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DETERMINATION OF SIZE DISTRIBUTION FUNCTION *

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ABSTRACT

The theory of a method is outlined which gives the size distribution function (SDF) of a polydispersed system of non-interacting colloidal and microscopic spherical particles, having sizes in the range $0 - 10^{-5}$ cm., from a gedanken experimental scheme. It is assumed that the SDF is differentiable and the result is obtained for rotational frequency in the order of 10^{3} $(\mathrm{sec})^{-1}$. The method may be used independently, but is particularly useful in conjunction with an alternate method described in a preceding paper (Ref.1).

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An earlier work [1] dealt with the practical method for determining the size distribution curve in colloidal suspensions of spheres from the measurement of amplitude of modulation. The present paper is concerned with an extension of the theory used in Ref.1 to an alternate method via the equations of motion of a particle during the centrifusion experiment.

This alternate method is attractive for two reasons:

a) It is relatively simple and better precision is possible;

b) far less computational work is necessary because the function is assumed to be smooth over a wide range of particle size, $0\text{-}10^{-5}$ cm.

PRINCIPLE OF THE METHOD

The basic assumption made, as in the preceding paper [1], is that the number of particles per unit length is constant, and the size distribution function to be determined can be obtained from the relation

$$\Phi(r) = \frac{1}{N}\,\frac{dn(r)}{dr} \quad , \tag{1}$$

where $\Phi(r)$ is the size distribution function, N is the total number of particles, and $n(r)$ is the number of particles which have radii between r and $r + \Delta r$.

In order to obtain the SDF of the ensemble, spherical colloids in water, the system must be disturbed from its equilibrium state so that each particle will respond in accordance to its size. For this purpose installation of a centrifusion experiment, as in the case of cream extraction, could be called upon (see Fig.1). $\hat{\omega}$ is the rotational angular velocity, V_1 and V_2 are occupants of the system and pure water, respectively, P is the partition and L is the co-ordinate at which the system is found in its equilibrium state.

During the process of centrifusion with constant angular frequency ω, each particle will obey the equation of motion

$$m\,\frac{d\vec{V}'}{dt} = (m-m')\omega^{2}\,\vec{r}' - 2m(\hat{\omega}\times\vec{V}') - 6\pi\eta r\vec{V}' \quad , \tag{2}$$

where m is the mass of the particle, $m'\omega^{2}\vec{r}'$ is the bouyant force, $\vec{V}'$ is the velocity of the particle relative to the medium, $6\pi\eta\vec{V}'r$ is the resistance force [2], $2m(\hat{\omega}\times\vec{V}')$ is the Coriolis force, m is the mass of water involved in the bouyant force, and r is the size of the particle.

In Cartesian co-ordinates, Eq.(2) becomes

$$\ddot{x} = (1-\alpha)\omega^2 x + 2\omega\dot{y} - \frac{9\alpha\nu}{2r^2}\dot{x} \quad (3a)^{*)}$$

$$\ddot{y} = (1-\alpha)\omega^2 y - 2\omega\dot{x} - \frac{9\alpha\nu}{2r^2}\dot{y} \quad , \quad (3b)^{*)}$$

where $\alpha = \frac{\rho'}{\rho}$, $\nu = \frac{\eta}{\rho}$ is the dynamical viscosity, ρ' and ρ are densities of water and the system, respectively, and η is viscosity of water.

Introducing the parameters

$$A = (1-\alpha)\omega^2 , \quad B = \frac{9\alpha\nu}{2r^2}$$

one finally obtains the equation

$$\ddot{x} - 2\omega\dot{y} + B\dot{x} - Ax = 0 \quad . \quad (4)$$

The last equation can further be simplified for the same order of velocities along the two axes and for a particular choice of ω around 10^3 $(\text{sec})^{-1}$. The middle two terms for a maximum range of size 10^{-5} cm are compared and $\frac{B}{\omega}$ is found to be greater by a factor of 10^5. Therefore, this equation reduces to

$$\ddot{x} + B\dot{x} - Ax = 0 \quad (5)$$

and the solution for the i^{th} particle is given by

$$x_i(t) = e^{-\frac{Bt}{2}} \left[c_1 e^{\frac{\sqrt{B^2+4A}}{2} t} + c_2 e^{\frac{\sqrt{B^2+4A}}{2} t} \right] \quad (6)$$

Using the initial conditions

$$x_i(t)\Big|_{t=0} = x_i(0); \quad V_i'(t)\Big|_{t=0} = 0$$

one obtains the equation

$$x_i(t) = x_i(0)\, e^{\frac{-B}{2}t} \left\{ \cosh\left(\frac{\sqrt{B^2+4A}}{2}t\right) + \frac{B}{\sqrt{B^2+4A}} \sinh\left(\frac{\sqrt{B^2+4A}}{2}t\right) \right\} \quad (7)^{**)}$$

*) For spherical particles, the relations $m = \frac{4\pi r^3}{3}\rho$ and $m' = \frac{4\pi r^3}{3}\rho'$ are used in order to obtain these equations.

**) This equation is obtained by assuming that all particles have started their motion from rest because the system is assumed to be in a state of equilibrium before centrifusion.

Since B is of the order of 10^8, the last equation will be

$$x_i(t) \sim x_i(0)\, e^{\frac{A}{B}t} \quad (8)^{*)}$$

Analysis of Eq.(8) shows that each particle having size r_i is distinctly related to the spatial co-ordinate for a given time t. Further, during centrifusion, the larger particles would leak to volume V_2 before the smaller ones. Suppose L is the final co-ordinate of a particle having size $r + \Delta r$ for a given time t, this equation then becomes

$$L = x(r+\Delta r)\, e^{\frac{A}{B}t} \quad , \quad (9a)$$

where

$$x(r+\Delta r) = x(t)\Big|_{t=0} \quad .$$

Using the expressions of A and B, and introducing the constant

$$C = \frac{2(1-\alpha)\omega^2}{9\nu\alpha}$$

the initial co-ordinate of the particle having size $r + \Delta r$, will be given by

$$x(r+\Delta r) = L\ e^{-c(r+ r)^2 t} \quad (9b)$$

Putting $\Delta r = 0$ in Eq.(9b), one obtains

$$x(r) = L\ e^{-cr^2 t} \quad (9c)$$

for the same time t.

The determination of the SDF can easily be done once the function $n(r)$ is obtained via Eq.(1) and making use of the assumption made about the number of particles per unit length, which is $\frac{N}{L}$ for the system. For the interval $[x(r),L]$ (Fig.1), the function $n(r)$ can be obtained from the relation

$$\frac{n(r)}{L - x(r)} = \frac{N}{L} \quad (10a)$$

which gives

$$n(r) = N(1 - e^{cr^2 t}) \quad . \quad (10b)$$

Introducing the constant $k = ct$, for specifically chosen time t, one has the equation

*) This equation is obtained by employing Bianomial expansion upto first order of the term $\sqrt{B^2 + 4A}$ and an approximation $\frac{A}{B^2} \sim 0$, since $B^2 \sim 10^{16}$ and $A \sim 10^6$.

$$n(r) = N(1 - e^{-kr^2}) \quad . \tag{10c}$$

Combining equations (1) and (10c), the size distribution function will therefore be

$$\Phi(r) = 2kr\, e^{-kr^2} \quad , \tag{11a}$$

where all experimental parameters are absorbed in the constant k. The constant can be expressed in terms of the property of the system by demanding the existence of extremum values of the SDF. When this assertion is satisfied the SDF will be

$$\Phi(r) = \frac{r}{r_c^2}\, e^{\frac{-r^2}{2r_c^2}} \quad , \tag{11b}$$

where r_c is the size of the maximum number of particles in the system and accordingly the constant k is found to be

$$k = \frac{1}{2r_c^2} \quad . \tag{11c}$$

Therefore, the SDF comes out to be dependent on the value of r_c and the plot is shown in Fig.2.

CONCLUSION

Several methods (Refs.3, 4 and 5) have been suggested for the determination of the SDF for different size ranges. The method developed in this paper can be used for size ranges $0 - 10^{-5}$ cm in a much simpler way than the method used in Ref.1. The ranges of size considered are useful in laser physics [6]. The result is in good agreement with the experimental values obtained in Ref.1, and is also used for a system consisting of non-spherical particles by the help of the shape factor corrections. The critical size r_c, can be determined by light scattering method [7] or with the help of an electron microscope [8]. The numerical data necessary for the practical application of the method are provided in Ref.1.

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FIGURE CAPTIONS

Fig.1 Centrifusion experimental scheme

Fig.2 The graph of the size distribution function.

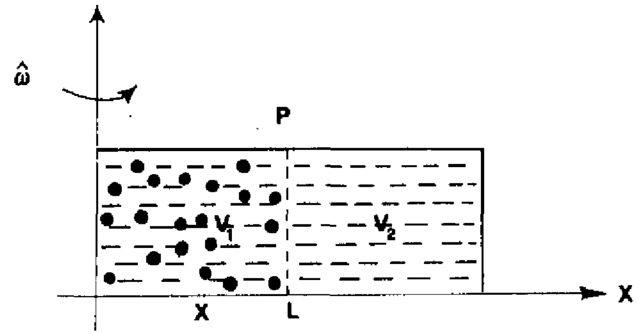

Fig.1

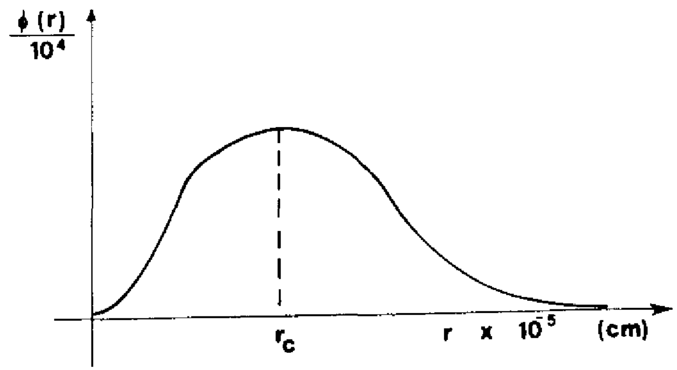

Fig.2