$$r_i = V_{wi}/V_{ws} \qquad \text{(B1)}$$

$$q_i = A_{wi}/A_{ws} \qquad \text{(B2)}$$

where V_{wi} and A_{wi} are the van der Waals volumes and areas of the molecule given by Bondi (1968) and where V_{ws} and A_{ws} are the van der Waals volume and area of a standard segment. The choice of a standard segment is somewhat arbitrary. Here it is defined as a sphere such that for a linear polymethylene molecule of infinite length the identity

$$(z/2)(r - q) = r - 1 \qquad \text{(B3)}$$

is satisfied. The coordination number z is set equal to 10. The volume of the standard sphere in terms of its radius R_{ws} is given by

$$V_{ws} = 4/3\,\pi\,R_{ws}^3 \qquad \text{(B4)}$$

and the area by

$$A_{ws} = 4\,\pi\,R_{ws}^2 \qquad \text{(B5)}$$

The van der Waals volume and area of an n-mer of polymethylene are n times the volume and area of a methylene group as given by Bondi; that is

$$V_{wi} = n(10.23)\ \text{cm}^3/\text{mole} \qquad \text{(B6)}$$

$$A_{wi} = n(1.35) \times 10^9\ \text{cm}^2/\text{mole} \qquad \text{(B7)}$$

Substitution of Equations (B1), (B2), and (B4) to (B7) into (B3) as n tends to infinity yields an equation which fixes $R_{ws} = 10.95 \times 10^{15}$ cm/mole.† Substitution into Equations (B4) and (B5) yields a standard segment volume of 15.17 cm^3/mole and a standard segment area of 2.5×10^9 cm^2/mole. Equations (B1) and (B2) then become

$$r_i = V_{wi}/15.17 \qquad \text{(B1a)}$$

$$q_i = A_{wi}/(2.5 \times 10^9) \qquad \text{(B2a)}$$

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† Per molecule $R_w = \dfrac{10.95 \times 10^{15}}{6.023 \times 10^{23}}$ cm/molecule. This number is substituted into Equations (B4) and (B5).

Two Kinds of Self-Preserving Size Spectra of a Cloud of Particles

The population balances describing the time dependence of the size distribution can, under some conditions, be transformed by means of a similarity transformation into an ordinary integro-differential equation containing two instead of three variables. If there is compatibility between the transformed equation and the constraints given by the total mass conservation equation and the equation for the total number of particles, a self-preserving spectrum of the first kind can be obtained. There are, however, many situations such as the sintering controlled aging of supported metal catalysts, coagulation of colloidal particles in laminar shear flow, and coagulation of colloidal particles in a turbulent flow when the particles are smaller than the size of the smallest eddy for which, although a similarity transformation is possible, the transformed equation has no solution because of incompatibility with the above mentioned constraints. A second kind of self-preserving spectrum is suggested for these situations. The new variables are induced from a particular case for which an analytical result is available. A detailed presentation of the sintering controlled aging of supported metal catalysts is presented.

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SCOPE

There are numerous physical processes for which it is of interest to know the time dependence of the size distribution of particles. Colloid coagulation, sintering of the crystallites of a supported metal, microbial cell mass distribution, crystallization, and bubbling in a fluidized bed are some examples. The time dependence of the size distribution can be described by a population balance containing the density distribution as a function of sizes and time. For some conditions, using a similarity transformation, it is possible to transform the equation containing partial derivatives into an ordinary integro-differential equation. In this manner the number of variables is reduced from three to two and a single curve, the self-preserving spectrum, is obtained for the size spectrum (Swift and Friedlander, 1964; Friedlander and Wang, 1966). Time does not appear explicitly in these variables but indirectly via the total number of particles. There are, however, a large number of cases of practical interest: sintering controlled aging of supported metal catalysts; coagulation of colloidal particles in laminar shear flow; coagulation of colloidal particles in turbulent flow when the particles are smaller than the size of the smallest eddy, for which, although the similarity transformation is possible, the transformed equation has no solution because of incompatibility with constraints imposed by the total mass conservation equation and by the total number of particles (Pulvermacher and Ruckenstein, 1974). The goal of the present paper is to find a second kind of self-preserving spectrum which can be used in those cases where the first kind does not exist.

CONCLUSIONS AND SIGNIFICANCE

The analysis of the structure of the similarity variables shows that three steps are involved in their construction: (1) an invariant transformation of the population balance, (2) the use of the mass conservation condition to obtain an expression for an exponent [exponent A of Equation (4a)], (3) the use of the equation for the total number of particles to eliminate the time t from the similarity variables. If there is compatibility between these steps, a self-preserving spectrum of the first kind exists; if not it does not exist. For a restricted range of the size spectrum one can ignore the conservation equation and the equation giving the total number of particles. The similarity variables obtained in the first step may thus remain valid, even when incompatibility exist between the three mentioned steps. Because the determination of the exponent A and the elimination of the time are no longer possible, the form of the similarity variables must be induced from a particular situation for which the self-preserving spectrum of the first kind does not exist but for which an analytical solution is available. It is shown that the new self-preserving spectrum can describe satisfactorily the time dependence of the size distribution for sintering controlled aging of supported metals. The new similarity variables can be used to choose among various mechanisms and to obtain the time dependence of the total number of particles when the commonly used measuring devices have a lower size limit of detection. An interesting byproduct is the observation that the new self-preserving spectrum leads, in the intermediary range of sizes, to a power law while the first kind of self-preserving spectrum leads to an exponential decay. Experiments have shown that the atmospheric aerosols have a power law decay.

The time evolution of the size distribution of a cloud of particles is of interest in numerous physical processes. Colloid coagulation, supported metal catalysts, granulation, crystallization, growth of microbial cells, and bubbling in fluidized beds are a few examples. If the particle size distribution is spatially homogeneous and if changes in size occur only via coalescence of the colliding particles, the size distribution satisfies the equation

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

where $n(v, t)dv$ is the number of particles having at time t a volume between v and $v + dv$, and $\beta(v, \tilde{v})$ is the collision frequency factor between particles of volumes v and $\tilde{v}$.

Todes (1949) and Swift and Friedlander (1964) have observed that if the collision frequency factor is a homogeneous function in v and $\tilde{v}$ Equation (1) can be changed by means of a similarity transformation into an ordinary integro-differential equation containing a single independent variable. Depending, however, upon the particular form of $\beta(v, \tilde{v})$, the equation obtained by the transformation may or may not have a solution. In a previous paper Pulvermacher and Ruckenstein (1974) established a necessary condition for the existence of a similarity solution. If a solution exists, it represents the asymptotic behavior of Equation (1) for sufficiently long times. No general proof for this assertion is available. The conclusion was induced from comparisons made in numerous cases between the numerical solutions of Equation (1) and the equation obtained by the transformation (Hidy, 1965; Lai et al., 1972; Ruckenstein and Pulvermacher, 1973). The similarity solution represents the time dependence of the size distribution by a single curve—the self-preserving spectrum.

There are, however, a large number of cases of practical interest for which, although a similarity transformation is possible, the equation obtained by the transformation has no solution. Such cases include sintering controlled aging of supported metal catalysts, coagulation of particles in laminar shear flow, and coagulation of spherical particles in a turbulent flow with particle radii smaller than the size of the smallest eddies. The goal of this paper is to find a second kind of self-preserving spectrum which can be used in those cases where transformations of the first kind do not lead to solutions. Because the analysis of the structure of the first transformation has clarified the way by which new variables are obtained, the first section of the paper is devoted to a discussion of Todes' and Swift and Friedlander's approaches. Considerations from the first section suggest a new similarity solution which may be useful when that of Swift and Friedlander does not succeed. The new similarity solution covers, however, a restricted range of the size spectrum. Its usefulness is demonstrated in the last section in connection with the size distribution of supported metal crystallites.

SELF-PRESERVING SPECTRUM OF THE FIRST KIND

The collision frequency factor $\beta(v, \tilde{v})$ is considered a homogeneous function of degree m in v and $\tilde{v}$

$$\beta(wv, w\tilde{v}) = w^m \beta(v, \tilde{v}) \tag{2}$$

Equation (1) is invariant under a one parameter group transformation consisting of the following set of transformations:

$$\bar{t} = a^{\alpha_1} t \tag{3a}$$

$$\bar{v} = a^{\alpha_2} v \tag{3b}$$

and

$$\bar{n}(\bar{v}, \bar{t}) = a^{\gamma_1} n(v, t) \tag{3c}$$

provided a certain relation exists between the exponents α_1, α_2, and γ_1.

The group transformation, Equations (3), gives rise to the following similarity variables:

$$n^+(v^+) = \frac{n(v, t)}{t^{\gamma_1/\alpha_1} A^*} \tag{4a}$$

$$v^+ = \frac{B^* v}{t^{\alpha_2/\alpha_1}} \tag{4b}$$

Substituting n, v, t from Equations (3) into Equation (1), one obtains

$$a^{\alpha_1 - \gamma_1} \frac{\partial \bar{n}}{\partial \bar{t}} = a^{-\alpha_2 m - 2\gamma_1 - \alpha_2} \left\{ \frac{1}{2} \int_0^{\bar{v}} \beta(\tilde{\bar{v}}, \bar{v} - \tilde{\bar{v}}) n(\tilde{\bar{v}}, \bar{t}) n(\bar{v} - \tilde{\bar{v}}) d\tilde{\bar{v}} - \int_0^\infty \beta(\bar{v}, \tilde{\bar{v}}) n(\bar{v}, \bar{t}) n(\tilde{\bar{v}}, \bar{t}) d\tilde{\bar{v}} \right\} \tag{5}$$

The condition for invariance leads to

$$\alpha_1 - \gamma_1 = -\alpha_2 m - 2\gamma_1 - \alpha_2 \tag{6}$$

Denoting

$$A = \frac{\gamma_1}{\alpha_1} \tag{7}$$

it follows that

$$\frac{\alpha_2}{\alpha_1} = -\frac{1 + A}{1 + m} \tag{8}$$

The similarity variables, Equations (4), thus take the form

$$n^+(v^+) = \frac{n(v, t)}{A^* t^A} \tag{4a'}$$

and

$$v^+ = \frac{B^* v}{t^{-(1+A)/(1+m)}} \tag{4b'}$$

where A^* and B^* are constants, independent of v, t, and n. The constant A can be determined from the condition of mass conservation

$$\phi = \int_0^\infty v n(v, t) dv = \text{const.} \tag{9}$$

where ϕ is the total volume of the particles.
One obtains

$$\phi = \frac{t^{A - (2(1+A)/(1+m))} A^*}{B^{*2}} \int_0^\infty v^+ n^+(v^+) dv^+ \tag{10}$$

Consequently (for m ≠ 1),

$$A = \frac{2}{m - 1} \tag{11}$$

and

$$\frac{\phi B^{*2}}{A^*} = \int_0^\infty v^+ n^+(v^+) dv^+ \tag{12}$$

The similarity variables become

$$n^+(v^+) = \frac{n(v, t)}{A^* t^{2/(m-1)}} \tag{13a}$$

and

$$v^+ = \frac{B^* v}{t^{1/(1-m)}} \tag{13b}$$

When $\beta(v, \tilde{v})$ is a homogeneous function of degree zero in v and $\tilde{v}$, Expressions (13a) and (13b) lead to the similarity variables suggested by Todes (1949).

There is a close relationship between the similarity variables (13) and those suggested by Swift and Friedlander (1964) and Friedlander and Wang (1966). Indeed the total number of particles N is given by

$$N = \int_0^\infty n(v, t) dv = \frac{A^*}{B^*} t^{1/(m-1)} \int_0^\infty n^+(v^+) dv^+ \tag{14}$$

Therefore

$$n^+(v^+) = \frac{n(v, t) \left[\int_0^\infty n^+(v^+) dv^+ \right]^2 A^*}{N^2 B^{*2}} \tag{15a}$$

and

$$v^+ = \frac{B^{*2} vN}{A^* \int_0^\infty n^+(v^+) dv^+} \tag{15b}$$

If we choose

$$\int_0^\infty n(v^+) dv^+ = 1 \tag{16}$$

and

$$\int_0^\infty v^+ n(v^+) dv^+ = 1 \tag{17}$$

and take into account Equation (9), Expressions (15a) and (15b) become the similarity variables of Swift and Friedlander (1964) and Friedlander and Wang (1966)

$$n^+(v^+) \equiv \psi(\eta) = \frac{n(v, t)\phi}{N^2} \tag{18a}$$

and

$$v^{+} \equiv \eta = \frac{vN}{\phi} \tag{18b}$$

Using the similarity variables (18a) and (18b), Equation (1) becomes

$$\left(\eta \frac{d\psi}{d\eta} + 2\psi\right)\left(\int_0^\infty \int_0^\infty \beta(\eta, \tilde{\eta})\psi(\eta)\psi(\tilde{\eta})\, d\eta d\tilde{\eta}\right)$$
$$+ \int_0^\eta \beta(\tilde{\eta}, \eta - \tilde{\eta})\psi(\tilde{\eta})\psi(\eta - \tilde{\eta})\, d\tilde{\eta}$$
$$- 2\int_0^\infty \beta(\eta, \tilde{\eta})\psi(\eta)\psi(\tilde{\eta})\, d\tilde{\eta} = 0 \tag{19}$$

where ψ is subject to the constraints of Equations (16) and (17).

It was shown in a previous paper (Pulvermacher and Ruckenstein, 1974) that Equation (19) has a solution compatible with the above mentioned constraints if

$$\eta\psi \to 0 \quad \text{when} \quad \eta \to 0 \tag{20}$$

If condition (20) is not satisfied, either the integral from (16), or both integrals from (16) and (17) diverge. This condition has been written in a more explicit form to show the effect of $\beta(v, \tilde{v})$ (Pulvermacher and Ruckenstein, 1974). For sintering controlled aging of supported metals, for coagulation of particles in laminar shear flow, and for coagulation of spherical particles in turbulent flow when the particle radius is small compared to the size of the smallest eddy, condition (20) is not satisfied and consequently Equation (19) has no solution (Pulvermacher and Ruckenstein, 1974). In these cases, the similarity variables ψ and η alone cannot represent the time dependence of the size spectrum. In the construction of the similarity variables using a one parameter group transformation (Equations (18)), three steps are involved:

(1) the invariant transformation of Equation (1) which leads to the similarity variables (4);

(2) the use of the mass conservation condition, Equation (9), which leads to an equation for the exponent A;

(3) the use of Equation (14) for the total number of particles which eliminate the time from the similarity variables (4).

Swift and Friedlander (1964) have used Birkhoff's method of separation of variables to construct the similarity variables. The following three steps are involved in their treatment:

(1) introduction of variables of the form

$$\psi(\eta) = \frac{n(v, t)}{g(t)} \quad \text{and} \quad \eta = \frac{v}{v^{*}(t)} \tag{21}$$

(2) the use of Equation (14) for the total number of particles and

(3) the use of Equation (9) for the total volume of particles to determine the form of the functions $g(t)$ and $v^{*}(t)$.

When condition (20) is not satisfied, no similarity solution exists because the similarity variables are incompatible with the constraint introduced by the mass conservation equation. However, for a restricted range of the size spectrum one can ignore the mass conservation equation requirement. The similarity variables may then remain valid although not in the form of (18). Since only a part of the spectrum is now represented by the similarity variables, it is no longer possible to use them in the conservation equation and in the equation for the total number of particles. Thus one can no longer determine the exponent A and eliminate the time in the one parameter group transformation, nor determine the functions $g(t)$ and $v^{*}(t)$ introduced in the method of separation of variables.

In what follows new similarity variables are induced from a particular situation for which condition (20) is not satisfied, but for which an analytical solution is available. It is then shown that these similarity variables are useful in other cases.

SELF-PRESERVING SPECTRUM OF THE SECOND KIND

If the collision frequency factor has the form

$$\beta(v, \tilde{v}) = b\,(v + \tilde{v}) \tag{21}$$

analytical solutions to Equation (1) are possible. They have been obtained by Golovin (1963) for two initial distributions.

For an initial distribution of the form

$$n(v) = \frac{N_0^2}{\phi} \exp\left[-\frac{vN_0}{\phi}\right] \tag{22}$$

Golovin obtained

$$\frac{n(v, t)}{N_0} = \frac{1 - \tau_1}{v\tau_1^{1/2}} I_1\left(2\frac{vN_0}{\phi}\tau_1^{1/2}\right)$$
$$\exp\left[-(1 + \tau_1)\frac{vN_0}{\phi}\right] \tag{23}$$

where $\tau_1 = 1 - N/N_0$.

If the initial distribution has the form

$$n(v) = N_0\,\delta\left(v - \frac{\phi}{N_0}\right) \tag{24}$$

the solution to Equation (1) for $v \geqq \phi/N_0$ is

$$\frac{n(v, t)}{N_0} = (1 - \tau_1)$$
$$\times \frac{(1 - \tau_1 + \tau_1^2)^{1/2}}{\tau_1(v - (\phi/N_0))} I_1\left(2\frac{v - (\phi/N_0)}{\phi/N_0}(1 - \tau_1 + \tau_1^2)^{1/2}\right)$$
$$\times \exp\left[-(1 - \tau_1 + 2\tau_1^2)\frac{(v - (\phi/N_0))}{\frac{\phi}{N_0}\tau_1}\right] \tag{25}$$

For large times $N << N_0$, and consequently $\tau_1 \to 1$. Equation (23) then becomes

$$\frac{n\phi}{NN_0} = \frac{\phi}{N_0 v} I_1\left(\frac{2vN_0}{\phi}\right) \exp\left[-\frac{2vN_0}{\phi}\right] \quad \text{for} \quad v \geqq 0 \tag{23a}$$

and Equation (25) leads to

$$\frac{n\phi}{NN_0} = \frac{\phi}{N_0(v - (\phi/N_0))} I_1\left(2\frac{v - (\phi/N_0)}{\phi/N_0}\right)$$
$$\exp\left[-2\frac{v - (\phi/N_0)}{\phi/N_0}\right] \quad \text{for} \quad v \geqq \frac{\phi}{N_0} \tag{25a}$$

Equations (23a) and (25a) show that the particle size distribution can be represented for large times by a single curve in the coordinates

$$\psi^{+} = \frac{n\phi}{NN_0} \tag{26a}$$

and

$$\eta^{+} = \frac{vN_0}{\phi} \tag{26b}$$

Furthermore, for $0 \neq N/N_0 << 1$, Equations (23a)

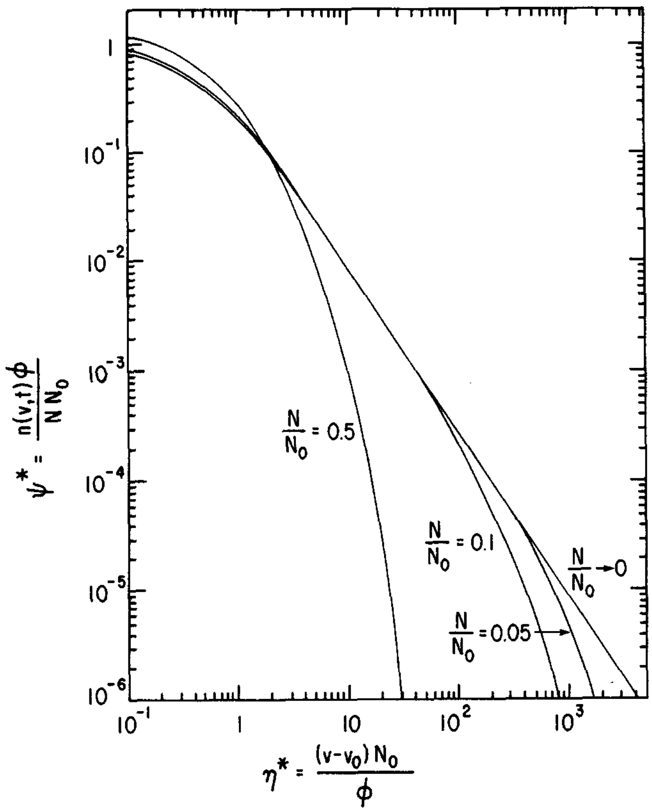

Fig. 1. Similarity solution of the second kind for a collision frequency factor of the form $\beta(v,\tilde{v}) = b(v + \tilde{v})$; unisized initial distribution.

and (25a) lead to the same equation

$$\psi^* = \frac{1}{\eta^*} I_1 (2\eta^*) \exp(-2\eta^*) \tag{27}$$

where

$$\psi^* (\eta^*) = \frac{n\phi}{NN_0} \tag{28a}$$

$$\eta^* = \frac{(v - v_0)N_0}{\phi} \tag{28b}$$

and v_0 is the volume of the smallest particle which is present at time $t = 0$. Thus, in the ψ^*, η^* representation, the same spectrum is approached for large times by two distributions which, for $t = 0$, are represented by Equations (22) and (24).

In order to have an appreciation for the range of sizes for which the similarity variables ψ^* and η^* can be used, Golovin's results are plotted in Figure 1 for various values of N/N_0. The figure shows that a unique curve is approached at short times only for the small particles but that the range of sizes for which the unique curve is valid increases with time. For purposes of comparison the results are also plotted in Figure 2 in terms of the similarity variables ψ and η. No unique curve is obtained by this representation.

The behavior in Figure 1 has a simple physical explanation. The structure of the variables ψ^*, η^* shows that no other parameter is needed to represent the size spectrum in that range of sizes for which $n(v, t)$ and $N(t)$ have the same time dependence. Because N is a decreasing function of time, only the range of sizes for which $n(v, t)$ decreases can be represented by the unique curve ψ^* vs. η^*. At short times, the concentration of the small particles decreases while the large particles are generated; at larger times the range of sizes for which $n(v, t)$ decreases becomes larger. Thus the range of sizes for which the unique curve is approached will increase in time.

SINTERING CONTROLLED AGING OF SUPPORTED METAL CATALYSTS REPRESENTED BY MEANS OF THE VARIABLES ψ^+ AND η^+

The kinetics of aging of supported metal crystallites was treated in previous papers by means of population balances of the form of Equation (1) (Ruckenstein and Pulvermacher 1973a,b). The collision frequency factor was obtained on the basis of a model accounting for diffusion of crystallites on the support and sintering of the colliding crystallites. Two limiting situations occur. If the interaction between the colliding crystallites is so strong that they form a single unit within a time which is short compared to the diffusional time, the rate of sintering is diffusion controlled. If the time for merging the colliding particles into a single unit is long compared to the diffusional time, then the merging process is the rate-determining step and the overall rate is sintering controlled. For diffusional control, we have demonstrated that the collision frequency factor is compatible with a similarity solution of the first kind. For sintering control the collision frequency factor has the form (Ruckenstein and Pulvermacher, 1973a,b):

$$\beta(v, \tilde{v}) = b_1(v^{2/3} + \tilde{v}^{2/3}) \tag{29}$$

In this case condition (20) is not satisfied (Pulvermacher and Ruckenstein, 1974) and a similarity solution of the first kind cannot be used. It was shown previously (Ruck-

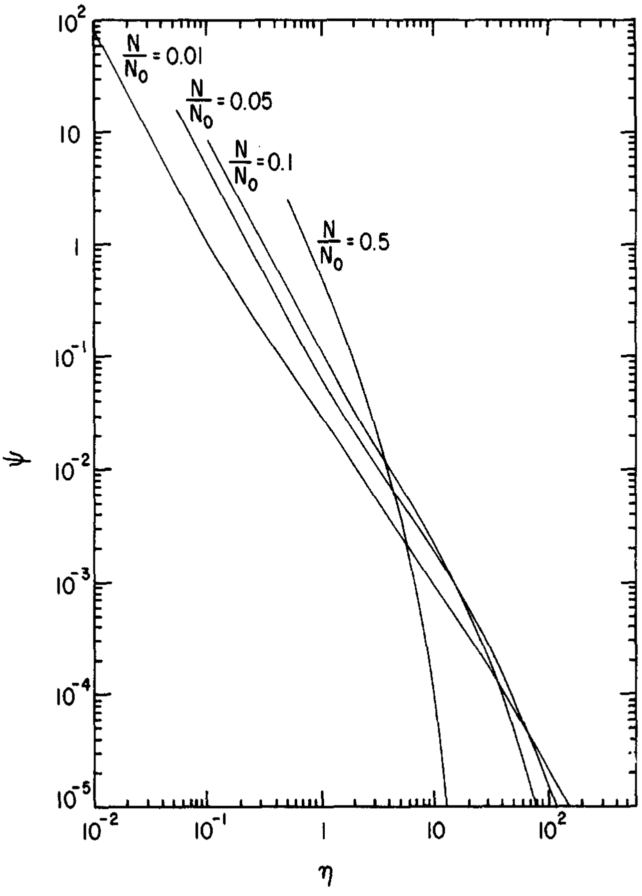

Fig. 2. Time dependence of particle size distribution for collision frequency factor of the form $\beta(v,\tilde{v}) = b(v + \tilde{v})$ in the Ψ, η representation; unisized initial distribution.

enstein and Pulvermacher, 1973; Pulvermacher and Ruckenstein, 1974) for three different initial distributions that no unique curve in the representation ψ, η can be obtained. The supplementary parameters $\tau = t\alpha_{11}2\pi r_1 N_0$ and $\phi^* = \phi/v_1 N_0$ have to be used along with the coordinates ψ, η. However, if the data are plotted in the coordinates ψ^+ and η^+ the range of sizes in which the curves approach each other increases with time: The numerical solution of Equations (1) and (29) is plotted in the coordinates ψ^+ and η^+ for the unisized initial distribution (Figure 3), for a two parameter gamma-function initial distribution (Figure 4), and for an exponential initial distribution (Figure 5). The figures show that as time increases the range of sizes in which the curves approach each other extends to larger particles. For comparison, we have plotted the numerical solution of Equation (1) in Figure 6 for a two-parameter gamma-function initial distribution. The comparison between Figures 4 and 6 shows that indeed the numerical solution of Equation (1) can be represented in a very satisfactory manner in the coordinates ψ^+, η^+.

The main characteristics of the new similarity variable is the proportionality between n and N. It is shown below that this proportionality can be obtained from the population balance, Equation (1), for that range of sizes for which the term representing particle formation due to collision of the smaller particles is small compared to the term representing the disappearance of particles due to collision with other particles.

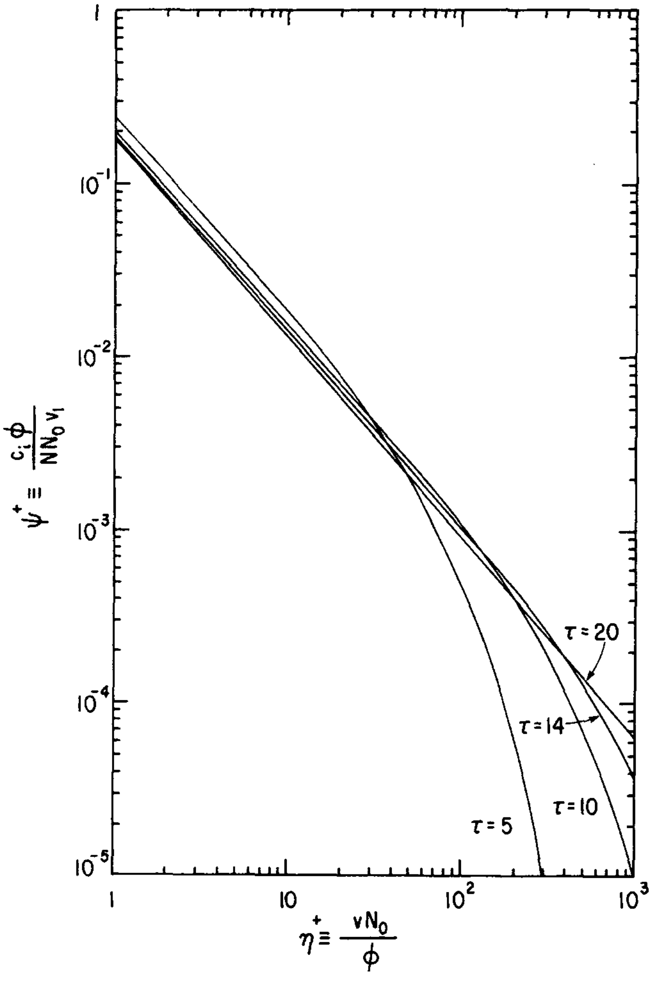

Fig. 3. Similarity solution of the second kind for a collision frequency factor of the form $\beta(v,\tilde{v}) = b_1(v^{2/3} + \tilde{v}^{2/3})$; unisized initial distribution.

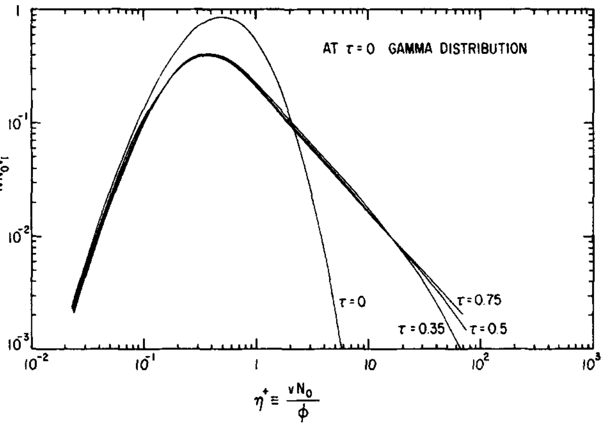

Fig. 4. Similarity solution of the second kind for a collision frequency factor of the form $\beta(v,\tilde{v}) = b_1(v^{2/3} + \tilde{v}^{2/3})$; initial distribution of the form of a two parameter gamma-function distribution:

$$n(r,t_0) = N_0\, r^\alpha \exp\,(-r/B)/\Gamma(\alpha + 1)\beta^{\alpha+1}$$

where

$$\beta = \frac{\sigma^2}{<r>};\ \alpha = \frac{<r>}{\beta} - 1;$$

Example shown: $<r> = 58$Å; $\sigma = 13.5$Å; radius of smallest particle in discrete representation 17.5Å.

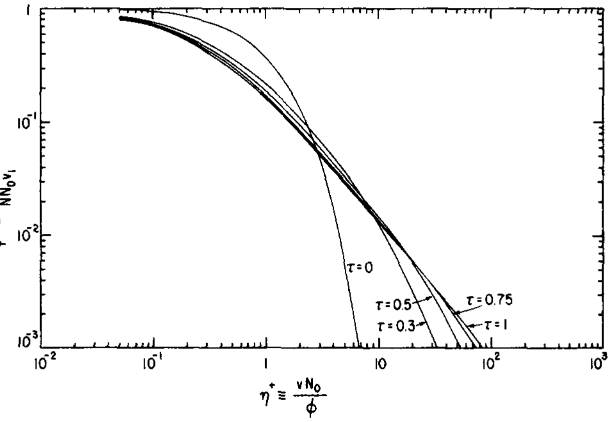

Fig. 5. Similarity solution of the second kind for a collision frequency factor of the form $\beta(v,\tilde{v}) = b_1(v^{2/3} + \tilde{v}^{2/3})$; initial distribution

$$\frac{c_i}{N_0} = \frac{\exp\left(-\frac{v_i}{20v_1}\right)}{\sum_1^\infty \exp\left(-\frac{v_i}{20v_1}\right)}$$

In this situation the population equation may be approximated by

$$\frac{\partial n(v,t)}{\partial t} \simeq -n(v,t)\int_0^\infty \beta(v,\tilde{v})n(\tilde{v},t)d\tilde{v} \quad (30)$$

The decay of the total number of particles is given by

$$\frac{dN(t)}{dt} = -\frac{1}{2}\int_0^\infty \int_0^\infty \beta(v,\tilde{v})n(v,t)n(\tilde{v},t)dv d\tilde{v} \quad (31)$$

Using Equation (29) for β Equations (30) and (31) become

$$\frac{\partial n(v,t)}{\partial t} \simeq -n(v,t)\ b_1(v^{2/3}N + M_{2/3}) \quad (32)$$

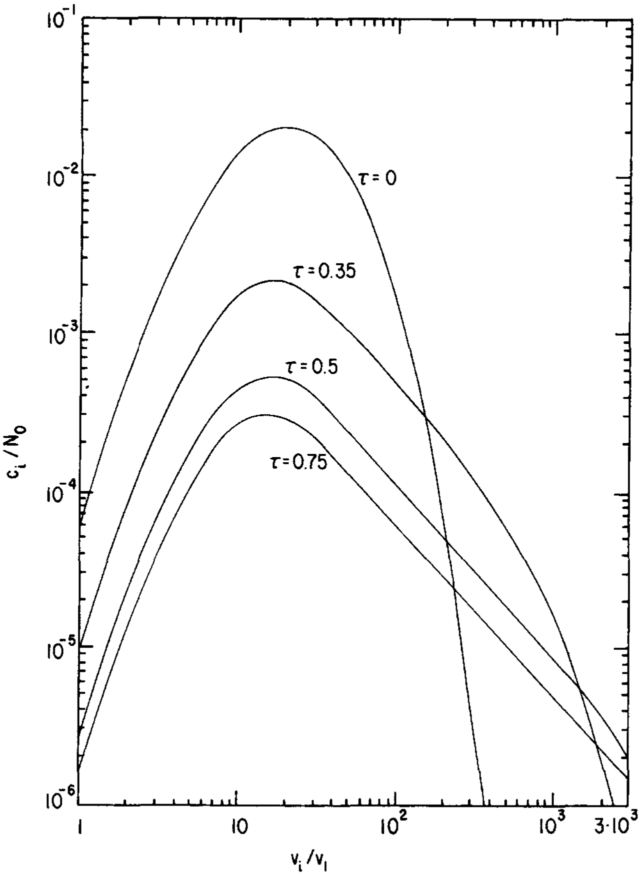

Fig. 6. Time dependence of particle size distribution for collision frequency factor of the form $\beta(v,\tilde{v}) = b_1(v^{2/3} + \tilde{v}^{2/3})$; initial distribution of the form of a two parameter gamma function distribution (see Figure 4).

and

$$\frac{dN}{dt} = -\, b_1 M_{2/3} N \tag{33}$$

where $M_{2/3}$ is the moment of order 2/3 defined by

$$M_{2/3} = \int_0^\infty v^{2/3} n(v, t)\, dv \tag{34}$$

For large times but not too large sizes

$$M_{2/3} >> v^{2/3} N \tag{35}$$

Therefore, Equations (32) and (33) lead to

$$\frac{\partial N}{\partial n} \simeq \frac{N}{n} \tag{36}$$

which, upon integrating, becomes

$$\ln \frac{n(v, t)}{N(t)} = F(v) \tag{37}$$

DISCUSSION AND COMPARISON BETWEEN THE TWO KINDS OF SELF PRESERVING SPECTRA

Two kinds of self-preserving spectra have been contrasted here. In one of them the variables are

$$\psi = \frac{n\phi}{N^2} \quad \text{and} \quad \eta = \frac{vN}{\phi} \tag{I}$$

whereas in the second they are

$$\psi^+ = \frac{n\phi}{NN_0} \quad \text{and} \quad \eta^+ = \frac{vN_0}{\phi} \tag{II}$$

The variables I may be used for those forms of $\beta(v, \tilde{v})$ which allow a similarity transformation and for which condition (20) is satisfied. In these situations, the curve $\psi = \psi(\eta)$ represents the asymptotic behavior of the solution of Equation (1) for large times. The form of this curve can be obtained by solving the transformed Equation (19), with the boundary condition $\psi \to 0$ when $\eta \to \infty$. In the cases for which the similarity variables I can be used, the initial distribution affects the asymptotic behavior only via the total volume ϕ of the particles; other details of the initial distribution disappear in time. The similarity solution is reached first by the larger particles and as time increases the smaller sizes approach the similarity solution.

The variables II can be used for those forms of $\beta(v, \tilde{v})$ which do allow a similarity transformation but do not satisfy condition (20). The representation in the coordinates ψ^+ and η^+ of the numerical solution of Equation (1) leads, for short times, to a family of curves which are very close to each other in the small size range. As time increases the range of sizes of the spectrum represented by the curve $\psi^+ = \psi^+(\eta^+)$ gets larger. The form of the curve $\psi^+ = \psi^+(\eta^+)$ cannot be obtained by solving the transformed equation since the variables ψ^+ and η^+ are only valid in a restricted range of the size spectrum. The initial distribution strongly affects the quasi-self preserving spectrum (see Figures 3 to 5). In general, the initial distribution determines the shape of the spectrum in the small size range (compare for instance Figures 3 and 5). The figures also show that in an intermediate range a power law dependence of the form $n/N \propto v^{-\alpha}$ develops with an exponent α independent of the initial distribution. The proportionality constant depends only very weakly upon the initial distribution. A power law also develops for the collision frequency factor given by Equation (21) (compare Equation (27) and Figure 1).

Perhaps it is of interest to mention that a power law dependence of the particle size spectrum has been found experimentally for atmospheric aerosols (Hidy and Brock, 1970; Junge, 1957). If one assumes that Brownian coagulation is the controlling mechanism of the spectrum of atmospheric aerosols, numerical calculations show that the decay in the high range sizes has to be exponential. However, if one assumes that turbulent coagulation is the controlling mechanism, the collision frequency factor has the form (Wang and Friedlander, 1967)

$$\beta \propto (v^{1/3} + \tilde{v}^{1/3})^3 \tag{38}$$

which is incompatible with a self preserving spectrum of the first kind (Pulvermacher and Ruckenstein 1974a), but compatible with a self preserving spectrum of the second kind and, consequently, with a power law.

While the similarity variables I can be used to predict the time dependence of any moment of the size distribution and to calculate the magnitude of certain process parameters (Friedlander and Wang, 1966; Ruckenstein and Pulvermacher, 1973a; Pulvermacher and Ruckenstein, 1974) the usefulness of the variables II is more restricted. However, some useful information can be extracted from them. For example, they may be used to choose among various coagulation mechanisms and to obtain information about the time dependence of the total number of particles when the total number of particles cannot be measured.

Experimental data may be used to prove or disprove the validity of a particular form of the collision frequency factor. Assume for instance that after a short transient time the experimentally observed size distributions taken at different times of the coagulation process superpose in the small size range when plotted in the ψ^+, η^+ representation. Only mechanisms compatible with similarity variable of the second kind can have this behavior. In the intermediary range, the power law which develops is closely related to the form of the collision frequency factor and identifies the rate determining mechanism. The power law for a given mechanism may be obtained relatively easy if Equation (1) is solved numerically for an initially unisized distribution (see Figure 3).

In some problems, as for instance in the coagulation of spherical particles in laminar or turbulent shear flow, it is difficult to measure the total number of particles in the system because the commonly used measuring devices have a lower size limit of detection which is larger than the smallest particle in the system. A cumulative distribution for different threshold volumes is usually obtained. If one assumes that the particles size distribution below a certain volume v^* can be represented by the variables II, the cumulative distribution for v^* or smaller threshold volumes can be used to obtain the total number of particles and its time dependence. If v^* is the threshold volume, the total number of particles can be written as

$$N(t) = \int_0^{v^*} n(v,t)\,dv + \int_{v^*}^{\infty} n(v,t)\,dv \qquad (39)$$

Denoting

$$N_{v^*} = \int_{v^*}^{\infty} n(v,t)\,dv \qquad (40)$$

and using the variables II, Equation (39) can be written as

$$\frac{N_{v^*}}{N} = 1 - \int_0^{\eta^{+*}} \psi^+(\eta^+)\,d\eta^+ \equiv \text{const.} \qquad (41)$$

where

$$\eta^{+*} = \frac{v^* N_0}{\phi} \equiv \frac{v^*}{v_{\text{av},0}} \qquad (42)$$

If the similarity spectrum, $\psi^+(\eta^+)$, and $v_{\text{av},0}$ are known, Equation (41) allows the determination of N from the measured values of N_{v^*}.

NOTATION

A = constant independent of volume and time
A^* = constant independent of volume and time
a = scaling factor
B^* = constant independent of volume and time
b, b_1 = constant independent of volume and time
c_i = number of particles containing i units
$F(v)$ = function of volume
I_1 = modified Bessel function of the first kind and order 1
$M_{2/3}$ = moment of order 2/3 defined by Equation (34)
m = exponent independent of volume and time
N_0, N = total number of particles at time $t = 0$ and $t = t$, respectively
N_{v^*} = cumulative distribution function defined by Equation (40)
$n(v, t)$ = continuous density distribution function
$n^+(v^+)$ = dimensionless density distribution function defined by Equation (4a)
$\bar{n}(\bar{v}, \bar{t})$ = transformation defined by Equation (3c)
$\langle r \rangle$ = average particle radius
r_1 = radius of smallest particle present in system
t = time
$\bar{t}$ = transformation defined by Equation (3a)
v = volume of a particle
v_i = volume of a particle containing i units
$\bar{v}$ = transformation defined by Equation (3b)
v_0 = volume of smallest particle present at time $t = 0$
$v_{\text{av},0}$ = average volume at time $t = 0$
v^+ = dimensionless volume defined by Equation (4b)
w = constant, independent of volume

Greek Letters

α, α_1, α_2 = exponents
α_{11} = reaction rate constant
$\beta(\eta, \tilde{\eta})$ = dimensionless collision frequency factor
$\beta(v, \tilde{v})$ = collision frequency factor between particles of size v and v
γ_1 = exponent
σ = dispersion
η = similarity variable, dimensionless volume defined by Equation (18b)
η^+ = similarity variable, dimensionless volume defined by Equation (26b)
η^* = similarity variable, dimensionless volume defined by Equation (28b)
τ = $t\alpha_{11}2\pi r_1 N_0$ dimensionless time
τ_1 = dimensionless total number of particles
ϕ = total volume of particles
ϕ^* = ϕ/v_1N_0 dimensionless volume
ψ = similarity variable, dimensionless distribution function defined by Equation (18a)
ψ^+ = similarity variable, dimensionless distribution function defined by Equation (26a)
ψ^* = similarity variable, dimensionless distribution function defined by Equation (28a)

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