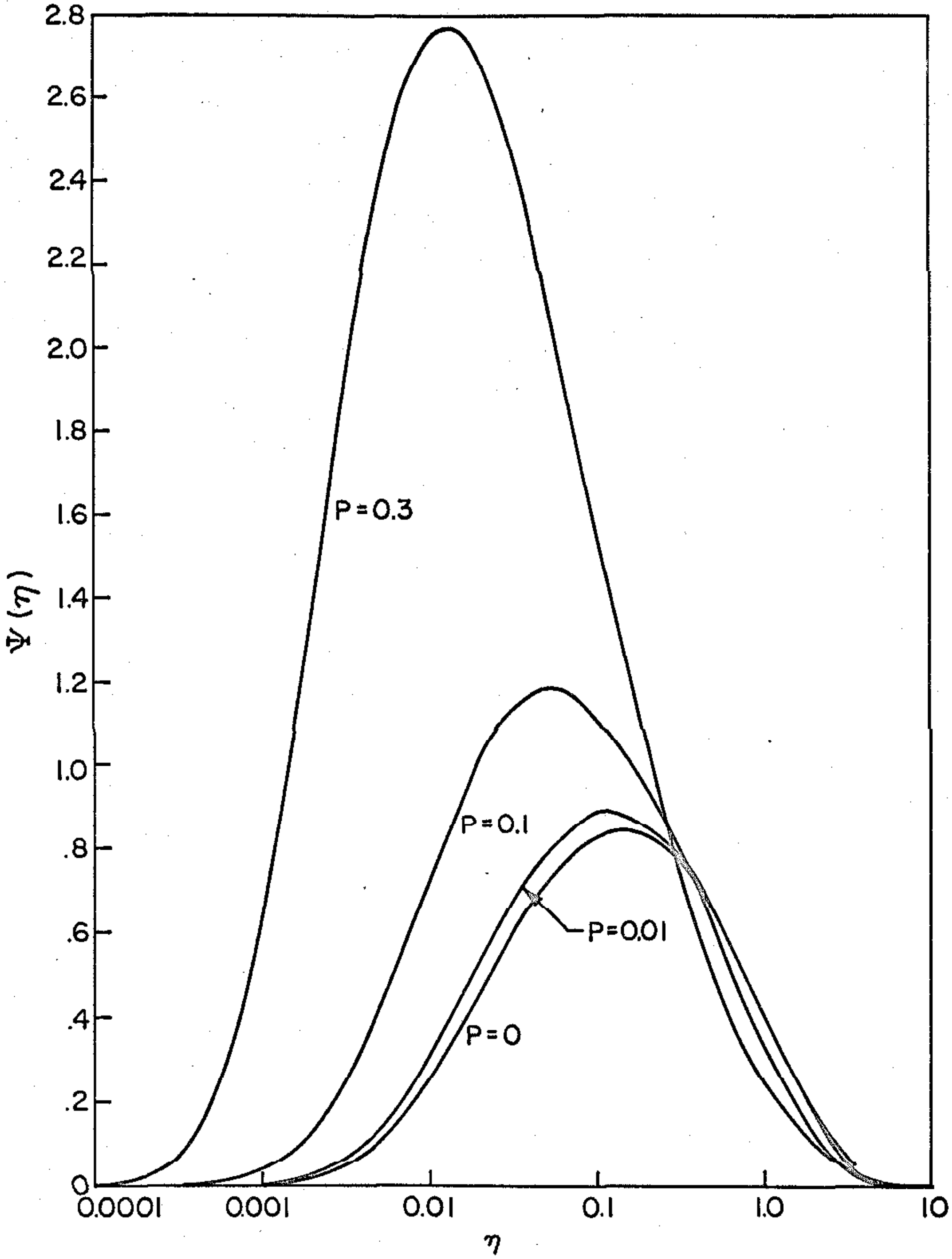

Fig. 5 Self-preserving particle size distributions for coagulation by Brownian motion with simultaneous shear flow

The value of $\psi(\eta)$ in Table 4 were used to evaluate the cummulative distribution defined as

$$\frac{N_v}{N} = \frac{1}{N}\int_v^{\infty} n(v,t)\,dv = \int_{\eta}^{\infty}\psi(\eta)\,d\eta$$

in which N_v represents the total number of particles with volume larger than v in a unit volume of the system. Fig. 6 shows two curves corresponding to P = 0.1 and 0.3 obtained by numerical integration (32). Two cumulative distribution curves reported by Swift and Friedlander (26) for shear coagulation experiments with oil-water emulsions are also shown in Fig. 6 for comparison. Since their experiments were carried out at constant shear rates, these experimental curves cannot be used to confirm the theoretical results. However, it is interesting to note that both experimental and theoretical curves show the same trend that the lower end of the spectrum tends to shift down as P increases.

B. Coagulation by Brownian Motion with Simultaneous Isotropic Turbulent Shear

For particles much smaller than the small eddies of the turbulence, the collision frequency factor is given by Eq. (6), viz.

$$\beta(v_i, v_j) = 0.31\left(\frac{\varepsilon}{\nu}\right)^{1/2}\left(v_i^{1/3} + v_j^{1/3}\right)^3 \qquad (6)$$

which is similar in form to that for laminar shear flow. In fact Eq.(6) can be obtained from Eq. (5) by replacing the laminar shear rate G by

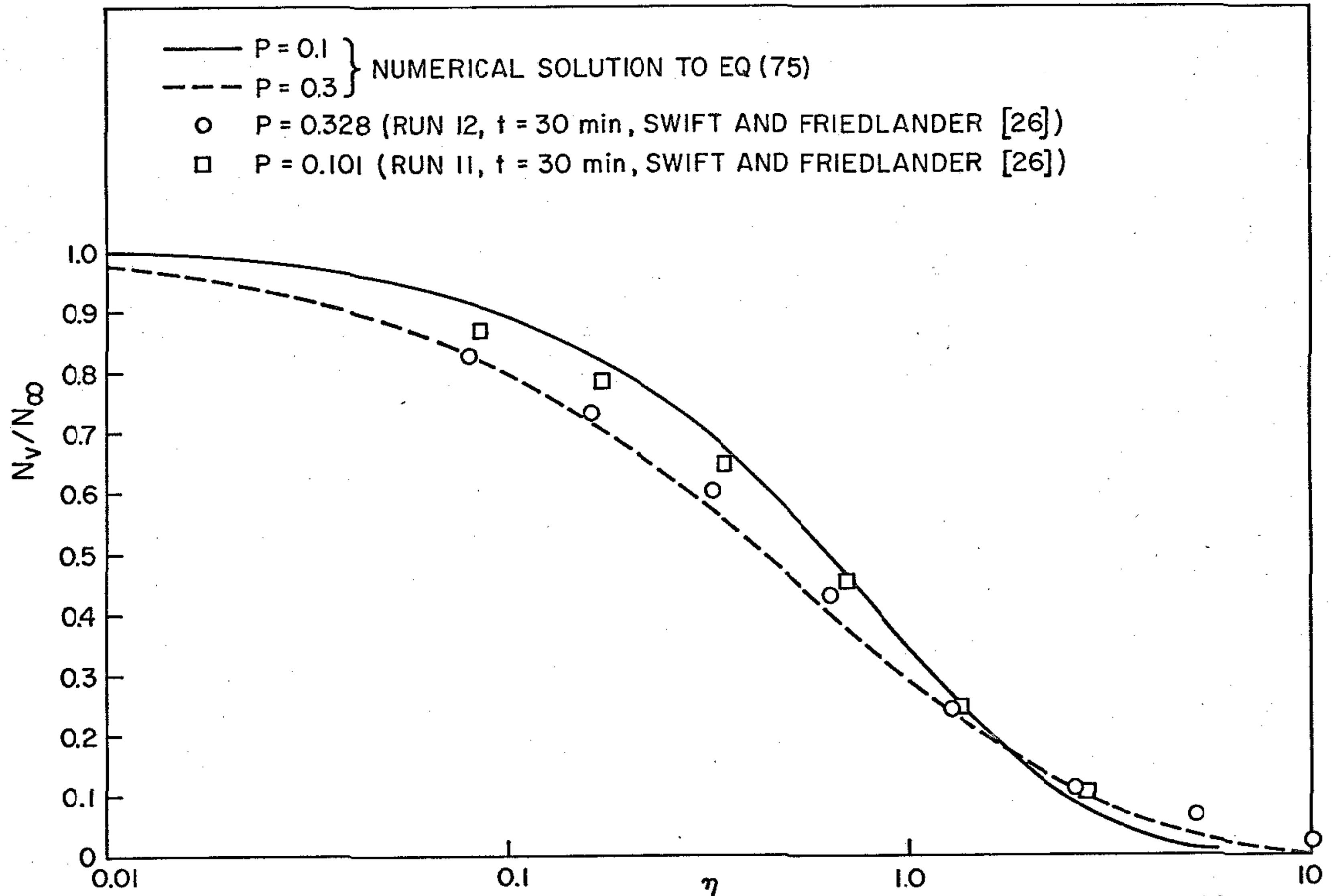

Fig. 6. Dimensionless cumulative distributions for coagulation by Brownian motion with simultaneous shear flow

$0.975 \; (\epsilon/\nu)^{1/2}$, in which ϵ is the local rate of energy dissipation and ν the kinetic viscosity of the fluid. Consequently, the self-preserving size spectra obtained for coagulation by laminar shear flow is applicable to coagulation by isotropic turbulence if the parameter $\mathcal{P}$ is now defined as

$$\mathcal{P} = \frac{1.46 \mu \phi}{\pi k T N} \left(\frac{\epsilon}{\nu}\right)^{1/2}$$

To maintain $\mathcal{P}$ as a constant throughout the process of coagulation, ϵ must vary with time as N^2 or

$$\epsilon = \frac{\epsilon(0)}{\left[1 + K_{SBS} N(0) t \right]^2} \tag{81}$$

in which $\epsilon(0)$ is the value of ϵ at t = 0.

According to the experimental results, the early part of the decay process of turbulence is described by (33):

$$\epsilon = \frac{c_0}{(t + t_0)^2} \tag{82}$$

in which c_0 and t_0 are constants determined by the initial conditions of the turbulence.

It can be seen from Eqs. (81) and (82) that the self-preserving size spectrum will be preserved in the early period of an isotropic turbulent flow if the initial conditions are such that

$$t_o = \frac{1}{K_{SBS}\, N(0)}$$

This result must be accepted with caution since Eq. (6) is applicable only for v_i/v_j between one and eight.

VII. SUMMARY AND CONCLUSIONS

If the collision frequency factor $\beta(v, \tilde{v})$ is a homogeneous function of its arguments, the partial integro-differential equation describing the coagulation kinetics can be transformed into an ordinary integro-differential equation by a similarity transformation originally proposed by Friedlander (24). The solution to the resulting equation is a particular solution to the coagulation equation and is called the self-preserving spectrum. The shape of the self-preserving spectrum is greatly influenced by the form of the collision frequency factor.

The ordinary integro-differential aquation obtained by the similarity transformation can be solved analytically for the case of constant $\beta(v, \tilde{v})$. For Brownian coagulation in the absence of the slip correction, approximate solutions are derived in closed form for the lower and upper end of the spectrum, and a numerical solution can be obtained for the whole spectrum.

If a slip correction for the particle drag is included, the function $\beta(v, \tilde{v})$ for Brownian motion is no longer homogeneous. The coagulation equation, however, can be written in terms of a reduced size spectrum with a reduced volume η and a reduced time τ as independent variables. According to the quasi-self-preserving hypothesis, the reduced size spectrum varies slowly with time. By suppressing the τ-derivative term, the equation can be solved as an ordinary integro-differential equation containing a parameter Λ, which is a function of the mean free path of the fluid, the total volume concentration ϕ and the total number concentration N of particles. The shapes of the quasi-self-preserving spectra depend on the parameter Λ. If the mean free path of the fluid increases with time as $N^{-1/3}$, these solutions are exact self-preserving solutions. For a system with constant mean free path, the reduced size spectrum varies slowly with time, confirming the quasi-self-preserving hypothesis.

The collision frequency factor for coagulation caused by simultaneous Brownian motion and shear flow is not a homogeneous function. However, the coagulation equation will have self-preserving solutions if the shear rate decreases with time as $\frac{G(0)}{1 + K_{SBS} N(0) t}$, in which K_{SBS} is the coagulation rate constant, G(0) and N(0) are the initial values of the shear rate and the total number concentration of particles. The shape of the self-preserving spectrum depends on the value ofa parameter P, which is a function of the shear rate, the total volume concentration and the total number concentration of particles.

The self-preserving hypothesis can be stated as follows:

> "The particle size spectra of coagulating dispersions approach a form independent of the initial distribution after a sufficiently long time. This holds true for certain classes of particle collision mechanisms."

The hypothesis is shown to be true for the case of constant $\beta(v, \tilde{v})$. For Brownian coagulation, arguments are presented to support the hypothesis, but the proof is incomplete.

Appendix I. Applicability of the Method of Series Decomposition in Solving the Coagulation Equation.

Martynov and Bakanov (21) claimed that a method of series decomposition, originally proposed by Tunitskii (34) for solving the coagulation equation with constant collision frequency factor $\beta(v,\tilde{v})$ can be generalized to the case in which $\beta(v,\tilde{v})$ is not a constant. The purpose of this appendix is to show by a counter example that this method is not always applicable.

Martynov and Bakanov introduced a new variable $\tau_1 = \frac{N(0)-N(t)}{N(0)}$ for time, and a new function $\varphi(v,\tau_1) = n(v,t)/N(0)$ for the size spectrum. In terms of $\varphi(v,\tau_1)$, the coagulation equation becomes

$$\frac{\partial\varphi(v,\tau_1)}{\partial\tau_1} = \frac{\int_0^v \beta(\tilde{v},v-\tilde{v})\varphi(\tilde{v},\tau_1)\varphi(v-\tilde{v},\tau_1)\,d\tilde{v} - 2\int_0^\infty \beta(v,\tilde{v})\varphi(v,\tau_1)\varphi(\tilde{v},\tau_1)\,d\tilde{v}}{\int_0^\infty\int_0^\infty \beta(v,\tilde{v})\,\varphi(v,\tau_1)\,\varphi(\tilde{v},\tau_1)\,dv\,d\tilde{v}} \tag{I-1}$$

According to the method of series decomposition, the function $\varphi(v,\tau_1)$ can be represented by

$$\varphi(v,\tau_1) = \sum_{n=0}^{\infty} \frac{1}{n!}\,\varphi_n(v)\,\tau_1^n \qquad 0 \leq \tau \leq 1 \tag{I-2}$$

in which $\varphi_n(v)$ is the n-th τ_1-derivative of $\varphi(v,\tau_1)$ evaluated at $\tau_1 = 0$. The first derivative is given in Eq. (I-1): the higher derivatives can be obtained from Eq. (I-1) by successive differentiation.

For Brownian coagulation with the initial distribution $\varphi(v,0) = \frac{N(0)}{\phi} e^{-N(0)v/\phi}$, the function $\varphi_1(v)$ is obtained from Eq. (I-1) by straightforward integration.

$$\varphi_1(v) = \left.\frac{\partial\varphi}{\partial\tau_1}\right|_{\tau_1=0} = \frac{\frac{N(0)}{\phi} e^{-\frac{N(0)v}{\phi}} \left\{ \left[1+B\left(\tfrac{2}{3},\tfrac{4}{3}\right)\right]\frac{N(0)v}{\phi} - 2 - \Gamma\left(\tfrac{2}{3}\right)\left[\frac{N(0)v}{\phi}\right]^{1/3} - \Gamma\left(\tfrac{4}{3}\right)\left[\frac{N(0)v}{\phi}\right]^{-1/3}\right\}}{1 + B\left(\tfrac{2}{3},\tfrac{4}{3}\right)} \tag{I-3}$$

It follows from Eq. (I-3) that $\varphi_1(v)$ approaches infinity as $v \to 0$. Thus the function $\varphi(v,\tau_1)$ cannot be represented by the series given in Eq. (I-2). This simple example demonstrates that the method of series decomposition is not applicable to Brownian coagulation with initial distribution in exponential form. It is not difficult to show that the series representation fails if the dispersion initially possesses a gamma distribution.

Appendix II. Some Self-preserving Size Spectra in Closed Form

Because of its complexity, the ordinary integro-differential equation for the self-preserving size spectrum can be solved analytically only for certain forms of the collision frequency factor $\beta(v,\tilde{v})$. An analytical solution was derived in Chapter IV for the case of constant $\beta(v,\tilde{v})$. In this appendix, solutions in closed form are obtained for two other cases. These solutions do not represent any known physical problems and are presented here simply for their mathematical interest.

The equation for the self-preserving size spectrum is given in Eq. (16), viz.

$$\left[\int_0^\infty\int_0^\infty \psi(\eta)\psi(\tilde\eta)\beta(\eta,\tilde\eta)\,d\eta\,d\tilde\eta\right]\left[\eta\frac{d\psi}{d\eta}+2\psi\right] + \int_0^\eta \beta(\tilde\eta,\eta-\tilde\eta)\psi(\tilde\eta)\psi(\eta-\tilde\eta)\,d\tilde\eta \quad - 2\int_0^\infty \beta(\eta,\tilde\eta)\psi(\eta)\psi(\tilde\eta)\,d\tilde\eta = 0 \tag{16}$$

The function $\psi(\eta)$ must satisfy the two normalization conditions given in Eqs. (13) and (14)

$$\int_0^\infty \psi(\eta)\,d\eta = 1 \tag{13}$$

$$\int_0^\infty \eta\,\psi(\eta)\,d\eta = 1 \tag{14}$$

Since the function $\beta(v,\tilde v)$ and the product $\psi(\eta)\,\psi(\tilde\eta)$ always appear together in Eq. (16), a new function $F(\eta,\tilde\eta)$ can be introduced to replace them:

$$F(\eta,\tilde\eta) = \frac{\beta(\eta,\tilde\eta)\,\psi(\eta)\,\psi(\tilde\eta)}{\int_0^\infty\int_0^\infty \beta(\eta,\tilde\eta)\,\psi(\eta)\,\psi(\tilde\eta)\,d\eta\,d\tilde\eta} \tag{II-1}$$

It follows from Eq. (II-1) that F $(\eta, \tilde{\eta})$ has the normalization condition:

$$\int_0^\infty \int_0^\infty F(\eta, \tilde{\eta})\, d\eta\, d\tilde{\eta} = 1 \qquad \text{(II-2)}$$

In terms of this new function, Eq. (16) becomes:

$$\eta \frac{d\psi}{d\eta} + 2\psi + \int_0^\eta F(\tilde{\eta}, \eta - \tilde{\eta})\, d\tilde{\eta} - 2\int_0^\infty F(\eta, \tilde{\eta})\, d\tilde{\eta} = 0 \qquad \text{(II-3)}$$

It is clear that, if F $(\eta, \tilde{\eta})$ is a known function, Eq. (II-3) reduces to a first order ordinary differential equation. This leads to the possibility of finding self-preserving spectra in closed form from Eq. (II-3). By assuming a form for F $(\eta, \tilde{\eta})$ and normalizing it by Eq. (II-2), Eq. (II-3) can be solved for $\psi(\eta)$. If the solution satisfies the two normalization conditions given in Eqs. (13) and (14), it is a self-preserving spectrum for the following collision frequency factor:

$$\beta(\eta, \tilde{\eta}) = \frac{c\, F(\eta, \tilde{\eta})}{\psi(\eta)\, \psi(\tilde{\eta})} \qquad \text{(II-4)}$$

in which c is an arbitrary constant.

For example, if F $(\eta, \tilde{\eta})$ takes the form

$$F(\eta, \tilde{\eta}) = \frac{a^2 b^2}{a^2 + b^2} \left[e^{-a(\eta+\tilde{\eta})} + e^{-b(\eta+\tilde{\eta})} \right]$$

in which a and b are positive constants, Eq. (II-3) becomes:

$$\eta \frac{d\psi}{d\eta} + 2\psi + \frac{a^2 b^2}{a^2+b^2} \eta (e^{-a\eta} + e^{-b\eta}) - \frac{2a^2 b^2}{a^2+b^2} \left(\frac{e^{-a\eta}}{a} + \frac{e^{-b\eta}}{b} \right) = 0$$

The general solution to this equation is

$$\psi(\eta) = \frac{a^2 b^2}{a^2+b^2} \left(\frac{e^{-a\eta}}{a} + \frac{e^{-b\eta}}{b} \right) + C$$

in which C is an integration constant. The normalization conditions given in Eqs. (13) and (14) require

$$C = 0$$

$$a^3 + b^3 = a^3 b + a b^3 \qquad \text{(II-5)}$$

Consequently, the self-preserving spectrum is

$$\psi(\eta) = \frac{a^2 b^2}{a^2+b^2} \left(\frac{e^{-a\eta}}{a} + \frac{e^{-b\eta}}{b} \right)$$

From Eq. (II-4) it follows that the corresponding collision frequency factor is given by:

$$\beta(\eta,\tilde{\eta}) = \frac{c_1\left[e^{-a(\eta+\tilde{\eta})} + e^{-b(\eta+\tilde{\eta})}\right]}{\left(\frac{e^{-a\eta}}{a} + \frac{e^{-b\eta}}{b}\right)\left(\frac{e^{-a\tilde{\eta}}}{a} + \frac{e^{-b\tilde{\eta}}}{b}\right)}$$

in which c_1 is an arbitrary constant.

In a similar manner, if F $(\eta,\tilde{\eta})$ has the form

$$F(\eta,\tilde{\eta}) = \frac{a^3b^3}{2(a^3+b^3)}(\eta+\tilde{\eta})\left[e^{-a(\eta+\tilde{\eta})} + e^{-b(\eta+\tilde{\eta})}\right]$$

the self-preserving spectrum and the collision frequency factor are found to be

$$\psi(\eta) = \frac{a^3b^3}{2(a^3+b^3)}\left[\frac{(a\eta+1)\,e^{-a\eta}}{a^2} + \frac{(b\eta+1)\,e^{-b\eta}}{b^2}\right]$$

$$\beta(\eta,\tilde{\eta}) = \frac{c_2(\eta+\tilde{\eta})\left[e^{-a(\eta+\tilde{\eta})} + e^{-b(\eta+\tilde{\eta})}\right]}{\left[\frac{(a\eta+1)e^{-a\eta}}{a^2} + \frac{(b\eta+1)e^{-b\eta}}{b^2}\right]\left[\frac{(a\tilde{\eta}+1)e^{-a\tilde{\eta}}}{a^2} + \frac{(b\tilde{\eta}+1)e^{-b\tilde{\eta}}}{b^2}\right]}$$

in which c_2 is an arbitrary constant; a and b are positive constants satisfying

$$3a^4 + 3b^4 = 2a^4 b + 2a b^4$$

Appendix III. Checking the Normalization Conditions for the Solution to the Transformed Coagulation Equation with Constant $\beta(v,\tilde{v})$

The solution to the transformed coagulation equation with constant $\beta(v,\tilde{v})$ for a system initially possessing a particular class of gamma distributions is given by Eq. (30), viz.

$$\bar{\Phi}(\eta,\tau) = \frac{1}{(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \exp\left(\frac{2k\pi i}{n} + p_k\eta\right) \qquad (30)$$

in which

$$p_k = \frac{n}{\sqrt{\tau}}\left[(1-\sqrt{\tau})^{1/n}\exp(2k\pi i/n) - 1\right]$$

To show that this is indeed a solution, it is necessary to prove that it satisfies the two normalization conditions given in Eqs. (22) and (23):

$$\int_0^\infty \Phi(\eta,\tau)\,d\eta = 1 \tag{22}$$

$$\int_0^\infty \eta\,\Phi(\eta,\tau)\,d\eta = 1 \tag{23}$$

For this purpose, Eq. (30) is rewritten as

$$\Phi(\eta,\tau) = \frac{1}{(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \omega^k \exp(p_k \eta) \tag{III-1}$$

in which

$$p_k = \frac{n}{\sqrt{\tau}} \left[(1-\sqrt{\tau})^{1/n} \omega^k - 1 \right]$$

ω = a primitive n-th root of unity = $e^{2\pi i/n}$

The following two identities are used in the proof:

$$\frac{n \xi^{n-1}}{1-\xi^n} = \sum_{k=1}^{n} \frac{\omega^k}{1-\xi\omega^k} \tag{III-2}$$

$$\frac{n^2 \xi^{n-1}}{(1-\xi^n)^2} = \sum_{k=1}^{n} \frac{\omega^k}{(1-\xi\omega^k)^2} \tag{III-3}$$

in which ξ is any real number between zero and one. These two relationships can be established as follows: Integrating both sides of Eq. (III-2) with respect to ξ from 0 to ξ yields:

$$1-\xi^{n} = \prod_{k=1}^{n} (1-\xi\omega^{k})$$

which can be shown to be an identity by noting that both sides are n-th degree polynomials having the same n roots (= $1, \omega, \omega^2, \ldots, \omega^{n-1}$) and the same coefficient for ξ^n. Consequently, Eq. (III-2) is itself an identity.

If both sides of Eq. (III-3) are integrated with respect to ξ from 0 to ξ, the following relationship is obtained:

$$\frac{n}{1-\xi^{n}} = \sum_{k=1}^{n} \frac{1}{1-\xi\omega^{k}} \qquad \text{(III-4)}$$

By series expansions of both sides, it can be shown that Eq. (III-4) is an identity for $0 \leq \xi < 1$. This proves that Eq. (III-3) is valid for ξ in the same range.

Integrating both sides of Eq. (III-1) with respect to η from 0 to ∞ gives:

$$\int_0^{\infty} \Phi(\eta,\tau)\,d\eta = \frac{\sqrt{\tau}}{n(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \frac{\omega^{k}}{1-(1-\sqrt{\tau})^{1/n}\omega^{k}} \qquad \text{(III-5)}$$

It follows from Eqs. (III-5) and (III-2) that

$$\int_0^\infty \Phi(\eta,\tau)\,d\eta = 1$$

which is the first normalization condtion.

The second normalization condition, Eq. (23), can be proved in a similar way.

Appendix IV. Derivation of Eq. (31) from Eq. (30)

For the case of constant $\beta(v,\vec{v})$, the reduced size spectrum for a system initially possessing a particular class of gamma distribution is represented by Eq. (30), viz.

$$\Phi(\eta,\tau) = \frac{1}{(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \exp\left(\frac{2k\pi i}{n} + p_k \eta\right) \qquad (30)$$

in which

$$p_k = \frac{n}{\sqrt{\tau}}\left[(1-\sqrt{\tau})^{1/n} \exp(2k\pi i/n) - 1\right]$$

For the purpose of the analysis, it is more convenient to express $\Phi(\eta,\tau)$ in terms of trigonometric functions. Substituting Euler's formula into Eq. (30) gives after some simplifications:

$$\Phi(\eta,\tau) = \frac{e^{-n\eta/\sqrt{\tau}}}{(1-\sqrt{\tau})^{(n-1)/n}} \left\{ \sum_{k=1}^{n} \exp\left[\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\cos\frac{2k\pi}{n}\right]\cos\left[\frac{2k\pi}{n}+\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\sin\frac{2k\pi}{n}\right]\right.$$

$$\left. + i\sum_{k=1}^{n} \exp\left[\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\cos\frac{2k\pi}{n}\right]\sin\left[\frac{2k\pi}{n}+\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\sin\frac{2k\pi}{n}\right]\right\}$$

(IV-1)

By making use of the identity

$$\sum_{k=1}^{n} \exp\left[x\cos\frac{2k\pi}{n}\right]\sin\left(\frac{2k\pi}{n}+x\sin\frac{2k\pi}{n}\right) = 0 \qquad \text{(IV-2)}$$

Eq. (IV-1) reduces to

$$\Phi(\eta,\tau) = \frac{e^{-n\eta/\sqrt{\tau}}}{(1-\sqrt{\tau})^{(n-1)/n}} \sum_{k=1}^{n} \exp\left[\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\cos\frac{2k\pi}{n}\right]\cos\left[\frac{2k\pi}{n}+\frac{n\eta(1-\sqrt{\tau})^{1/n}}{\sqrt{\tau}}\sin\frac{2k\pi}{n}\right]$$

(31)

which is the desired expression for $\Phi(\eta,\tau)$

Eq. (IV-2) is obtained from the following identity by differentiation with respect to x:

$$\sum_{k=1}^{n} e^{x\cos\frac{2k\pi}{n}} \sin\left(x\sin\frac{2k\pi}{n}\right) = 0 \qquad \text{(IV-3)}$$

That Eq. (IV-3) is valid for any real x can be proved by noting that the k-th term and the (n-k)-th term in the summation always cancel out, and that the n-th term is identically equal to zero. If the summation has even terms, the $(\frac{n}{2})$-th term always vanishes.

Appendix V. The Asymptotic Behavior of the Moments of the Reduced Size Spectrum for the Case of Constant $\beta(v,\vec{u})$

The moments of the reduced size spectrum for the case of constant $\beta(v,\vec{u})$ is described by Eq. (33):

$$\frac{d\mu_n}{d\theta} = -(n+1)\mu_n + \sum_{i=0}^{n} \binom{n}{i} \mu_i \mu_{n-i} \qquad (33)$$

$$n = 1, 2, \cdots$$

By letting $\mu_n = n!\,(\mu_n^{\circ}+1)$, Eq. (33) becomes

$$\frac{d\mu_n^{\circ}}{d\theta} = -(n-1)\mu_n^{\circ} + \sum_{i=2}^{n-2} \mu_i^{\circ}\mu_{n-i}^{\circ} + 2\sum_{i=2}^{n-1}\mu_i^{\circ} \qquad \text{(V-1)}$$

$$n = 2, 3, \cdots$$

It is not difficult to show that the solutions to Eq. (V-1) for n = 2 and 3 are

$$\mu_2^0 = \mu_2^0(0)\, e^{-\theta}$$

$$\mu_3^0 = 2\mu_2^0(0)\, e^{-\theta} + [\mu_3^0(0) - 2\mu_2^0(0)]\, e^{-2\theta}$$

It can be seen from Eq. (V-1) and these two solutions that the n-th moment should take the form

$$\mu_n^0 = \sum_{k=1}^{n-1} c_{n,k}\, e^{-k\theta} \tag{V-2}$$

The coefficients $c_{n,k}$ can be determined by substituting Eq. (V-2) into Eq. (V-1) and equating terms of like power in $e^{-\theta}$.

It follows from Eq. (V-2) that

$$\lim_{\theta\to\infty} \mu_n^0(\theta) = 0$$

Consequently, the limiting value of $\mu_n(\theta)$ as $\theta \to \infty$ is $n!$

Appendix VI. The Sequence of Moments for the Distribution $e^{-\eta}$

The purpose of this appendix is to prove that the sequence of moments $n!$ determines a unique distribution.

According to Reference (29), a sufficient condition for the uniqueness of a distribution with moments μ_n is that the series $\sum_{n=1}^{\infty} (\mu_{2n})^{-1/2n}$ diverges.

If $\mu_n = n!$, the series can be written as

$$\sum_{n=1}^{\infty} (\mu_{2n})^{-1/2n} = \sum_{n=1}^{\infty} \frac{1}{\left[(2n)!\right]^{1/2n}} \qquad \text{(VI-1)}$$

To prove that this is a divergent series, it suffices to show that each term in this series, after a certain term, is numerically greater than the corresponding term of the divergent series $\sum_{n=1}^{\infty} \frac{1}{n}$

It is equivalent to proving the inequality

$$n^{2n} > (2n)! \qquad \text{for n sufficiently large}$$

The asymptotic expansion for $(2n)!$ is

$$(2n)! = e^{-2n}\sqrt{4\pi n}\,(2n)^{2n} = \left(\frac{e}{2}\right)^{-2n}\sqrt{4\pi n}\;\; n^{2n}$$

It is clear that $(e/2)^{-2n}\sqrt{4\pi n} << 1$ for large n. Consequently, $n^{2n} > (2n)!$ if n is sufficiently large. This completes the proof that the sequence of moments $n!$ determines a unique distribution.

NOMENCLATURE

a	dimensionless constant
$a_{i,j}(\theta)$	$= \mu_{i+1/3}\,\mu_{j-1/3}\,/\,\mu_i\,\mu_j$
A_i	coefficient in Stokes-Cunningham correction, dimensionless
A_s	total surface area of particles per unit volume, cm^2/cc
b	dimensionless constant
c_0	a constant in Eq. (82), cm^2/sec
c, c_1, c_2	dimensionless constants
C, C_1, C_2, C_3 C_4, C_5, C_6	dimensionless constants
D_i	diffusion coefficient of particles of volume v_i, cm^2/sec
f_{ij}	collision frequency between particles of volume v_i and v_j, collisions/(cc) (sec)
$f(\eta/\tau^{1/2})$	an arbitrary function of $\eta/\tau^{1/2}$, dimensionless
$F(\eta,\tilde{\eta})$	$= \beta(\eta,\tilde{\eta})\psi(\eta)\psi(\tilde{\eta}) / \int_0^\infty\int_0^\infty \beta(\eta,\tilde{\eta})\psi(\eta)\psi(\tilde{\eta})\,d\eta\,d\tilde{\eta}$, dimensionless
G	shear rate, sec^{-1}
k	Boltzmann constant
K	coagulation rate constant, cc/sec
m_ν	ν-th moment of the distribution function n(v,t)
$M(v,t)$	mass of particles with volume larger than v in a unit volume of the system, gm/cc

NOMENCLATURE (Cont'd.)

$n_i(t)$	number of particles per unit volume with volume v_i, particles/cc
$n(r,t)$, $n(v,t)$	particle size distribution function, particles/cm^6
$N(t)$	total number concentration of particles, particles/cc
N_v	number of particles with volume larger than v in a unit volume of the system, particles/cc
p	parameter of Laplace transform
P	$= 3\mu G\phi/(2\pi kTN)$ or $1.46\mu\phi\varepsilon^{1/2}/(\pi kTN\nu^{1/2})$, dimensionless
Q	$= \mu^*_{-1/3} + 3P\mu^*_{2/3}$
r	particle radius, cm
t	time, sec
t_0	a constant in Eq. (82), sec
T	absolute temperature, °K
v, v_i	particle volume, cm^3
x	$= \ln \xi$
$Y(x)$	dimensionless function of x

Greek Symbols

α	$= \mu^*_{1/3}\mu^*_{-1/3}/(1+\mu^*_{1/3}\mu^*_{-1/3})$
$\beta(v_i,v_j)$	collision frequency factor between particles of volume v_i and v_j, cc/sec
γ	a proportionality constant in Eq. (78)
ϵ	rate of energy dissipation per unit mass by turbulence, cm^2/sec^3
ξ	$= (1+\mu^*_{1/3}\mu^*_{-1/3})^3\eta/(\mu^*_{1/3})^3$

η	reduced particle volume, dimensionless
θ	$= -\frac{1}{2} \ln \tau$
θ_1	$= \frac{1}{2} \int_{\tau}^{1} \frac{d\tau}{(1+\mu_{1/3}\mu_{-1/3})\tau}$
λ	mean free path, cm
Λ	$= 1.257 \ \lambda \left(\frac{4\pi N}{3\phi} \right)^{1/3}$, dimensionless
μ	viscosity, gm/(cm)(sec)
μ_n	n-th moments of $\Phi(\eta,\tau)$
μ_n^*	n-th moments of $\psi(\eta)$
ν	kinematic viscosity, cm^2/sec
ρ_p	particle density, gm/cm^3
τ	$= \left[\frac{N(t)}{N(0)} \right]^2$, dimensionless
ϕ	total volume concentration of particles, cc/cc
$\Phi(\eta,\tau)$	reduced particle size distribution function, dimensionless
$\chi(\xi)$	$= (\mu^*_{1/3})^3 \ \psi(\eta) / (1 + \mu^*_{1/3} \mu^*_{-1/3})^4$
$\psi(\eta)$	self-preserving particle size distribution function, dimensionless
$\psi_{LN}(\eta)$	log normal distribution
ω	a primitive root of unity

Subscripts

C	the case of constant collision frequency factor
SB	self-preserving systems coagulating by Brownian motion
SBS	self-preserving systems coagulating by simultaneous Brownian motion and shear flow

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PROPOSITION I

OPTIMUM VOLUME RATIOS FOR MINIMUM RESIDENCE TIME IN STIRRED-TANK REACTOR SEQUENCES.

It was first pointed out by Denbigh (1) that maximum conversion can be obtained by a suitable choice of the ratio of the reactor volumes for irreversible reactions occurring in a sequence of two reactors with a fixed total volume. In his paper, Denbigh reported that for a first-order reaction both reactors should be of the same size, but in the case of second- and third-order reactions the optimum ratios were 2.0 and 3.0, respectively. Working on the problem of minimizing the total reactor volume for a fixed conversion, Leclerc (2) confirmed the conclusion of Denbigh regarding first-order reactions and pointed out that Denbigh's conclusions regarding second- and third-order reactions depend on the assumption that the concentration of the reactant leaving each reactor is much smaller than the concentration of the reactant entering that reactor. By a graphical trial-and-error procedure, Leclerc obtained the results that the optimum volume ratios for second- and third-order reactions are 1.3 and 1.7 respectively for the conversion of a reactant from a concentration of 0.7 to a concentration of 0.5. Subsequently, Wood and Stevens (3) used the method of Lagrangian multipliers and the dynamic programming technique to compute the optimum volume ratios, and found that Leclerc's results for second- and third-order reactions are in error. Using an IBM 709 computer, Wood and Stevens also calculated the optimum volume ratios for the three reactor sequence and concluded that the optimum volume ratios are functions of the overall conversion only.

The purpose of this proposition is to show that by using the technique of the discrete maximum principle, this particular optimization problem can be solved with less amount of computing labor. A set of equations relating the optimum volume ratios and the overall conversion is presented. For a second-order reaction occurring in a sequence of two reactors, the optimum volume ratio is expressed as a function of the overall conversion in a closed form.

An N-stage stirred tank reactor sequence is schematically shown in Fig. 1. The concentration of the reactant is represented by C and the reactor volume by V. The subscript n denotes the stage number. The flow rate is represented by Q. The residence time, defined as the ratio of the reactor volume to the flow rate, is designated by θ.

If the reaction occurring in the reactor is ν-th order with a rate constant k, a steady-state material balance for the nth reactor gives:

$$C_{n-1} = C_n + k\,\theta_n C_n^{\nu} \tag{1}$$

The problem is to find the values of the ratio, $\frac{\theta_n}{\theta_1}$, $n = 2,3,\ldots,N$, so as to minimize $\sum_{n=1}^{N} \theta_n$, with given C_0 and C_N.

It follows from Eq. (1) that C_n can be considered as a function of C_{n-1} and θ_n.

$$C_n = T\,(C_{n-1},\ \theta_n) \qquad n = 1,2,\ldots,N \tag{2}$$

The optimization problem belongs to the class of one-dimensional processes discussed in Reference (4). According to Reference (4), a one-dimensional process is a multi-stage process whose performance equation is identical with Eq. (2) and the function to be minimized can be expressed as a sum $\sum_{n=1}^{N} G(C_{n-1}, \theta_n)$, in which C is the state variable and θ the decision variable. The optimum values of θ_n, n = 1,2,...,N, for such a process can be determined by the following N relationships:

$$\frac{\dfrac{\partial G(C_{n-1}, \theta_n)}{\partial \theta_n}}{\dfrac{\partial T(C_{n-1}, \theta_n)}{\partial \theta_n}} = \frac{\dfrac{\partial G(C_n, \theta_{n+1})}{\partial \theta_{n+1}}}{\dfrac{\partial T(C_n, \theta_{n+1})}{\partial \theta_{n+1}}} \cdot \frac{\partial T(C_n, \theta_{n+1})}{\partial C_n} - \frac{\partial G(C_n, \theta_{n+1})}{\partial C_n}$$

$$n = 1,2,\ldots,N-1 \qquad (3)$$

C_N = given value

For this particular problem, $G(C_{n-1}, \theta_n) = \theta_n$ and hence Eq. (3) reduces to

$$\frac{\partial T(C_{n-1}, \theta_n)}{\partial \theta_n} = \frac{\dfrac{\partial T(C_n, \theta_{n+1})}{\partial \theta_{n+1}}}{\dfrac{\partial T(C_n, \theta_{n+1})}{\partial C_n}} \qquad n = 1,2,\ldots,N-1 \qquad (4)$$

From Eqs. (1) and (2), it can be found that

$$\frac{\partial T(C_{n-1}, \theta_n)}{\partial \theta_n} = -\frac{k\, C_n^{\nu}}{1 + \nu k\, \theta_n C_n^{\nu-1}} \qquad n = 1,2,\ldots,N \qquad (5)$$

and

$$\frac{\partial T(C_{n-1},\theta_n)}{\partial C_{n-1}} = \frac{1}{1+\nu k\,\theta_n C_n^{\nu-1}} \qquad n = 1,2,\ldots,N \qquad (6)$$

Substituting Eqs. (5) and (6) into Eq. (4) gives:

$$1+\nu k\,\theta_n C_n^{\nu-1} = \left(\frac{C_n}{C_{n+1}}\right)^{\nu} \qquad n = 1,2,\ldots,N-1 \qquad (7)$$

It follows from Eq. (1) that

$$\theta_n = \frac{C_{n-1} - C_n}{k\,C_n^{\nu}} \qquad n = 1,2,\ldots,N \qquad (8)$$

Substituting this expression for θ_n into Eq. (7) yields

$$\frac{1}{y_{n+1}^{\nu}} - 1 = \nu\left(\frac{1}{y_n} - 1\right) \qquad n = 1,2,\ldots,N-1 \qquad (9)$$

in which $y_n = c_n/c_{n-1}$. It can be readily seen that $C_N/C_0 = \prod_{n=1}^{N} y_n$. and the overall conversion ξ is related to y_n's by

$$\xi = \frac{C_0 - C_N}{C_0} = 1 - \prod_{n=1}^{N} y_n \qquad (10)$$

The values of y_n, n = 1,2,...,N, can be obtained by solving simultaneously the N relationships in Eqs. (9) and (10). If the volume ratio V_n/V_1 is denoted by γ_n, it can be found from Eqs. (9) and (10) that

$$\gamma_n = \nu^{n-1} \prod_{k=2}^{n} \frac{1-y_k}{1-y_k^{\nu}} \qquad n = 1,2,\ldots,N \tag{11}$$

Eq. (11) indicates that the optimum volume ratio is a function of y_n's, which in turn are functions of the overall conversion only,

For the simple case with $\nu = 2$ and N = 2 Eqs. (9), (10) and (11) can be solved to give:

$$\gamma_2 = \frac{2}{1 + A + B + \frac{1-\xi}{6}}$$

in which

$$A = \frac{1-\xi}{6}\left\{1 + \frac{54}{(1-\xi)^2}\left[1 + \sqrt{\frac{(1-\xi)^2}{27} + 1}\,\right]\right\}^{1/3}$$

$$B = \frac{1-\xi}{6}\left\{1 + \frac{54}{(1-\xi)^2}\left[1 - \sqrt{\frac{(1-\xi)^2}{27} + 1}\,\right]\right\}^{1/3}$$

Since $\frac{(1-\xi)^2}{27} << 1$, A and B can be approximated by

$$A \cong \left(\frac{1-\xi}{2}\right)^{1/3}$$

$$B \cong \frac{1}{9}\left(\frac{1-\xi}{2}\right)^{5/3}$$

The approximate solution for the optimum volume ratio is

$$\gamma_2 = \frac{2}{1 + \frac{1-\xi}{6} + \left(\frac{1-\xi}{2}\right)^{1/3} + \frac{1}{9}\left(\frac{1-\xi}{2}\right)^{5/3}} \qquad (12)$$

The values of γ_2 calculated from Eq. (12) are shown in Fig. 2. The result is in good agreement with that obtained by Wood and Stevens.

Nomenclature

C	concentration
k	reaction rate constant
N	total number of stages
Q	flow rate
V	reactor volume
y_n	C_n/C_{n-1}
γ_n	V_n/V_1
θ	residence time
ν	order of reaction
ξ	overall conversion

Subscript

n	stage designation

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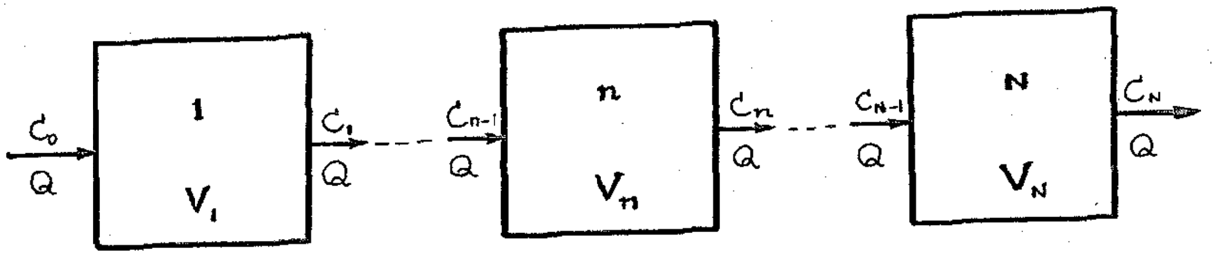

Figure 1. An N-stage Stirred Tank Reactor Sequence

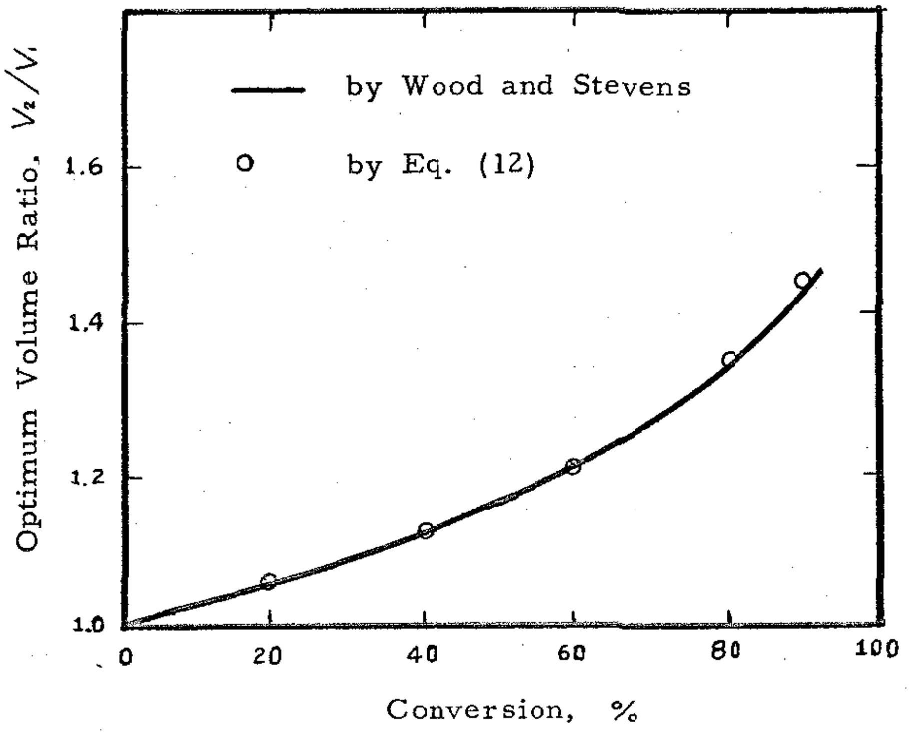

Figure 2. Comparison of the Result Obtained by Wood and Stevens with that Calculated from Eq. (12).

PROPOSITION II

Reprinted from
JOURNAL OF ELECTRONICS AND CONTROL, Vol. 17, No. 2, p. 199, August 1964

The Optimization of Continuous Complex Processes by the Maximum Principle†

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[Received January 1, 1964]

ABSTRACT

A scheme which can be used to optimize a continuous complex process by means of the maximum principle is presented. The continuous complex process is a process which is composed of interconnected branches whose performances can be described by a set of differential equations. An example of optimizing a simple feedback process is given to illustrate the use of the method.

§ 1. INTRODUCTION

THE maximum principle was originally formulated by Pontryagin (1962) for the optimization of continuous simple processes, i.e. the processes which dynamically follow simple paths, with each following only one path as depicted in fig. 1. Many processes employed in industry are, however, composed of several interconnected branches. While such a complex process usually can be decomposed into several simple sub-processes which can be optimized separately, special care must be taken in dealing with the state vector at the junction point of the sub-processes. Thus, it is desirable to devise a scheme which can be directly used to optimize a complex process without decomposing it. The purpose of this paper is to propose such a scheme.

§ 2. DEFINITION

A process refers to the dynamical change of the state of a system. A process can be classified either as a time-wise or as a space-wise process, depending on whether the change of the state is along the time or the space coordinate. Since these two types of processes are mathematically identical, the coordinate, t, will be used to denote either time or space in the following discussion.

For a deterministic process, the state of a system at a certain time or position, t, is completely described by the state vector, $x(t)$. The change of the state is a result of the action of the decision vector, $\theta(t)$,

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which can be manipulated independently. In a simple continuous process (see fig. 1), the change of the state can be described by the following performance equation :

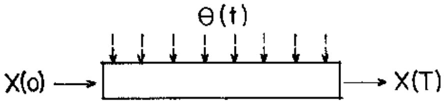
$$\frac{dx_i}{dt}=f_i(x_1,\ldots,x_s\,;\quad \theta_1,\ldots,\theta_r),\quad i=1,2,\ldots,s$$

or in vector form

$$\frac{dx}{dt}=f(x;\quad \theta), \qquad \ldots\ldots\ldots \quad (1)$$

where s and r are the dimensions of x and θ respectively. The length of the process is denoted by T which is the distance between two end points in the t-coordinate.

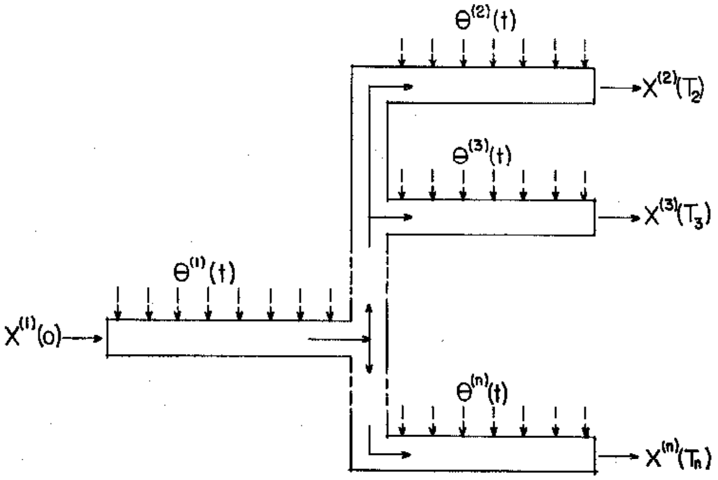
Fig. 1



Simple process.

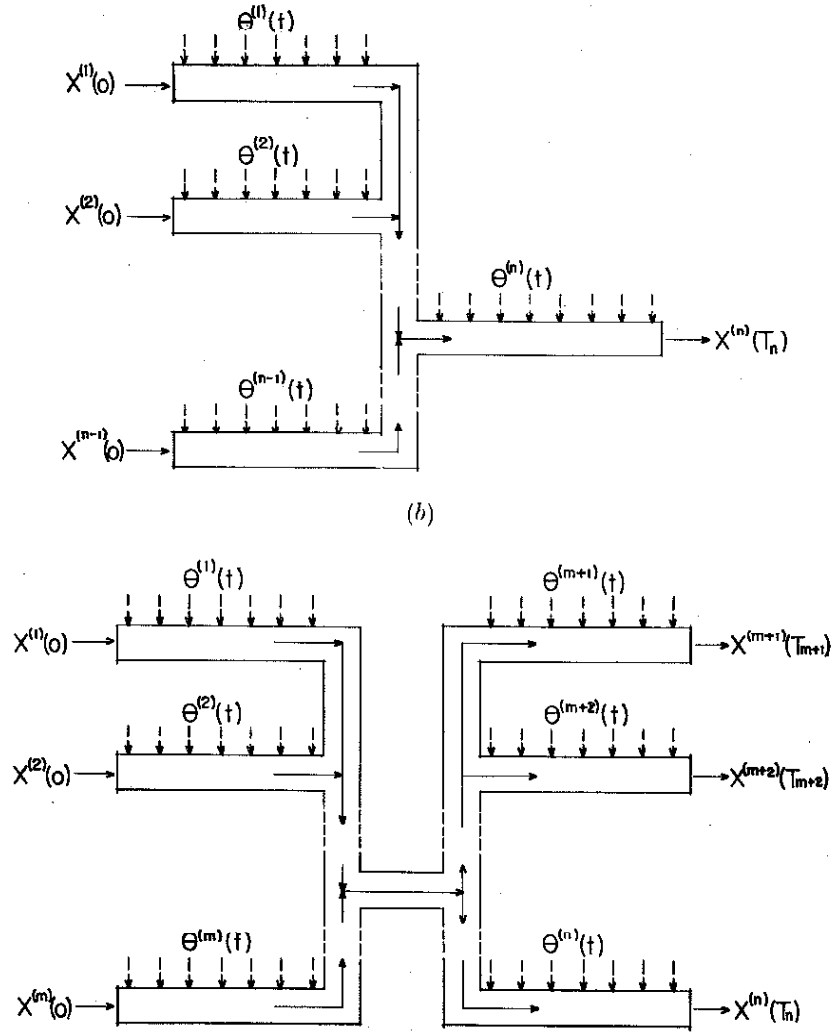
As mentioned in § 1, all of the complex processes are composed of several interconnected branches. The point where two or more branches connect is called a junction point. There may be, as shown in fig. 2, three different types of junction points : (*a*) separating point, (*b*) combining point, and (*c*) crossing point. A separating point represents a point where one branch of the path splits into several branches. A combining point is a

Fig. 2



(*a*)

Fig. 2 (*continued*)



(*b*)

(*c*)

(*a*) Separating point ; (*b*) combining point ; (*c*) crossing point.

point where several branches combine into one single branch. A junction point where several branches combine together and then split again into several branches may be called a crossing point.

Each branch in a complex process is described by a performance equation of the type categorized by eqn. (1). The form of the function, $f(x\,;\,\theta)$, and the length, T, may differ for different branches. A number may be arbitrarily assigned to each branch for convenience. The superscripts in $f^{(k)}(x^{(k)}\,;\,\theta^{(k)})$ and the subscript of T_k represent the branch number.

The arrows at the junction point show the direction of the flow of the process streams. The relationships between the state vectors of different branches at the junction points are described by the 'junction equations'. They are (for convenience, all the stage numbers are referred to fig. 2) :

(1) Separating points :

$$\left.\begin{aligned} x^{(2)}(0) &= g^{(2)}(x^{(1)}(T_1)), \\ x^{(3)}(0) &= g^{(3)}(x^{(1)}(T_1)), \\ &\cdot \\ &\cdot \\ &\cdot \\ x^{(n)}(0) &= g^{(n)}(x^{(1)}(T_1)). \end{aligned}\right\} \quad \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \quad (2)$$

(2) Combining points :

$$x^{(n)}(0) = g^{(n)}(x^{(1)}(T_1), x^{(2)}(T_2), \ldots, x^{(n-1)}(T_{n-1})). \quad \cdot\ \cdot \quad (3)$$

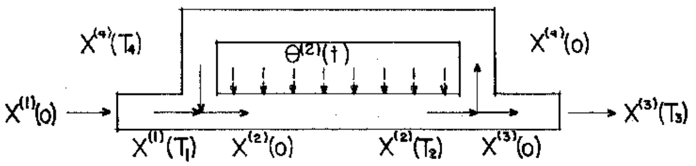
(3) Crossing points :

$$\left.\begin{aligned} x^{(m+1)}(0) &= g^{(m+1)}(x^{(1)}(T_1), x^{(2)}(T_2), \ldots, x^{(m)}(T_m)), \\ x^{(m+2)}(0) &= g^{(m+2)}(x^{(1)}(T_1), x^{(2)}(T_2), \ldots, x^{(m)}(T_m)), \\ &\cdot \\ &\cdot \\ &\cdot \\ x^{(n)}(0) &= g^{(n)}(x^{(1)}(T_1), x^{(2)}(T_2), \ldots, x^{(m)}(T_m)), \end{aligned}\right\} \quad \cdot\ \cdot \quad (4)$$

where the function $g^{(n)}(x^{(k)}(T_k))$ is the vector form of $g^{(n)}(x_1^{(k)}(T_k), x_2^{(k)}(T_k), \ldots, x_{s^{(k)}}^{(k)}(T_k))$. It may be noted that the dimensions of the state vector may be different from branch to branch. Superscripts, such as in $s^{(k)}$, are used to distinguish the differences.

In a complex process, there may be some branches which do not possess the decision vector, such as the upper branch of a simple feedback loop shown in fig. 3. The performance equation for such a non-decision branch is :

Fig. 3



Simple feedback loop.

$$\frac{dx}{dt} = f(x). \quad \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \quad (5)$$

A complex process may have several initial points and final points, and the values of the state vectors at these points are called initial states and final states respectively.

The optimization problem under consideration may be stated as follows.

Given all of the performance equations, junction equations, lengths, and initial states of a complex process consisting of a path with N branches, b initial points, and f final points, find the decision vector function of each branch so as to maximize a certain linear function of the final states of the process, such as

$$\sum_{k=1}^{f} \sum_{i=1}^{s^{(k)}} c_i^{(k)} x_i^{(k)}(T_k),$$

where $c_i^{(k)}$ are constants ; the summations are taken over all the components of the state vectors and over all the final states.

The set of the decision vector functions, $\theta^{(k)}(t)$, $k=1, 2, \ldots, N$, thus found is called the optimal policy. The function to be maximized is called the objective function.

§ 3. OPTIMIZATION PROCEDURE

The procedure to find the optimal policy for a complex process can be divided into two steps.

Step 1. Introduce a covariant vector, $z^{(k)}(t)$, and a Hamiltonian function $H^{(k)}(x, z, \theta)$ for each branch satisfying :

$$H^{(k)}(x, z, \theta) = \sum_{i=1}^{s^{(k)}} z_i^{(k)} f_i^{(k)}(x_1^{(k)}, \ldots, x_{s^{(k)}}^{(k)} ; \theta_1^{(k)}, \ldots, \theta_{r^{(k)}}^{(k)}), \quad . \quad (6)$$

$$\frac{\partial H^{(k)}(x, z, \theta)}{\partial x_i^{(k)}} = -\frac{dz_i^{(k)}(t)}{dt}, \quad i=1, 2, \ldots, s^{(k)}, \quad . \quad . \quad . \quad (7)$$

with the values of $z_i^{(k)}$ at the junction points and final points satisfying (for convenience, all the stage numbers are referred to fig. 2) :

(*a*) Separating points :

$$z_i^{(1)}(T_1) = \sum_{k=2}^{n} \sum_{j=1}^{s^{(k)}} \frac{\partial g_j^{(k)}}{\partial x_i^{(1)}} z_j^{(k)}(0) \; ; \quad i=1, 2, \ldots, s^{(1)}. \quad . \quad . \quad (8)$$

(*b*) Combining points :

$$z_i^{(k)}(T_k) = \sum_{j=1}^{s^{(n)}} \frac{\partial g_j^{(n)}}{\partial x_i^{(k)}} z_j^{(n)}(0) \; ; \quad i, =1, 2, \ldots, s^{(k)}, \quad k=1, 2, \ldots, n-1. \quad (9)$$

(*c*) Crossing points :

$$z_i^{(p)}(T_p) = \sum_{k=m+1}^{n} \sum_{j=1}^{s^{(k)}} \frac{\partial g_j^{(k)}}{\partial x_i^{(p)}} z_j^{(k)}(0) \; ; \quad i=1, 2, \ldots, s^{(p)}, \quad p=1, 2, \ldots, m. \quad (10)$$

(*d*) Final points :

$$z_i^{(k)}(T_k) = -c_i^{(k)} \; ; \quad i=1, 2, \ldots, s^{(k)}, \quad k=1, 2, \ldots, f. \quad . \quad . \quad (11)$$

Step 2. Find the decision vector function, $\theta^{(k)}$, from the following conditions :

$$H^{(k)}(x, z, \theta) = \text{minimum at every point } t, k-1, 2, \ldots, N. \quad . \quad (12)$$

In other words, the optimal functions, $\bar{\theta}^{(k)}$, are obtained by varying $\theta^{(k)}$ until the minimum value of $H^{(k)}$ is attained at each point.

§ 4. DERIVATION

The condition, eqn. (12), will now be briefly derived.

Let $\bar{\theta}^{(k)}(t)$ be the optimal decision vector functions and $\bar{x}^{(k)}(t)$ the optimal state vector functions of the kth branch, then :

$$\frac{d\bar{x}^{(k)}(t)}{dt} = f^{(k)}(\bar{x}^{(k)}\,;\,\bar{\theta}^{(k)}). \qquad (13)$$

If an independent small perturbation of the decision vector is made at every point of the process, such that :

$$\theta^{(k)}(t,\epsilon) = \bar{\theta}^{(k)}(t) + \epsilon\phi^{(k)}(t) + 0(\epsilon^2), \qquad (14)$$

the state vector function will be perturbed to :

$$x^{(k)}(t,\epsilon) = \bar{x}^{(k)}(t) + \epsilon y^{(k)}(t) + 0(\epsilon^2), \qquad (15)$$

where $\phi^{(k)}(t)$ and $y^{(k)}(t)$ are arbitrary functions of t, having the same dimensions and order of magnitude as $\theta^{(k)}$ and $x^{(k)}$ respectively ; ϵ represents a very small number ; $0(\epsilon^2)$ denotes the terms including ϵ^2 and of higher order.

By means of Taylor's expansion, a variational equation can be obtained from eqns. (13) and (15) as :

$$\epsilon\frac{dy_i^{(k)}}{dt} = f_i^{(k)}(\bar{x}^{(k)}\,;\,\theta^{(k)}) - f_i^{(k)}(\bar{x}^{(k)}\,;\,\bar{\theta}^{(k)}) + \sum_{j=1}^{s^{(k)}} \epsilon y_j^{(k)} \times \frac{\partial f_i^{(k)}(\bar{x}^{(k)}\,;\,\bar{\theta}^{(k)})}{\partial \bar{x}_j^{(k)}} + 0(\epsilon^2). \qquad (16)$$

The relationships between the variations of the state vectors of different branches at the junction points are obtained by expanding the junction equations in powers of ϵy_i as follows :

(1) Separating points :

$$\epsilon y_i^{(k)}(0) = \sum_{j=1}^{s^{(1)}} \epsilon y_j^{(1)}(T_1)\frac{\partial g_i^{(k)}(x_1^{(1)}(T_1),\ldots,x_{s^{(1)}}^{(1)}(T_1))}{\partial x_j^{(1)}} + 0(\epsilon^2),$$
$$i=1,2,\ldots,s^{(k)},\quad k=2,3,\ldots,n. \qquad (17)$$

(2) Combining points :

$$\epsilon y_i^{(n)}(0) = \sum_{k=1}^{n-1}\sum_{j=1}^{s^{(k)}} \epsilon y_j^{(k)}(T_k)\frac{\partial g_i^{(n)}(x^{(1)}(T_1),\ldots,x^{(n-1)}(T_{n-1}))}{\partial x_j^{(k)}} + 0(\epsilon^2),$$
$$i=1,2,\ldots,s^{(n)}. \qquad (18)$$

(3) Crossing points :

$$\epsilon y_i^{(p)}(0) = \sum_{k=1}^{m}\sum_{j=1}^{s^{(k)}} \epsilon y_j^{(k)}(T_k)\frac{\partial g_i^{(p)}(x^{(1)}(T_1),\ldots,x^{(m)}(T_m))}{\partial x_j^{(k)}} + 0(\epsilon^2),$$
$$i=1,2,\ldots,s^{(p)},\quad p=m+1,m+2,\ldots,n. \qquad (19)$$

Since all the initial states of the process are given and fixed, we have :

$$y_i^{(k)}(0)=0\ ;\quad i=1,2,\ldots,s^{(k)},\quad k=1,2,\ldots,b. \qquad (20)$$

Now if we substitute the expression for $dz_i^{(k)}/dt$ from eqn. (7) and that for $dy_i^{(k)}/dt$ from eqn. (16) into the following equation :

$$\frac{d}{dt}\sum_{i=1}^{s^{(k)}} \epsilon y_i^{(k)} z_i^{(k)} = \sum_{i=1}^{s^{(k)}} \epsilon z_i^{(k)} \frac{dy_i^{(k)}}{dt} + \sum_{i=1}^{s^{(k)}} \epsilon y_i^{(k)} \frac{dz_i^{(k)}}{dt},$$

we obtain :

$$\frac{d}{dt}\sum_{i=1}^{s^{(k)}} \epsilon y_i^{(k)} z_i^{(k)} = \sum_{i=1}^{s^{(k)}} z_i^{(k)}[f_i^{(k)}(\bar{x}^{(k)};\, \theta^{(k)}) - f_i^{(k)}(\bar{x}^{(k)};\, \bar{\theta}^{(k)})],\ k=1,\ 2,\ldots,N.$$

In obtaining the above equation, the term $0(\epsilon^2)$ is deleted on the assumption that all of the functions, $f^{(k)}(x,\theta)$, depend smoothly on x and θ. The same assumption will also be made for the junction functions, $g^{(k)}(x)$, so that the term $0(\epsilon^2)$ also can be deleted from eqns. (17) through (19).

Integrating from $t=0$ to $t=T_k$ and summing over all branches give

$$\sum_{k=1}^{N}\sum_{i=1}^{s^{(k)}} \epsilon[y_i^{(k)}(T_k)z_i^{(k)}(T_k) - y_i^{(k)}(0)z_i^{(k)}(0)] = \sum_{k=1}^{N}\int_0^{T_k}\sum_{i=1}^{s^{(k)}} z_i^{(k)} \times [f_i^{(k)}(\bar{x}^{(k)}\ ;\ \theta^{(k)}(- f_i^{(k)}(\bar{x}^{(k)}\ ;\ \bar{\theta}^{(k)})]\,dt. \qquad (21)$$

Applying eqns. (8) through (10) and eqns. (17) through (20) to the left-hand side of eqn. (21) yields :

$$\sum_{k=1}^{f}\sum_{i=1}^{s^{(k)}} \epsilon y_i^{(k)}(T_k)z_i^{(k)}(T_k) = \sum_{k=1}^{N}\int_0^{T_k}\sum_{i=1}^{s^{(k)}} z_i^{(k)}[f_i^{(k)}(\bar{x}^{(k)}\ ;\ \theta^{(k)}) - f_i^{(k)}(\bar{x}^{(k)}\ ;\ \bar{\theta}^{(k)})]\,dt. \qquad (22)$$

Since $\bar{\theta}^{(k)}, k=1,2,\ldots,N$, is the sequence that maximizes

$$\sum_{k=1}^{f}\sum_{i=1}^{s^{(k)}} c_i^{(k)} x_i^{(k)}(T_k),$$

the effect of the perturbation represented by eqn. (14) can only be to make :

$$\sum_{k=1}^{f}\sum_{i=1}^{s^{(k)}} \epsilon c_i^{(k)} y_i^{(k)}(T_k) \leqslant 0. \qquad (23)$$

Combination of eqns. (11), (22) and (23) gives :

$$\sum_{k=1}^{N}\int_0^{T_k}\sum_{i=1}^{s^{(k)}} z_i^{(k)}[f_i^{(k)}(\bar{x}^{(k)}\ ;\ \theta^{(k)}) - f_i^{(k)}(\bar{x}^{(k)}\ ;\ \bar{\theta}^{(k)})]\,dt \geqslant 0. \qquad (24)$$

Now since the perturbed functions, $\theta^{(k)}$, are independent of each other, it may be concluded that the integrand of each integral in eqn. (24) must itself be non-negative ; thus :

$$\sum_{i=1}^{s^{(k)}} z_i^{(k)}[f_i^{(k)}(\bar{x}^{(k)} ; \theta^{(k)}) - f_i^{(k)}(\bar{x}^{(k)} ; \bar{\theta}^{(k)})] \geqslant 0,$$

$$k = 1, 2, \ldots, N,$$

which is equivalent to eqn. (12).

From the above derivation, it follows immediately that if the objective function is to be minimized instead of maximized, the optimal policy can be found by the same procedure except that eqn. (12) is replaced by :

$$H^{(k)}(x, z, \theta) = \text{maximum}. \qquad (25)$$

§ 5. AN EXAMPLE

To illustrate the use of the optimization procedure presented, let us consider the simple feedback loop shown in fig. 3.

The process consists of four branches with the following performance equations :

$$\frac{dx_1^{(1)}}{dt} = 0, \qquad (26)$$

$$\frac{dx_1^{(2)}}{dt} = -ax_1^{(2)} + \theta_1^{(2)}, \qquad (27)$$

$$\frac{dx_1^{(3)}}{dt} = 0, \qquad (28)$$

$$\frac{dx_1^{(4)}}{dt} = 0. \qquad (29)$$

The junction equations are :

$$x_1^{(2)}(0) = \alpha x_1^{(1)}(T_1) + \beta x_1^{(4)}(T_4), \qquad (30)$$

$$x_1^{(3)}(0) = x_1^{(2)}(T_2), \qquad (31)$$

$$x_1^{(4)}(0) = x_1^{(2)}(T_2). \qquad (32)$$

It is desired to find the decision function $\theta_1^{(2)}(t)$ to minimize the integral

$$\tfrac{1}{2}\int_0^{T_2} [(x_1^{(2)})^2 + (\theta_1^{(2)})^2]\, dt$$

with the initial state given as :

$$x_1^{(1)}(0) = \gamma. \qquad (33)$$

To solve this problem, we introduce a second state variable :

$$x_2^{(2)}(t)=\tfrac{1}{2}\int_0^t[(x_1^{(2)})^2+(\theta_1^{(2)})^2]\,dt.$$

It follows immediately that the performance equations for x_2 are :

$$\frac{dx_2^{(1)}}{dt}=\frac{dx_2^{(3)}}{dt}=\frac{dx_2^{(4)}}{dt}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$\frac{dx_2^{(2)}}{dt}=\tfrac{1}{2}(x_1^{(2)})^2+\tfrac{1}{2}(\theta_1^{(2)})^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The junction equations are :

$$x_2^{(2)}(0)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$x_2^{(3)}(0)=x_2^{(2)}(T_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

$$x_2^{(4)}(0)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

The initial state is :

$$x_2^{(1)}(0)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

The optimization problem is now transformed into one of minimizing $x_2^{(3)}(T_3)$ for a process described by eqns. (26) through (39). Since the objective function is $x_2^{(3)}(T_3)$, we have $c_1^{(3)}=0$ and $c_2^{(3)}=1$.

According to eqns. (6) and (7), we write :

$$H^{(1)}=H^{(3)}=H^{(4)}=0,$$

$$H^{(2)}=az_1^{(2)}x_1^{(2)}+\tfrac{1}{2}z_2^{(2)}(x_1^{(2)})^2+z_1^{(2)}\theta_1^{(2)}+\tfrac{1}{2}z_2^{(2)}(\theta_1^{(2)})^2, \quad . \quad (40)$$

$$\frac{dz_1^{(1)}}{dt}=\frac{dz_1^{(3)}}{dt}=\frac{dz_1^{(4)}}{dt}=\frac{dz_2^{(1)}}{dt}=\frac{dz_2^{(3)}}{dt}=\frac{dz_2^{(4)}}{dt}=0, \quad . \quad . \quad (41)$$

$$\frac{dz_1^{(2)}}{dt}=+az_1^{(2)}-z_2^{(2)}x_1^{(2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$\frac{dz_2^{(2)}}{dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

According to eqns. (9) and (8), we have at the combining point :

$$z_1^{(1)}(T_1)=\alpha z_1^{(2)}(0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

$$z_1^{(4)}(T_4)=\beta z_1^{(2)}(0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

$$z_2^{(1)}(T_1)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$z_2^{(4)}(T_4)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

and at the separating point :

$$z_1^{(2)}(T_2)=z_1^{(3)}(0)+z_1^{(4)}(0), \quad . \ . \ . \ . \ . \ . \ . \quad (48)$$

$$z_2^{(2)}(T_2)=z_2^{(3)}(0). \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (49)$$

Applying eqn. (11), we have

$$z_1^{(3)}(T_3)=0, \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (50)$$

$$z_2^{(3)}(T_3)=-1. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (51)$$

It is seen from eqns. (41) and (43) that :

$$z_i^{(k)}(t)=\text{constant}\ ; \quad i=1,2, \quad k=1,3,4 \text{ and } i=2, \quad k=2. \quad (52)$$

Inserting eqns. (50) and (51) into eqns. (48) and (49) and employing eqn. (52) give :

$$z_1^{(2)}(T_2)=z_1^{(4)}(0)=z_1^{(4)}(T_4), \quad . \ . \ . \ . \quad (53)$$

$$z_2^{(2)}(t)=-1. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (54)$$

From eqns. (45) and (53), we obtain :

$$\beta z_1^{(2)}(0)=z_1^{(2)}(T_2). \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (55)$$

Substituting $z_2^{(2)}(t)=-1$ into eqn. (40) gives :

$$H^{(2)}=-az_1^{(2)}x_1^{(2)}-\tfrac{1}{2}(x_1^{(2)})^2+z_1^{(2)}\theta_1^{(2)}-\tfrac{1}{2}(\theta_1^{(2)})^2. \quad . \ . \quad (56)$$

According to eqn. (25), with the assumption that the maximum of $H^{(2)}$ occurs at the stationary point, we can obtain $\theta_1^{(2)}(t)$ by putting :

$$\frac{\partial H^{(2)}}{\partial \theta_1^{(2)}}=0.$$

The result is :

$$\theta_1^{(2)}(t)=z_1^{(2)}(t). \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (57)$$

Inserting the above expression of $\theta_1^{(2)}(t)$ into eqn. (27) gives :

$$\frac{dx_1^{(2)}}{dt}=-ax_1^{(2)}+z_1^{(2)}. \quad . \ . \ . \ . \ . \ . \ . \quad (58)$$

From eqn. (42), we have :

$$\frac{dz_1^{(2)}}{dt}=+x_1^{(2)}=az_1^{(2)}. \quad . \ . \ . \ . \ . \ . \ . \quad (59)$$

Equations (58) and (59) can be readily integrated to give :

$$x_1^{(2)}(t)=A_1\exp(\lambda t)+A_2\exp(-\lambda t), \quad . \ . \ . \ . \quad (60)$$

$$z_1^{(2)}(t)=A_3\exp(\lambda t)+A_4\exp(-\lambda t), \quad . \quad . \quad . \quad . \quad (61)$$

where

$$\lambda=\sqrt{(a^2+1)}, \quad A_3=(a+\lambda)A_1, \quad \text{and } A_4=(a-\lambda)A_2.$$

The constants A_1 and A_2 are to be determined by eqns. (30) and (55).

It is seen from eqns. (26) and (29) that $x_1^{(1)}$ and $x_1^{(4)}$ are constant. Substitution of eqns. (32) and (33) into eqn. (30) yields :

$$x_1^{(2)}(0)=\alpha\gamma+\beta x_1^{(2)}(T_2). \quad . \quad . \quad . \quad . \quad . \quad (62)$$

Applying eqns. (55) and (62) to eqns. (60) and (61), we have :

$$A_1=\frac{[\alpha\gamma/1-\beta\exp(\lambda T_2)]}{1-[(a+\lambda)(1-\beta\exp(-\lambda T_2))(\beta-\exp(\lambda T_2))]/[(a-\lambda)\times(1-\beta\exp(+\lambda T_2))(\beta-\exp(-\lambda T_2))]}$$

and

$$A_2=\frac{[\alpha\gamma/1-\beta\exp(\lambda T_2)]}{[1-\beta\exp(-\lambda T_2)]/[1-\beta\exp(\lambda T_2)]-[(a-\lambda)(\beta-\exp(-\lambda T_2))]/[(a+\lambda)(\beta-\exp(\lambda T_2))]}.$$

Since $\theta_1^{(2)}(t)=z_1^{(2)}(t)$, the optimal policy is :

$$\theta_1^{(2)}(t)=(a+\lambda)A_1\exp(\lambda t)+(a-\lambda)A_2\exp(-\lambda t).$$

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PROPOSITION III

THE RELATION BETWEEN RATE CONSTANTS AND EQUILIBRIUM CONSTANT

Blum and Luus (1) gave a mathematical proof for the relation that the ratio of the forward and the reverse reaction rate constants is a simple power of the equilibrium constant. They stated that this relation is valid for the entire class of reversible reactions for which the overall reaction rate is written "conventionally" as the difference of two separable rate terms. It is felt that the conditions under which this relation holds have not been clearly stated. The purpose of this proposition is (1) to discuss the conditions under which this relation will be applicable and (2) to give an alternative mathematical proof for this relation.

This discussion will be limited to the class of reversible reactions which can be represented as

$$0 \rightleftharpoons \sum_{i=1}^{m} \nu_i A_i \qquad (1)$$

in which ν_i are the stoichiometric coefficients, positive for products and negative for reactants, and A_i represent the chemical species involved.

If Eq. (1) represents an elementary reaction, the overall reaction rate for any species A_j can be expressed as the difference of the forward and the reverse reaction rate:

$$\frac{1}{\nu_j}\,\frac{d[A_j]}{dt} = k \prod_{\substack{i \\ (\nu_i<0)}} (A_i)^{|\nu_i|} - k' \prod_{\substack{i \\ (\nu_i>0)}} (A_i)^{\nu_i} \qquad (2)$$

in which k and k′ are the forward and the reverse reaction rate constants; (A_i) and [A_i] are the activity and concentration of A_i . $\prod_{\substack{i \\ (\nu_i<0)}} (A_i)^{|\nu_i|}$ represents the product of $(A_i)^{|\nu_i|}$ over all negative ν_i .

If the coefficients ν_i in Eq. (1) have a highest common divisor n, the equilibrium constant K is expressed as

$$K = \prod_{i=1}^{m} (A_{ie})^{\nu_i/n} \qquad (3)$$

in which the subscript e indicates the state of equilibrium. Since the net reaction rate vanishes at equilibrium, it follows immediately from Eqs. (2) and (3) that the ratio of the forward and the reverse reaction rate constants is a simple power of the equilibrium constant.

A complex reaction consisting of ρ elementary reactions

$$0 \rightleftharpoons \sum_{i=1}^{m} \nu_{ir} A_i \qquad r = 1, 2, \cdots, \rho \qquad (4)$$

can also be represented as Eq. (1) by adding the individual equations in Eq. (4), each individual equation being multiplied by an appropriate integer S_r called the stoichiometric number (2). The overall reaction rate for any species A_j in this complex reaction is

$$\frac{d[A_j]}{dt} = \sum_{r=1}^{\rho} \nu_{jr} \left[k_r \underset{\substack{i \\ (\nu_{ir}<0)}}{\pi} (A_i)^{|\nu_{ir}|} - k_r' \underset{\substack{i \\ (\nu_{ir}>0)}}{\pi} (A_i)^{\nu_{ir}} \right] \qquad (5)$$

which, in general, cannot be reduced to a difference of two single rate terms. The simple relation between the rate constants ratio and the equilibrium constant therefore does not exist in a general complex reaction. However, when there is only one rate-determining step in Eq. (4) and when the stationary-state approximation is applicable, it is possible to express the net overall reaction rate as a difference of two rate terms. This special case has been treated by Horiuti (2), who obtained the conclusion that

$$\frac{k}{k'} = K^{n/S_d} \qquad (6)$$

in which k and k' are the forward and the reverse reaction rate constants for the complex reaction; S_d is the stoichiometric number of the rate-determining reaction; and n is the highest common divisor in Eq. (1). The proof given by Horiuti is based on the transition-state theory. A mathematical proof which does not depend on the transition-state theory will be presented in the following.

When there is only one rate-determining step, the net reaction rate of species A_j in a complex reaction can be approximated by:

$$\frac{1}{\nu_j} \frac{d[A_j]}{dt} = k \phi \prod_{i=1}^{m} (A_i)^{\alpha_i} - k' \phi \prod_{i=1}^{m} (A_i)^{\alpha_i'} \qquad (7)$$

where the exponents α_i and α_i' in general differ from the stoichiometric coefficients; ϕ is a function of the activities of the intermediates.

Since the net reaction rate vanishes at equilibrium, it follows from Eq. (7) that

$$\frac{k}{k'} = \prod_{i=1}^{m} (A_{ie})^{\alpha_i' - \alpha_i} \tag{8}$$

Both the equilibrium constant K and the ratio k/k′ are functions of temperature only and therefore can be related as

$$\frac{k}{k'} = f(K) \tag{9}$$

Combining Eqs. (8) and (9) gives:

$$f(K) = \prod_{i=1}^{m} (A_{ie})^{\alpha_i' - \alpha_i} \tag{10}$$

Differentiating Eq. (10) with respect to (A_{je}) gives:

$$\frac{d f(K)}{d K} \cdot \frac{\nu_j K}{n (A_{je})} = \frac{(\alpha_j' - \alpha_j)}{(A_{je})} \prod_{i=1}^{m} (A_{ie})^{\alpha_i' - \alpha_i}$$

which may be simplified to

$$\frac{d \ln f(K)}{dK} = \frac{n(\alpha_j' - \alpha_j)}{\nu_j K} \tag{11}$$

The subscript j in Eq. (11) can be any number from 1 to m. It can be seen from Eq. (11) that the expression $(\alpha_j' - \alpha_j)/\nu_j$ must have the same value for any number of j. By representing the expression $(\alpha_j' - \alpha_j)/\nu_j$ by q, the solution to Eq. (11) can be written as:

$$f(K) = C K^{nq} \tag{12}$$

Since $k/k' = 1$ when $K = 1$, it follows from Eqs. (9) and (12) that

$C = 1$

Consequently,

$$\frac{k}{k'} = K^{nq} \tag{13}$$

which shows that the ratio of rate constants is a simple power of the equilibrium constant.

As an example, consider the dissociation of hydrogen on a hot tungsten surface. The overall reaction is

$$H_2 \rightleftharpoons 2H \tag{14}$$

Blum and Luus (1) have shown that the overall reaction rate is

$$\frac{1}{2}\frac{d[H]}{dt} = k\, p_{H_2}^{1/2} - k'\, p_H \tag{15}$$

where p_{H_2} and p_H are the partial pressures of H_2 and H.

The equilibrium constant and the ratio $\frac{k}{k'}$ are given by

$$K = \frac{p_{H,e}^2}{p_{H_2,e}} \qquad (16)$$

$$\frac{k}{k'} = \frac{p_{H,e}}{p_{H_2,e}^{1/2}} \qquad (17)$$

Comparing Eqs. (16) and (17) gives

$$\frac{k}{k'} = K^{1/2} \qquad (18)$$

Since the exponents of the partial pressures in Eq. (15) differ from the stoichiometric coefficients, the reaction must be a complex one. It may be postulated that the mechanism is

$$H_2 \rightleftharpoons H_2(a) \qquad (19)$$

$$H_2(a) \rightleftharpoons 2\,H(a) \qquad (20)$$

$$H(a) \rightleftharpoons H \qquad (21)$$

where (a) refers to the adsorbed state on the tungsten surface. The stoichiometric numbers for Eqs. (19), (20) and (21) are 1, 1 and 2 respectively. Eq. (18) shows that $n/S_d = 1/2$. Therefore the reaction represented by Eq. (21) is the rate determining step. The rate expression, Eq. (15), can be deduced from the postulated mechanism. Let K_1 and K_2 be the equilibrium constants for Eqs. (19) and (20); k_3 and k_3' be the forward and the reverse reaction rate constants for Eq.(21). If Eq. (21) is the rate-determining step, one may write:

$$p_{H_2(a)} = K_1 \, p_{H_2} \tag{22}$$

$$p_{H(a)} = (K_2 \, p_{H_2(a)})^{1/2} \tag{23}$$

and

$$\frac{d[H]}{dt} = k_3 \, p_{H(a)} - k_3' \, p_H \tag{24}$$

Combining Eqs. (22), (23) and (24) gives

$$\frac{d[H]}{dt} = k_3 \, K_1^{1/2} K_2^{1/2} p_{H_2}^{1/2} - k_3' \, p_H$$

which is the same as Eq. (15) if one puts $k = \frac{1}{2} k_3 K_1^{1/2} K_2^{1/2}$ and $k' = \frac{1}{2} k_3'$

Notation

(A_i)	activity of A_i
$[A_i]$	concentration of A_i
k	reaction rate constant
K	equilibrium constant
p	partial pressure
q	$(\alpha_j' - \alpha_j)/\nu_j$
S	stoichiometric number
t	time
α	exponent in the rate expression
ν	stoichiometric coefficient

Subscripts

e	state of equilibrium
i	refers to i-th species
r	refers to r-th reaction

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PROPOSITION IV

APPLICATION OF THE SELF-PRESERVING SIMILARITY TRANSFORMATION TO THE KINETIC EQUATION FOR SIMULTANEOUS COAGULATION AND CONDENSATION PROCESS

The purpose of this proposition is to derive the conditions under which the kinetic equation for simultaneous coagulation and condensation process can be transformed by the similarity transformation originally proposed by Friedlander (1) for the coagulation equation.

The growth rate of a drop with volume v resulting from condensation can be expressed as (2)

$$\frac{dv}{dt} = \frac{3^{1/3}(4\pi)^{2/3}(S-1)\, v^{1/3}}{\frac{JL^2M\rho}{KRT^2} + \frac{\rho RT}{p_s DM}} = D^*(S-1)\, v^{1/3} \qquad (1)$$

in which

S = saturation ratio = $\frac{p}{p_s}$

p = vapor pressure of the system

p_s = saturation vapor pressure of the system

J = mechanical equivalent of heat

L = latant heat of condensation of the vapor

M = molecular weight of the vapor

ρ = density of the liquid condensed from the vapor

K = thermal conductivity of the medium

R = universal gas constant

T = absolute temperature

D = diffusion coefficient of the vapor

Eq. (1) is derived by assuming (1) that the drop is at rest, (2) that the heat and mass transfers between the drop and its surroundings have attained steady state, and (3) that the drop should be sufficiently large so that the effect of the curvature on the equilibrium vapor pressure is negligible.

The rate of change of the particle size distribution resulting from Brownian coagulation and condensation is given by

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^{v} \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v},t)\, n(v-\tilde{v},t)\, d\tilde{v} - \int_0^{\infty} \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, d\tilde{v} - \frac{\partial}{\partial v}\left[\frac{dv}{dt}\, n(v,t)\right] \qquad (2)$$

in which $\frac{dv}{dt}$ is the drop growth rate given in Eq. (1); $\beta(v,\tilde{v})$ is the collision frequency factor:

$$\beta(v,\tilde{v}) = \frac{2kT}{3\mu}\left(v^{1/3} + \tilde{v}^{1/3}\right)\left(\frac{1}{v^{1/3}} + \frac{1}{\tilde{v}^{1/3}}\right)$$

The expressions for the rate of change of the total number concentration N and the total volume concentration ϕ of particles can be obtained from Eq. (2) by integration:

$$\frac{dN}{dt} = \frac{d}{dt}\int_0^{\infty} n(v,t)\, dv = -\frac{1}{2}\int_0^{\infty}\int_0^{\infty} \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, dv\, d\tilde{v} \qquad (3)$$

$$\frac{d\phi}{dt} = \frac{d}{dt}\int_0^\infty v\,n(v,t)\,dv = D^*(S-1)\int_0^\infty v^{1/3} n(v,t)\,dv \qquad (4)$$

The similarity transformation originally proposed by Friedlander (1) for the coagulation equation is

$$n(v,t) = \frac{N^2}{\phi}\psi(\eta) \quad ; \quad \eta = \frac{Nv}{\phi} \qquad (5)$$

It may be noted that ϕ is invariant for a pure coagulation, but increases with time in a simultaneous coagulation and condensation process.

Substituting Eq. (5) into Eqs. (3) and (4) gives:

$$\frac{dN}{dt} = -\frac{N^2}{2}\int_0^\infty\int_0^\infty \beta(\eta,\tilde{\eta})\,\psi(\eta)\psi(\tilde{\eta})\,d\eta\,d\tilde{\eta} \qquad (6)$$

$$\frac{d\phi}{dt} = D^*(S-1)\,N^{2/3}\phi^{1/3}\int_0^\infty \eta^{1/3}\psi(\eta)\,d\eta \qquad (7)$$

Substitution of Eqs. (5), (6) and (7) into Eq. (2) yields after some simplifications:

$$
\begin{aligned}
&(1+\mu^*_{1/3}\mu^*_{-1/3})\left(2\psi+\eta\frac{d\psi}{d\eta}\right)+\frac{3\mu D^*}{2kT}\,\frac{S-1}{N^{1/3}\phi^{2/3}}\,\mu^*_{1/3}\left(\psi+\eta\frac{d\psi}{d\eta}\right)\\
&+\int_0^{\eta}\left[1+\left(\frac{\eta-\tilde{\eta}}{\tilde{\eta}}\right)^{1/3}\right]\psi(\tilde{\eta})\psi(\eta-\tilde{\eta})\,d\tilde{\eta}-\left(2+\mu^*_{-1/3}\eta^{1/3}+\mu^*_{1/3}\eta^{-1/3}\right)\psi(\eta)\\
&-\frac{3\mu D^*}{2kT}\,\frac{S-1}{N^{1/3}\phi^{2/3}}\left[\frac{1}{3}\eta^{-2/3}\psi(\eta)+\eta^{1/3}\frac{d\psi}{d\eta}\right]=0
\end{aligned}
\tag{8}
$$

in which $\mu^*_{1/3}$ and $\mu^*_{-1/3}$ are given by

$$\mu^*_{\nu}=\int_0^{\infty}\eta^{\nu}\psi(\eta)\,d\eta \qquad \nu=\frac{1}{3},\ -\frac{1}{3} \tag{9}$$

If the quantity $\frac{3\mu D^*}{2kT}\cdot\frac{S-1}{N^{1/3}\phi^{2/3}}$ is a constant, Eq. (8) becomes an ordinary integro-differential equation independent of time explicitly. It is to be solved with the two constraints in Eq. (9) and the following two normalization conditions:

$$\int_0^{\infty}\psi(\eta)\,d\eta=1$$

$$\int_0^{\infty}\eta\,\psi(\eta)\,d\eta=1$$

The solution to Eq. (8), if it exists, is a particular solution to Eq. (2). This is a self-preserving spectrum, since its form remains unchanged throughout the process.

It follows from the above analysis that the condition for the system to be self-preserving is

$$\frac{3\mu D^*}{2kT}\,\frac{S-1}{N^{1/3}\phi^{2/3}} = \text{constant} = C^* \tag{10}$$

If the system is kept at constant temperature, the saturation ratio S must be varied with time as $2kTC^*N^{1/3}\phi^{2/3}/(3\mu D^*)+1$ to make the system self-preserving. Solving Eqs. (6) and (7) for N and ϕ gives:

$$N = \frac{1}{\frac{1}{N(0)} + \frac{2kT}{3\mu}(1+\mu^*_{1/3}\mu^*_{-1/3})t}$$

$$\phi = \phi(0)\left[1 + \frac{2kT}{3\mu}(1+\mu^*_{1/3}\mu^*_{-1/3})N(0)t\right]^{\frac{C^*\mu^*_{1/3}}{1+\mu^*_{1/3}\mu^*_{-1/3}}}$$

The saturation ratio for a self-preserving system is therefore given by:

$$S = 1 + \frac{2kT}{3\mu}\cdot\frac{C^*}{D^*}\cdot[N(0)]^{1/3}[\phi(0)]^{2/3}\left[1+\frac{2kT}{3\mu}(1+\mu^*_{1/3}\mu^*_{-1/3})N(0)t\right]^{\frac{2C^*\mu^*_{1/3}}{3(1+\mu^*_{1/3}\mu^*_{-1/3})}-\frac{1}{3}} \tag{11}$$

If the saturation ratio is kept constant (for example, by a chemical reaction), the system will be self-preserving provided its initial conditions are such that

$$\left[N(0)\right]^{1/3}\left[\phi(0)\right]^{2/3} = \frac{3\mu}{kT}\, D^{*}(S-1)\, \frac{\mu^{*}_{-1/3}}{1+\mu^{*}_{1/3}\,\mu^{*}_{-1/3}}$$

This relation can be derived from Eq. (11).

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PROPOSITION V

UNSTEADY-STATE EVAPORATION IN A TUBE OF FINITE LENGTH

In this proposition, a partial differential equation is derived for the evaporation of a volatile liquid A into a gas B in a tube of finite length. The method for solving this equation is discussed. The total pressure of the system can be predicted from the solution to the partial differential equation. Such a result may be used to determine the diffusivities of gases.

The system is sketched in Fig. 1. The tube has a length L and a cross-sectional area A. The liquid level is maintained at position $z = 0$ at all times. The entire system is maintained at constant temperature. It is assumed that (1) A and B form an ideal-gas mixture and (2) B is insoluble in A.

The equation of continuity for A and B are

$$\frac{\partial C_A}{\partial t} = - \frac{\partial N_{Az}}{\partial z} \tag{1}$$

$$\frac{\partial C_B}{\partial t} = - \frac{\partial N_{Bz}}{\partial z} \tag{2}$$

in which C_A = molar concentration of A

C_B = molar concentration of B

N_{Az} = molar flux of A relative to stationary coordinates

N_{Bz} = molar flux of B relative to stationary coordinates.

According to Fick's law of diffusion (1), N_{Az} is given by

$$N_{Az} = x_A (N_{Az} + N_{Bz}) - CD \frac{\partial x_A}{\partial z} \tag{3}$$

in which x_A is the mole fraction of A, C is the total molar concentration, and D the diffusivity.

Since there is no motion of B at the interface, N_{Az} and N_{Bz} have the following values at $z = 0$:

$$N_{AO} = - \frac{CD}{1 - x_{AO}} \left. \frac{\partial x_A}{\partial z} \right|_{z=0} \tag{4}$$

$$N_{BO} = 0 \tag{5}$$

in which x_{AO} is the equilibrium gas-phase concentration; for an ideal-gas mixture this is just the vapor pressure of pure A divided by the total pressure P.

Adding Eqs. (1) and (2) gives

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial z} (N_{Az} + N_{Bz}) \tag{6}$$

Since A and B are assumed to form an ideal-gas mixture, C is related to the total pressure P and the temperature T by

$$C = \frac{P}{RT} \tag{7}$$

in which R is the universal gas constant. It can be seen from Eq. (7) that C is a function of time only.

Eq. (6) can be integrated with respect to z to give:

$$N_{Az} + N_{Bz} = -\frac{dC}{dt} z + g(t) \qquad (8)$$

The arbitrary function g(t) is determined by Eqs. (4) and (5) to be

$$g(t) = N_{A0}$$

Since both N_{Az} and N_{Bz} vanish at $z = L$, it follows from Eq. (8) that

$$\frac{dC}{dt} = \frac{N_{A0}}{L}$$

Thus the sum $N_{Az} + N_{Bz}$ can be expressed as

$$N_{Az} + N_{Bz} = N_{A0} \left(1 - \frac{z}{L}\right) \qquad (9)$$

Substituting Eq. (9) into Eq. (3) gives:

$$N_{Az} = x_A N_{A0} \left(1 - \frac{z}{L}\right) - C D \frac{\partial x_A}{\partial z} \qquad (10)$$

Substitution of Eq. (10) into Eq. (1) yields for constant D

$$\frac{\partial C_A}{\partial t} = C D \frac{\partial^2 x_A}{\partial z^2} - N_{A0} \left(1 - \frac{z}{L}\right) \frac{\partial x_A}{\partial z} + \frac{x_A N_{A0}}{L}$$

By making use of the relation $x_A = C_A/C$, the above equation can be rewritten as

$$\frac{\partial x_A}{\partial t} = D \frac{\partial^2 x_A}{\partial z^2} + \frac{D}{1 - x_{A0}} \left.\frac{\partial x_A}{\partial z}\right|_{z=0} \cdot \left(1 - \frac{z}{L}\right) \frac{\partial x_A}{\partial z} \qquad (11)$$

This is the partial differential equation for the diffusion process in this system. It is to be solved with the initial and boundary conditions:

I.C. at $t = 0$, $x_A = 0$

B.C. 1 at $z = 0$, $x_A = x_{A0}$

B.C. 2 at $z = L$, $\frac{\partial x_A}{\partial z} = 0$

For short times, since the vapor A has not penetrated too far into the gas phase, the quantity $\frac{z}{L}$ in Eq. (11) can be neglected, and the B.C.2 can be replaced by "$x_A = 0$, at $z = \infty$ ". With these two simplifying assumptions, Eq. (11) can be solved by the method of combination of variables to give (2):

$$\frac{x_A}{x_{A0}} = \frac{1 - \operatorname{erf}\left(\frac{z}{\sqrt{4Dt}} - \varphi\right)}{1 + \operatorname{erf}\varphi} \tag{12}$$

in which
$$\varphi = -\frac{1}{2}\,\frac{x_{A0}}{(1-x_{A0})}\,\left.\frac{dX}{dZ}\right|_{z=0}$$

$$X = \frac{x_A}{x_{A0}}$$

$$Z = \frac{z}{\sqrt{4Dt}}$$

For large t, the above simplifying assumptions are not valid, but Eq. (11) can be solved by numerical method. Since x_{A0} and $\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$ are unknown functions of time, special analysis is required in solving Eq. (11) numerically. A relationship between x_{A0} and $\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$ can be found as follows:

The time rate of change of the total pressure is given by

$$\frac{dP}{dt} = RT\frac{dC}{dt} = -\frac{PD}{L(1-x_{A0})}\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$$

Integration with respect to t gives

$$P = P(0)\, e^{-\frac{D}{L}\int_0^t \frac{1}{1-x_{A0}} \frac{\partial x_A}{\partial z}\Big|_{z=0} dt} \tag{13}$$

If the vapor pressure of liquid A is represented by P_A°, it follows from Eq. (13) that

$$x_{A0} = \frac{P_A^{\circ}}{P} = \frac{P_A^{\circ}}{P(0)}\, e^{\frac{D}{L}\int_0^t \frac{1}{1-x_{A0}} \frac{\partial x_A}{\partial z}\Big|_{z=0} dt} \tag{14}$$

which is a relationship between x_{A0} and $\frac{\partial x_A}{\partial z}\Big|_{z=0}$

To avoid the difficulty in numerical solution caused by the discontinuity of x_A at $t = 0$ and $z = 0$, Eq. (12) can be used to compute the values of x_A for small t.

It can be seen from Eq. (13) that the diffusivity can be expressed as

$$D = \frac{-L \ln \frac{P}{P(0)}}{\int_0^t \frac{1}{1-x_{A0}} \frac{\partial x_A}{\partial z}\Big|_{z=0} dt} \tag{15}$$

This equation may be used to determine diffusivities of gases. The quantities P and x_{A0} in this expression can be measured experimentally: the value of $\frac{\partial x_A}{\partial z}\Big|_{z=0}$ can be obtained from the numerical solution to Eq. (11). Since $\frac{\partial x_A}{\partial z}\Big|_{z=0}$ is a function of D and t, it requires a trial and error procedure to determine D by Eq. (15).

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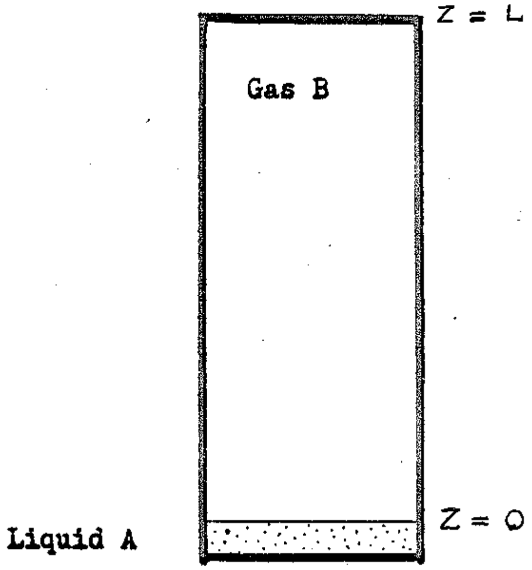

Fig. 1. A Diffusing System