A SIMPLE MODEL OF AGING OF A SET OF PARTICLES IN SUSPENSIONS OR DISPERSION SYSTEMS

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Dispersion systems of various kinds are subject to time variation of particle size distribution. A simple model is proposed describing this behaviour. The solution is presented of the appropriate differential equation for a particular case which serves to show principal properties of the model proposed.

The process of formation of a new phase in a fluid is usually associated with the appearance of individual particles of the new phase (crystallization, emulsification, aerosol formation or condensation, boiling). The process is usually viewed as a superposition of consecutive phenomena of nucleation and particle growth[1,2]. It has been known from experience [1-4] that such process is accompanied by aging or ripening of the particles causing the particle size distribution to change: the mean particle size grows while the total number of particles decreases. It is a natural consequence of the thermodynamic instability of the system exhibiting large interfacial area. A satisfactory model of the given phenomenon has not been proposed to date even for cases of utmost practical interest[2]. For instance, the phenomenon of ripening of crystalline suspensions has been known and technologically utilized for a longer time[3-5]. The aim of this work is to present a simple model of this process.

Let us suppose that a particle A_i consisting of i elementary particles (ions, atoms, molecules) loses or gains due to random collisions only one particle over an infinitesimal unit of time. The sequence of reactions of the particle A_i may be illustrated schematically by

$$\ldots A_{i-1} \underset{-A}{\overset{+A}{\rightleftharpoons}} A_i \underset{-A}{\overset{+A}{\rightleftharpoons}} A_{i+1} \ldots \qquad (1)$$

The rate of formation of particle A_i is then given by

$$\partial p(i, t)/\partial t = \lambda_{i-1} p(i-1, t) - (\lambda_i + \mu_i)\, p(i, t) + \mu_{i+1} p(i+1, t) \qquad (2)$$

where $p(i, t)$ is the probability density for the existence of particle A_i in an instant t in a unit volume of the system (a quantity proportional to concentration of particles A_i). λ_i and μ_i are the frequencies of conversion of particle A_i into A_{i-1} and A_{i+1}. Let us assume that the frequencies of the reaction events (conversions) are proportional to the surface area of the parcticles[6]

$$\lambda_i = \lambda i^{2/3}, \quad \mu_i = \mu i^{2/3} \tag{3}$$

and that the function $p(i, t)$ may be regarded as a continuous function of both arguments. Substituting the first and the third term on the right hand side of Eq. (2) by their Taylor expansions and neglecting the terms of higher than the third order one obtains

$$\frac{\partial p}{\partial t} = \frac{\mu + \lambda}{2} \frac{\partial^2 (i^{2/3} p)}{\partial i^2} - (\lambda - \mu) \frac{\partial (i^{2/3} p)}{\partial i}. \tag{4}$$

This relation can be rearranged to

$$\partial y/\partial \theta = a \partial^2 y/\partial x^2 - \partial (wy)/\partial x, \tag{5}$$

where $\theta = g^2 t$, $x = ci^{2/3}$, $g = (2/3)c$, $a = (\lambda + \mu)/2$, $b = \lambda - \mu$,

$$y(x, \theta) = p(i, t)(\mathrm{d}i/\mathrm{d}x), \quad w = (b/g)(x/c)^{1/2} - (a/2x).$$

For reaction events symmetric in time, when we assume

$$\lambda = \mu, \quad \text{or, equivalently,} \quad b = 0,$$

Eq. (5) reduces to the following simple form

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} + \frac{1}{2x} \frac{\partial y}{\partial x} - \frac{y}{2x^2} \tag{6a}$$

or, after transformation $z(x) = y(x)\, x^{1/2}$, to

$$\frac{\partial z}{\partial \tau} = \frac{\partial^2 z}{\partial x^2} - \frac{1}{2x} \frac{\partial z}{\partial x}, \tag{6b}$$

where $\tau = a\theta = g^2 at$.

In the following examination of the properties of the above model we shall restrict ourselves to the particular case of $b = 0$.

Eqs (6) possess rather complicated analytical solutions. For instance, for suitable initial and boundary conditions[5] as

$$z(0, \tau) = 0, \quad \lim_{x \to \infty} z(x, \tau) = 0 \tag{7}$$

and

$$z(x, 0) = n^n/(n-1)!\, x^n \exp(-nx) \tag{8}$$

the solution of Eq. (*6b*) is an expression obtained by the Hankel transform of the solution derived by the method of separation of variables[7]

$$z(x, \tau) = \frac{n^n}{(n-1)!}\, \Gamma(n+2) \int_{\lambda=0}^{\infty} \exp(-\lambda^2 \tau)\,(\lambda^2 + n^2)^{-1/2(n+5/4)} \,.$$

$$. \, P_{n+1/4}^{-3/4}\left(\frac{n}{\sqrt{(n^2+\lambda^2)}}\right) \sqrt{\lambda x}\, J_{3/4}(\lambda x)\, \mathrm{d}\lambda \,, \tag{9}$$

where Γ, P, J designate respectively the gamma the Legendre and the Bessel function[8]. A similar expression for the solution of Eq. (*6a*) and identical conditions may be found in ref.[2].

Examination of the properties of the function y using numerical methods of solving Eqs (*6*) seems more convenient than dealing with the expression of the type as in Eq. (*9*). A numerical solution for conditions analogous to those in Eqs (*7*) and (*8*) setting $n = 2$ (for more details see ref.[2]) yielded the time course of the distribution function $y(x, \tau)$. This course was characterized by the moments of the function y

$$I_n(\tau) = \int_{x=0}^{\infty} x^{n/2} y(x, \tau)\, \mathrm{d}x, \quad \text{for} \quad n = 0, 1, 2, 3, 4\,. \tag{10}$$

Mutual relation of the moments I_n of the transformed frequency function, y, to the moments J_n of the original frequency function, p, is given by

$$I_n = \int_{x=0}^{\infty} x^{n/2} y\, \mathrm{d}x = \int_{i=0}^{\infty} c^{n/2} i^{n/3} p\, \mathrm{d}i = c^{n/2} J_n\,, \tag{11}$$

where

$$J_n = \int_{i=0}^{\infty} i^{n/3} p\, \mathrm{d}i\,. \tag{12}$$

The expression $y\,\mathrm{d}x = p\,\mathrm{d}i$ represents the number of particles within the interval $\langle x, x + \mathrm{d}x\rangle$ or $\langle i, i + \mathrm{d}i\rangle$. Simultaneously x represents the surface area and i the volume of the particle. Thus $x^{n/2}$ or $i^{n/3}$ are proportional to the n-th power of the characteristic dimension of the particle. The product following the integration sign in Eq. (*10*) is thus the differential of the n-th moment of the frequency function in the usual sense of the definitions and with the usual physical meaning, see *e.g.* ref.[9].

The obtained time courses of individual moments are shown in Fig. 1. The figure indicates clearly that the model possesses the intuitively expected features of the process of aging: The zero-th moment (proportional to the number of particles) decreases similarly as the second moment (proportional to the total surface area of all particles). The constancy of the third moment reflects the principle of conservation of mass of the particles. The growth of the fourth moment characterizes the growth of

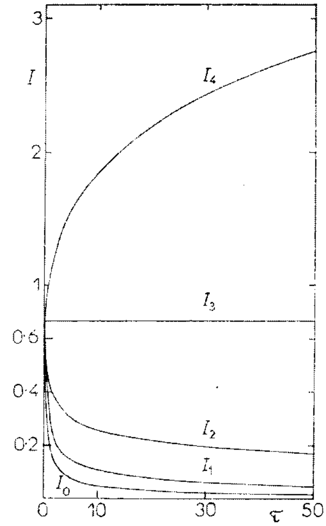

FIG. 1

Transient Development of Individual Moments

The scale of I axis changes at $I = I_3 = 0{\cdot}673$.

the mean particle diameter (the mean diameter of a set of particles may be conveniently defined as the fraction I_4/I_3). The above dependences are also in full agreement with the experimental observation of aging of crystalline suspensions undergoing recrystallization[2,10]. It is thus apparent that even a model based on highly simplified concepts is capable of describing certain important features of aging of the set of particles.

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