

# THE VISCOSITY OF A CONCENTRATED SUSPENSION OF SPHERICAL PARTICLES<sup>1</sup>

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## ABSTRACT

Einstein's viscosity equation for an infinitely dilute suspension of spheres is extended to apply to a suspension of finite concentration. The argument makes use of a functional equation which must be satisfied if the final viscosity is to be independent of the sequence of stepwise additions of partial volume fractions of the spheres to the suspension. For a monodisperse system the solution of the functional equation is  $\eta_r = \exp\left(\frac{2.5\phi}{1 - k\phi}\right)$ , where  $\eta_r$  is the relative viscosity,  $\phi$  the volume fraction of the suspended spheres, and  $k$  is a constant, the self-crowding factor, predicted only approximately by the theory. The solution for a polydisperse system involves a variable factor,  $\lambda_{ij}$ , which measures the crowding of spheres of radius  $r_i$  by spheres of radius  $r_j$ . The variation of  $\lambda_{ij}$  with  $r_i/r_j$  is roughly indicated. There is good agreement of the theory with published experimental data.

## INTRODUCTION AND THEORY

Since the publication of Einstein's basic analysis of the viscosity of a dilute suspension of rigid spheres in a viscous liquid, numerous equations have been developed in efforts to extend Einstein's formula to suspensions of higher concentrations (1-4). The various resulting formulas differ considerably from each other; and no one of them agrees with both sets of experimental data discussed later in this paper. Some papers deal with nonspherical particles, or with nonrigid particles such as dissolved polymer molecules.

The present analysis is limited to rigid, spherical particles. Also, the approach is partly empirical in that the interaction parameters are left for experimental determination, no effort being made to obtain their values from hydrodynamic theory. What the present analysis does consider is the space-crowding effect of the suspended spheres on each other; and there is no restriction imposed on the concentration or particle size distribution.

### *The Crowding Factor*

The Einstein viscosity equation postulates a suspension so dilute that there is no appreciable interaction between the spheres. In extending this

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equation to higher concentrations, we must take into account at least the first-order interaction. We may describe this interaction as essentially a crowding effect. That is, in a two-component system, for example, spheres of size  $r_1$  and partial volume concentration  $\phi_1$  crowd spheres of size  $r_2$  into the remaining free volume  $1 - \lambda_{12} \phi_1$ . The crowding factor,  $\lambda_{12}$ , may be different from unity as will be explained later.

We assume that  $\lambda_{12}$  is a function of the ratio  $r_1/r_2$ , but is independent of the value of  $\phi_i$ . In making this assumption we are neglecting second and higher order interactions. We shall use  $k$  to denote the particular value  $\lambda_{ii}$ , the self-crowding factor.

### *Monodisperse Suspension of Finite Concentration*

If spheres all of radius  $r_1$  are added to a suspension in two volume fractions  $\phi_1$  and  $\phi_2$ , the addition of the first fraction will increase the viscosity by a factor  $H(\phi_1) = \frac{\eta_1}{\eta_0}$ . All we know at present concerning  $H$  is that it must reduce to Einstein's formula for the relative viscosity at small values of  $\phi_1$ .

If the second fraction,  $\phi_2$ , is now added, there will be a further increase in viscosity. Part of this increase we may consider as being an increase, caused by  $\phi_2$ , in the viscosity of the remaining liquid in the space not occupied by  $\phi_1$ . This increase will therefore be of the form  $H(\psi_{21})$ , where  $\psi_{21} = \frac{\phi_2}{1 - k\phi_1}$  is the concentration of  $\phi_2$  in this remaining liquid, allowance being made for a crowding factor,  $k$ , different from unity.

But the crowding of fractions  $\phi_1$  and  $\phi_2$  being mutual, introducing  $\phi_2$  reduces the free volume accessible to  $\phi_1$ , and the effective concentration of  $\phi_1$  in the liquid is then  $\psi_{12} = \frac{\phi_1}{1 - k\phi_2}$ . To take account of this effect we must now replace  $H(\phi_1)$  by  $H(\psi_{12})$ . The product  $H(\psi_{12}) \times H(\psi_{21})$  is the viscosity of a suspension of total concentration,  $\phi_1 + \phi_2$ , and hence this product must be equal to  $H(\phi_1 + \phi_2)$ . This is

$$\begin{aligned} H(\phi_1 + \phi_2) &= \frac{\eta_{12}}{\eta_0} = H(\psi_{12}) \times H(\psi_{21}) \\ &= H\left(\frac{\phi_1}{1 - k\phi_2}\right) \times H\left(\frac{\phi_2}{1 - k\phi_1}\right). \quad [1] \end{aligned}$$

It is found that this functional equation is satisfied if  $H$  has the form

$$H(x) = \exp\left(\frac{2.5x}{1 - kx}\right). \quad [2]$$

$H(x)$ , in conventional terminology, is the relative viscosity,  $\eta/\eta_0$ . The constant 2.5 is chosen to agree with Einstein's equation for very dilute

suspensions, when  $\phi$  approaches zero. To check Eq. [2] mathematically, it can be verified that

$$\begin{aligned} \exp\left(\frac{2.5\phi}{1-k\phi}\right) &\equiv \exp\left[\frac{2.5(\phi_1 + \phi_2)}{1-k(\phi_1 + \phi_2)}\right] \\ &\equiv \exp\left[\frac{2.5\left(\frac{\phi_1}{1-k\phi_2}\right)}{1-k\left(\frac{\phi_1}{1-k\phi_2}\right)}\right] \exp\left[\frac{2.5\left(\frac{\phi_2}{1-k\phi_1}\right)}{1-k\left(\frac{\phi_2}{1-k\phi_1}\right)}\right]. \end{aligned} \quad [3]$$

More generally, if  $\phi$  is divided into  $n$  small fractions, it is easily verified that

$$\exp\frac{2.5\phi}{1-k\phi} \equiv \prod_1^n \exp\left[\frac{\frac{2.5\phi_i}{1-k(\phi-\phi_1)}}{1-\frac{k\phi_i}{1-k(\phi-\phi)_i}}\right]. \quad [4]$$

#### *Suspension of Spheres of Two Different Diameters*

For spheres of different diameters, the crowding factor will be different from  $k$ , and will be different, also, depending on which spheres are considered as being crowded, the large ones or the small ones. Hence in modifying the right-hand member of Eq [3] to fit this case, we must substitute  $\lambda_{21}\phi_2$  for  $k\phi_2$  in the first exponential term, and  $\lambda_{12}\phi_1$  for  $k\phi_1$  in the second exponential. Simplification of the resulting expression then leads to

$$H(\phi_1 + \phi_2) = \exp\left(\frac{2.5\phi_1}{1-k\phi_1-\lambda_{21}\phi_2}\right) \times \exp\left(\frac{2.5\phi_2}{1-k\phi_2-\lambda_{12}\phi_1}\right). \quad [5]$$

#### *Polydisperse Suspension*

If we have a suspension of  $n$  groups of spheres, each group of a different diameter, we may write, by extension of Eq. [5],

$$\ln H(\phi) = 2.5 \sum_{i=1}^n \frac{\phi_i}{1 - \sum_{j=1}^n \lambda_{ji}\phi_j}. \quad [6]$$

For a continuous distribution of diameters, Eq. [6] becomes in the limit

$$\ln H(\phi) = 2.5 \int_0^\phi \frac{d\phi_i}{1 - \int_0^\phi \lambda_{ji}d\phi_j}. \quad [7]$$

Let

$$\begin{cases} \sigma = \ln \frac{r}{\bar{r}}, \\ d\phi = P(\sigma)d\sigma, \\ \int_{\sigma_1}^{\sigma_2} P(\sigma)d\sigma = 1, \end{cases} \quad [8]$$

where  $\bar{r}$  is a mean radius, defined anyhow, and  $\sigma_2$  and  $\sigma_1$  are the upper and lower limits of  $\sigma$ . Then Eq. [7] takes the form,

$$\ln \frac{\eta}{\eta_0} = \ln H = 2.5\phi \int_{\sigma_1}^{\sigma_2} \frac{P_i d\sigma}{1 - \phi \int_{\phi_1}^{\sigma_2} \lambda_{ji} P_j d\sigma}. \quad [9]$$

With regard to the physical significance of the preceding equation, it may be clarifying to point out that the first integral sign does not represent the successive additions of the different components of the suspended material. Rather, it represents the successive evaluations of the effects of the different components, each component operating in the presence of all of the other components.

$$\text{Properties of } \lambda_{ij} \left( \frac{r_i}{r_j} \right)$$

While there will be no attempt here to determine by theoretical analysis the precise properties of  $\lambda_{ij}$  as a function of the radius ratio,  $\rho_{ij} = r_i/r_j$ , we can easily deduce certain important features of this function. For the case  $\rho_{ij} \rightarrow 0$ ,  $\rho_{ji} \rightarrow \infty$ , the suspension of the small spheres in the liquid between the large spheres behaves towards the large spheres like a homogeneous liquid of increased viscosity. Hence the large spheres are not crowded at all by the small ones; and the small spheres are crowded into the space left unoccupied by the large ones. Therefore

$$\lim_{\rho_{ij} \rightarrow 0} \lambda_{ij} = 0, \quad [10]$$

$$\lim_{\rho_{ij} \rightarrow \infty} \lambda_{ij} = 1, \quad [11]$$

If we use these values of  $\lambda_{ij}$  in Eq. [5], letting  $\phi_1$  be the component of small radius and  $\phi_2$  the component of large radius, we find

$$\eta = \eta_0 \exp \frac{2.5\phi_1}{1 - k\phi_1 - \phi_2} \exp \frac{2.5\phi_2}{1 - k\phi_2}. \quad [12]$$

The same equation can be obtained from two applications of Eq. [2], if we recognize only that the volume accessible to the fraction  $\phi_1$  is  $1 - \phi_2$ . Thus Eqs. [10] and [11] are checked.

The value of  $\lambda_{ij}$ , or  $k$ , is obviously of considerable importance. We can make a rough estimate of  $k$  from the following considerations. Densely packed spheres, in a face-centered cubic lattice, for example, would exhibit infinite viscosity, simply because of mechanical interlocking. The fractional volume,  $\phi_c$ , of the spheres in such packing is 0.74. Hence, if  $H(\phi_c)$  by Eq. [2] is to be infinite, we must have

$$k \doteq 1/0.74 = 1.35. \quad [13]$$

This method of estimating  $k$  gives a lower limit. A rough estimate of an upper limit can be similarly obtained by assuming that the densest packing which will permit continuous movement is simple cubic. For this case  $\phi_c = \pi/6$ , and

$$k \doteq 6/\pi = 1.91. \quad [14]$$

From this purely geometric argument we therefore conclude that

$$1.35 < k < 1.91. \quad [15]$$

This simple analysis of space-filling and crowding action at high concentrations does not in itself prove much about the value of  $k$  at low

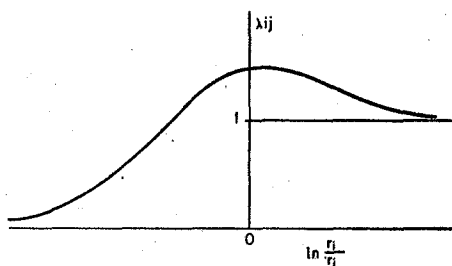


Fig. 1. Properties of  $\lambda_{ij}$ , the effective crowding of spheres of radius  $r_j$  by spheres of radius  $r_i$ .

concentrations. However, space-filling action cannot vary greatly with concentration, and if the associated crowding action is a major part of particle-to-particle hydrodynamic interaction, then we may expect that  $k$  will vary only slightly with  $\phi$ , if at all, and will have a value of approximately 1.5. Presumably the function  $\lambda_{ij}(\rho_{ij})$  has a maximum at or near  $\rho_{ij} = 1$ .

The properties of  $\lambda_{ij}$ , so far as they have been deduced, are shown in Fig. 1.

#### EXPERIMENTAL CHECK

The above theory provides three equations, [2], [5], and [9] or [6], by which the theory can be tested. Unfortunately the published literature does not provide the data necessary for rigorous tests of the more general equations. Relatively little work has been done at high concentrations of

rigid suspended spheres; and the control of particle diameter leaves much to be desired. Particles small enough to form colloidal solutions are increased in size by an adsorbed stabilizing layer of unknown thickness.

The best experimental data for testing Eq. [2] are those published by V. Vand (3) on nearly monodisperse suspensions of glass spheres, of diameters ranging from 0.010 to 0.016 cm. His suspension medium was an equally dense solution of zinc iodide in a mixture of water and glycerol.

The upper curve of Fig. 2 shows Vand's data for relative viscosity,  $\eta_r$ , or in our notation,  $H(\phi)$ , plotted against  $\phi$ . The curve fitted to these points represents Eq. [2] with  $k = 1.43$ . The agreement seems to be within experimental error over the full range of the data. The two branches of the experimental curve above  $\phi = 0.35$  represent two variations in experimental technique. Curve *S* was obtained by stirring the suspension immediately before measuring; curve *N* by not stirring.

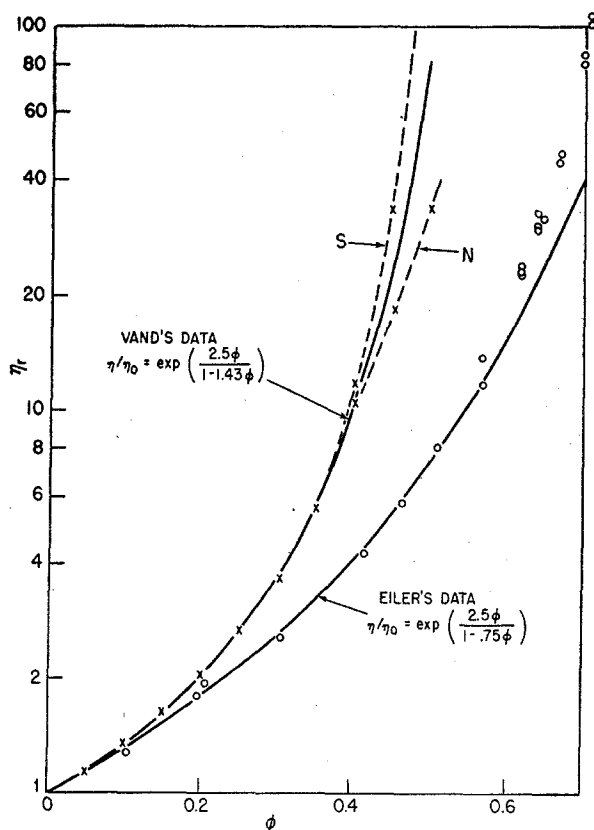


FIG. 2. Theoretical curves fitted to experimental data by Vand (x) and by Eilers (o).

The comparison between observed and calculated viscosity is shown more exactly in Table I.

This experimental test of the theory shows that, in spite of the slight spread in diameter of Vand's glass spheres, the theoretical equation fits the data with a constant value of  $k$  over the total variation in  $\phi$  from 0 to 0.5. Furthermore, the value of  $k$  comes within the limits set by the inequalities (see Eq. [15]).

H. Eilers (5) has published a series of viscosity measurements on concentrated emulsions of a bituminous material of high softening point, such that at room temperature the droplets were essentially rigid. The

TABLE I  
*Vand's Data: Observed and Calculated<sup>a</sup>*

Concentration $\phi$ , %	$\eta_r$ (obs.)	$\eta_r$ (calcd.)
0	1.000	1.000
5	1.145	1.144
10	1.342	1.340
15	1.621	1.613
20	2.024	2.016
25	2.632	2.648
30	3.636	2.716
35	5.556	1.75
40N	10.53	10.36
40S <sup>b</sup>	11.77	10.36
45N <sup>b</sup>	18.18	23.48
45S <sup>b</sup>	33.33	23.48
50N <sup>b</sup>	33.33	80.35
50S <sup>b</sup>	200.00	80.35

<sup>a</sup> Calculations by the formula  $\ln \eta_r = \frac{2.5\phi}{1 - 1.43\phi}$ .

<sup>b</sup> S signifies that suspension was stirred just before being measured; N signifies not stirred.

diameters varied from 1.6 to 4.7  $\mu$ , except for about 1% by volume of diameter less than 1.6  $\mu$ . The emulsions must therefore be considered as polydisperse. If we knew the  $\lambda_{ij}$  function in detail, and if we knew the  $P(\sigma)$  function for Eilers' material, we could then use Eq. [9] to express the viscosity as a function of the concentration. Lacking this information, we proceed to develop Eq. [9] as a power series in  $\phi$ , obtaining

$$\ln \frac{\eta}{\eta_0} = 2.5\phi \left[ 1 + \sum_1^{\infty} \phi^n \lambda_n \right], \quad [16]$$

where

$$\lambda_n = \int_{\sigma_1}^{\sigma_2} P_i \left[ \int_{\sigma_1}^{\sigma_2} \lambda_{ji} P_j d\sigma \right]^n d\sigma. \quad [17]$$

To the second degree in  $\phi$ , Eq. [16] may be written

$$\ln \frac{\eta}{\eta_0} = \frac{2.5\phi}{1 - \lambda_1\phi}, \quad [18]$$

which is of the same form as Eq. [2]. The lower curve in Fig. 2 shows Eilers' data, and also Eq. [18] with  $\lambda_1 = 0.75$ . The agreement is quite satisfactory in view of the fact that Eq. [18] is only an approximation, not expected to be valid at high concentrations. The fact that  $\lambda_1$  (Eilers)  $< k$  (Vand) also is in agreement with the theory.

### DISCUSSION

The crowding theory of viscosity that has been presented here yields an equation for the relative viscosity of a monodisperse suspension of spheres which agrees with the best published experimental data over the full concentration range from 0 to 0.5. In addition to the Einstein coefficient for dilute suspensions, the equation involves one adjustable parameter which is correctly predicted as to order of magnitude. In view of this success of the theory, the conclusion seems justified that the interaction between the spheres in a suspension is primarily the simple geometric crowding action which is the basis of the theory. The mutual disturbance of flow lines around two near particles is therefore a matter of secondary importance.

From Eqs. [17] and [18], and also from the two curves in Fig. 2, it is clear that the second-degree coefficient in the viscosity-concentration equation must be a function of the particle size distribution. This is a point which has been ignored in other published theories. For example, we have the following paradoxical situation. In de Bruijn's theory of viscosity (1) an unknown parameter is determined by assuming infinite viscosity for a suspension of spheres of volume concentration 0.74, corresponding to close packing of spheres of uniform size (just as, for example, we obtained Eq. [13] above). De Bruijn's fluidity formula was found to give excellent agreement with Eilers' data on bitumen suspensions. We would here consider these suspensions to be polydisperse systems, and would not expect good agreement. De Bruijn's formula should agree, on the other hand, with Vand's data, published in 1947; but the disparity between the two curves of Fig. 2 above shows that de Bruijn's formula agreeing with Eilers' data could not agree with Vand's data.

Presumably the equations of the present theory could be elaborated to apply to other than rigid, spherical particles; but before such an extension of the theory is attempted it would be desirable to have the necessary experimental data for a rigorous test of the theory as it now stands. This requires close control of particle size, and measurements on single-



dual-, and multiple-component suspensions covering a wide range of particle diameters and concentrations.

While this manuscript was in preparation a recent paper by James V. Robinson (6) came to the writer's attention. Robinson measured the viscosities of suspensions of glass spheres in S. A. E. No. 30 motor oil, S. A. E. No. 50 motor oil, castor oil, ethylene glycol, a sucrose solution, and corn sirup. Sphere diameters were mostly from 10 to 30  $\mu$ . All of Robinson's data are well fitted by Eq. [18] with  $\lambda_1 = 0.833$ , except for the initial points, at  $\phi = 0$ , on the curves for ethylene glycol, sucrose solution, and corn sirup. These three initial points do not fit well with the other experimental points on their respective curves, and some systematic error in the data seems to be indicated.

Robinson developed a theoretical viscosity equation of the form

$$\frac{\eta}{\eta_0} = 1 + \frac{Ak\phi}{1 - S\phi},$$

where  $A$  and  $S$  are adjustable constants. The product  $S\phi$  is interpreted as the sedimentation volume of the glass spheres, and  $1 - S\phi$  as the "free" volume of liquid. Obviously, in order to agree with Einstein's equation,  $A$  must have the value 2.5; but Robinson finds that, in order to fit his experimental data, he must choose various values of  $A$  from 3 to 5.

The concept of free volume introduced by Robinson is developed more rigorously in the present paper. The improvement in the present analysis, compared with Robinson's, is indicated in one way by the fact that, while fitting experimental data at high concentrations, we still agree with Einstein's equation at low concentrations.

*Note added in proof.* As a result of some correspondence with Professor F. R. Eirich, the author wishes to add a remark concerning V. Vand's (3) theoretical work. Equation [2] of the present paper occurs as an intermediate equation in Vand's theory. However, Vand's theory gives a value for  $k$  of .61, which is too low to make the equation fit his data. After further theoretical development Vand arrives at a final equation which fits his data quite well, but is in the form of a power series terminating with the second degree in the concentration.

There is, in this author's opinion, a serious error in Vand's theory of the collision effect. Vand assumes that after collision two spheres will separate along rectilinear paths; but it can be shown that the paths of recession must be curvilinear and are the mirror images of the paths of approach. Correction of this error in Vand's theory would lead to a higher theoretical value of  $k$ .

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