

Viscosity of concentrated suspensions: An approach based on percolation theory

G. A. Campbell

Department of Chemical Engineering, Clarkson University, Potsdam, New York 13676

G. Forgacs

Department of Physics, Clarkson University, Potsdam, New York 13676

(Received 29 June 1989)

A different approach to study the viscosity of concentrated suspensions is proposed. It is based on percolation theory. It is suggested that at the critical concentration of fillers, ϕ_c , a macroscopic interconnected cluster (secondary structure) of fillers is formed. This cluster extends from one wall of the rheometer to the other. It is the properties of this macroscopic cluster which determine the viscosity for $\phi \geq \phi_c$. An analytic formula is derived for $\eta_r(\phi)$ above ϕ_c , which is tested against a number of sets of experimental data.

The theoretical calculation of the zero shear viscosity of suspensions has a long history. Since the pioneering work of Einstein,¹ a number of expressions have been proposed.²⁻⁴ These expressions almost invariably are extensions of Einstein's formula and as such are valid only for dilute suspensions. No methods effectively treating dense suspensions have been established.

A different approach was followed by Thomas,⁵ who, using data from a number of authors, established an empirical relationship

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + 0.00273 \exp(16.6\phi). \quad (1)$$

Here $\eta_r = \eta/\eta_0$ (η is the viscosity of the suspension, η_0 is the viscosity of the suspending medium), and ϕ are the relative viscosity of the suspension and the volume fraction of the fillers, respectively. The above expression turned out to be so successful that results for $\eta_r(\phi)$ derived on the basis of theoretical considerations are tested against it. An extensive comparison of the theoretical $\eta_r(\phi)$ dependencies with Thomas' formula is given in Ref. 4. It has to be noted that (1) is valid only for $0 \leq \phi \leq 0.55$, it does not allow for $\eta_r \rightarrow \infty$ for any $\phi \leq 1$. An expression valid in the asymptotic region ($\phi \sim \phi_m$, where ϕ_m is the concentration of close packing at which no further flow is possible) was derived by Frankel and Acrivos⁶ on the basis of only hydrodynamic interactions between suspended particles.

Although the hydrodynamic characteristics of the flow and the microscopic interactions affecting the individual fluid and filler particles undoubtedly are important in establishing the correct $\eta_r(\phi)$ relation, it has been realized that the effect of structure formation also has to be considered. In Ref. 7 it was suggested that in a concentrated suspension of solid spheres relatively low shear may induce a structure. In Ref. 8 it was established that in an 8% solution of polyisobutylene in cyclohexane filled with chalk, a secondary structure formed at $\phi = 0.15$. In Ref. 9 the formation of clusters of fillers, their distribution, and effect on the relative viscosity was studied. Pair-correlation functions of fillers in noncolloidal suspensions were measured experimentally in Ref. 10.

In the present work the $\eta_r(\phi)$ dependence of concen-

trated suspensions ($0.16 \leq \phi$) is reexamined. Our approach, however, differs from all the previous theoretical studies of this problem. It is based on the consequences of structure formation. It employs percolation theory.¹¹ Using ideas of percolation theory, together with some simplifying physical assumptions about the flow, we propose a new expression for $\eta_r(\phi)$. Our expression, when tested against a number of sets of experimental data [including those based on (1)], gives excellent agreement for $0.16 \leq \phi \leq \phi_m$. The only adjustable parameter is ϕ_m .

Percolation theory was first applied to the problem of suspensions by de Gennes¹² who studied the equations of hydrodynamics in the presence of an infinite percolation cluster of the suspended particles. de Gennes's analysis predicted a plug flow and an anomaly in the plot of the relative viscosity versus ϕ . No attempt was made to determine the functional relationship $\eta_r = \eta_r(\phi)$. Numerical simulations by Brady and Bossis¹³ and experimental results by Blanc *et al.*¹⁴ do support some qualitative predictions of de Gennes' ideas.¹⁵ The importance of clustering for the understanding of the rheology of concentrated dispersions was also emphasized by Quemada.¹⁶ Very recently percolation theory was successfully applied to the analysis of experimental results on the viscosity of microemulsions by Peyrelasse, Moha-Ouchane, and Boned.¹⁷ What we propose here is the application of percolation theory to obtain *quantitative* results on the viscosity of a concentrated suspension.

We consider a suspension of monodispersed hard spheres. The solvent and the fillers are mutually buoyant. We assume a Newtonian flow, which can be characterized by a shear independent viscosity. The spheres are ideal in that except for hydrodynamic interactions all other forces are neglected or included in the parameters characterizing the percolation structure. (The spheres cannot penetrate each other, so that a contact interaction is present by definition.) Upon increasing their volume fraction the fillers form more and more complicated clusters. This is possible due to hydrodynamic forces alone. Indeed, two spheres can be brought together in a simple shear and form a temporary doublet whose average lifetime varies

with the shear rate γ as¹⁸

$$\tau \sim 2.5\gamma^{-1}. \quad (2)$$

In a fluid subjected to shear, the geometrical distribution of suspended fillers is continuously modified. Consequently, the clusters these fillers form have to be considered as dynamical ones, whose structure is constantly changing in the sense that they are losing and gaining particles. At any given moment there is a well-defined distribution of clusters and this distribution evolves in time in a stationary manner.¹⁴ We postulate, similarly to de Gennes, that at a critical volume fraction ϕ_c an "infinite" percolating cluster of fillers forms. In an actual experiment "infinite" means a macroscopic cluster which extends from one wall of the viscosimeter to the other. Below the percolation threshold only microscopic clusters exist and the flow is effectively the same as in the dilute limit. The effect of the microscopic clusters may be taken into account in a systematic way by including higher-order terms in the power series expansion of η_r in terms of ϕ . Early theories should, therefore, give a rather accurate account of the microscopic clusters. Above the percolation threshold, for the flow to persist the infinite cluster has to be rearranged. Such a rearrangement is possible only if the fillers in the infinite cluster can find empty space to move into. Clearly, at ϕ_m only the infinite cluster exists, the fillers cannot move, and the viscosity is infinite. For $\phi_c \leq \phi \leq \phi_m$ the fillers still can move, but this motion becomes more and more difficult as $\phi \rightarrow \phi_m$. This is illustrated in Fig. 1.

We then assume that for $\phi \geq \phi_c$ the viscosity is determined by the properties of the infinite cluster. In what follows, on the basis of this assumption we derive an analytic form for $\eta_r(\phi)$.

Transport coefficients in the presence of percolation structures like heterogeneous solids, composites, porous media, amorphous metals, etc. are calculated typically by solving the transport equations on a percolation cluster, either numerically or using some kind of effective medium theory.¹⁵ Here we follow another route which allows us to perform the calculations analytically.

From our earlier discussion it is clear that the lower the probability that a given particle in the infinite cluster finds empty space to move into, the larger the value of η_r should be. Therefore, it is reasonable to assume that the contribution of the individual fillers to the increase of the viscosity is inversely proportional to their probability finding empty space around themselves. To simplify the discussion we assume that the fillers occupy the vertices of a reg-

ular (say simple-cubic) lattice. Therefore, we wish to determine the probability that a given filler (which originally is part of the macroscopic cluster) is at the surface of a cluster of voids of N sites. These ideas (in the continuum limit; see later) are schematically illustrated in Fig. 1(b), where for particle a and c $N \neq 0$, whereas for particle b , $N = 0$. The filler particle b is blocked, it cannot move. The calculation of the above probability, in general, is a formidable task. The following mean-field-type approximation, however, makes the calculation rather straightforward. We assume that the probability of a given site in the N -site cluster to be empty is $q(\phi)$ independent of all the other sites, and therefore, the probability of an N -site void is

$$P_N = q^N. \quad (3)$$

Here $q = q(\phi)$ can be determined as follows. For a given ϕ the relative volume fraction of the empty sites is proportional to $(\phi_m - \phi)$ (we completely ignore the microscopic clusters). Since for us the completely "empty space" is that at $\phi = \phi_c$, $q(\phi_c) = 1$. Also at $\phi = \phi_m$ no empty space is available, and therefore $q(\phi_m) = 0$. We then arrive at

$$q(\phi) = \frac{\phi_m - \phi}{\phi_m - \phi_c}. \quad (4)$$

According to our assumption, the contribution of the N -site clusters to η_r is¹⁹

$$\eta_r(N) = \frac{1}{C(N)q^N}. \quad (5)$$

[A possible proportionality constant in (3) can be incorporated into η_0 .] Here $C(N)$ is the weight of the N -site clusters with the above discussed properties. A given filler at the surface of the N -site empty cluster can be pushed into any of the N sites, therefore the weight $C(N)$ in (5) should be proportional to N . Now imagine that a single filler indeed has been pushed into one of the empty sites. In the N -site void it becomes loose, since it can freely move between the empty sites and, therefore, it does not hinder the flow. The next filler at the surface can be placed now only at $N-1$ sites, the third at $N-2$, and so on, until the empty cluster disappears. (We assume that every time a filler from the surface enters the empty cluster its place is immediately occupied by another filler from the infinite cluster.) With this we arrive at $C(N) = N!$ and by summing (5) over N (Ref. 20) ($1 \leq N \leq \infty$) we obtain

$$\eta_r = e^{1/q} - 1. \quad (6)$$

This expression, in view of (4), is highly nonanalytic in ϕ and no power series in ϕ could reproduce it.

Until now we basically assumed that the fillers can move only in discrete steps. It was done only for convenience. In reality it is not so and we should use the results of continuous percolation theory.^{21,22} According to this theory, if clusters are formed by identical uncorrelated spherical particles, to a very good approximation, the percolation threshold ϕ_c is independent of the underlying structure and $\phi_c = 0.16$.^{21,22} (Note that this value is very close to the one reported in Ref. 8 for the appearance of a secondary structure.) Contrary to ϕ_c the value of ϕ_m depends on the structure. For a hexagonal structure

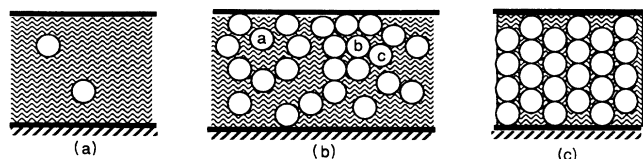


FIG. 1. (a) Schematic illustration of the very small ϕ region. (b) Possible cluster structures for $\phi \geq \phi_c$. Particle a can easily be displaced; particle c is constrained in its motion; particle b is entirely blocked. (c) The case $\phi = \phi_m$.

$\phi_m = 0.74$ and for any other structure of monodispersed spheres $\phi_m < 0.74$.³

Before comparing the simple formula (6) with experimental results, a few remarks on the effect of experimental errors on Eq. (6) are necessary. If $d\phi$ is the uncertainty in measuring the concentration of fillers, Eq. (6) leads to a relative error (in percents) of the viscosity

$$\frac{d\eta_r}{\eta_r} = 100 \left(\frac{e^{1/q}}{q(\phi_m - \phi)} \right) d\phi. \quad (7)$$

In Table I we list the relative errors for $d\phi = 0.005$ or half of a percent (with $\phi_m = 0.685$ and $\phi_c = 0.16$). It can be seen that in an expression like (6) a small uncertainty in ϕ can lead to a substantial error in η_r , especially for concentrations above 0.5. This has to be taken into account when Eq. (6) is compared with experimental results.

There exists a large number of experimental results for the relative viscosity of concentrated suspensions. Experiments, however, are never performed with an ideal system like the one we study in this work. In comparing our results with experiments, we tried to select experiments which in our opinion, approximate most closely the conditions at which our discussion has validity. This comparison is shown in Fig. 2.

As mentioned earlier we consider only the interval $0.16 \leq \phi \leq \phi_m$, with ϕ_m being the only adjustable parameter. Since the Thomas' curve (1) is the result of an extrapolation (in which 17 sets of experimental data were used) to minimize finite shear, non-Newtonian, inertial, and nonhomogeneous effects, an important test of our approach is the comparison of Eqs. (1) and (6). As can be seen from Fig. 2 the fit is excellent in the region where Eq. (1) is valid.

The next set of data to which Eq. (6) is fitted is an earlier one by Lewis and Nielson²³ (not present in Thomas' analysis). This data set represents a sample of glass beads with a fairly broad distribution in size (45–60 μm) and the reported shear rates were between 0.03 and 1 sec^{-1} . As can be seen from Fig. 2 the fit is excellent up to a concentration of 0.45. The fit at $\phi \sim 0.5$ is poor. However, as can be seen from Fig. 2, on the basis of the experimental results, $\eta(\phi)$ is not a convex function in the region around $\phi \sim 0.45$, which is contrary to the expectation $\eta(\phi = \phi_m) = \infty$. In addition, for high values of ϕ it is increasingly difficult to sustain experimentally the conditions necessary for a Newtonian flow.

TABLE I. Relative error in η_r due to the uncertainty in ϕ for different values of filler volume fraction. $\phi_m = 0.68$, $\phi_c = 0.16$.

ϕ	Error (%)
0.16	0.95
0.25	1.48
0.40	3.30
0.50	7.70
0.55	14.7
0.60	36.3

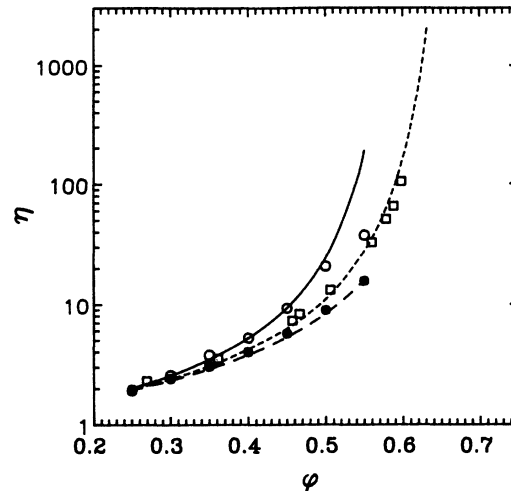


FIG. 2. Comparison of expression (6) with experimental results. ϕ_m is the only adjustable parameter. Solid circles, open circles, and open squares stand, respectively, for Thomas's data ($\phi_m = 0.685$), the data of Lewis and Nielsen ($\phi = 0.58$), and Pätzold's data ($\phi_m = 0.645$). The corresponding curves, obtained by using Eq. (6) are theoretical fits to the experimental results.

Finally, we compare our result with a data set published by Pätzold.²⁴ These data were taken in a specifically designed system which was constructed to minimize any segregation of fillers while the suspension was being tested. At the same time monodispersity was carefully controlled. The data compare very well in this case with Eq. (6).²⁵

The following remarks are in place concerning the presented ideas. We assume no correlations between the fillers. As mentioned, such correlations are considered here only inasmuch as the fillers cannot penetrate each other. Any more sophisticated correlation in our formulation would lead to correlated percolation and could be incorporated in a more complicated theory. Our discussion is valid only above the percolation threshold. Expression (6) for η_r , valid for $\phi \geq \phi_c$ should be matched with results valid for $\phi \leq \phi_c$ obtained by other methods. Our final expression (6) for η_r was obtained on the assumption that all the fillers are in the infinite cluster. In fact, at ϕ_c a substantial fraction of the particles are in the microscopic clusters, which are not in physical contact with the macroscopic cluster. The number of particles in the infinite cluster grows, however, very rapidly after the onset of percolation,¹¹ which could explain the excellent fit for $0.2 \leq \phi$. We fully realize that our discussion is highly oversimplified [especially on the form of $C(N)$]. We believe, however, that the good agreement with experimental results is not accidental; our model grabs the essentials of the flow and opens the possibility to study the rheology of concentrated solutions in a new way.

It is quite remarkable that despite the number of assumptions and simplifications we have made, our final result, Eq. (6), describes the presented experimental results so well over a large range of concentrations. We cannot expect our formula to fit any arbitrary data set. The

present work should be considered as a starting point towards the possible application of percolation theory to the quantitative analysis of the viscosity of concentrated suspensions. To make further progress and apply our ideas to other systems for which at this point our final result may not be a good fit, we will have to take into account more specific features of the individual physical systems,

rheometers, and conditions at which the experiments are carried out.

One of us (G.F.) acknowledges useful conversations with C. Doering. He was partially supported by the National Science Foundation under Grant No. DMR-8515519.

-
- ¹A. Einstein, *Ann. Phys.* **17**, 549 (1905); **19**, 289 (1906); **34**, 591 (1911).
- ²For an early review, see H. L. Frisch and R. Simha, in *Rheology*, edited by F. R. Eirich (Academic, New York, 1956) Chap. 14.
- ³For a more recent review, consult R. Herczynski and I. Pieńkowska, *Ann. Rev. Fluid Mech.* **12**, 237 (1980).
- ⁴L. A. Utracki and B. Fisa, *Polymer Composites* **3**, 193 (1982).
- ⁵D. G. Thomas, *J. Colloid Sci.* **20**, 267 (1965).
- ⁶N. A. Frankel and A. Acrivos, *Chem. Eng. Sci.* **22**, 847 (1967).
- ⁷F. Gadala-Maria and A. Acrivos, *J. Rheol.* **24**, 799 (1980).
- ⁸L. A. Faisalson and E. E. Jacobson, *Polym. Mech.* **6**, 898 (1977).
- ⁹A. L. Graham and R. B. Bird, *Ind. Eng. Chem. Fundam.* **23**, 406; **23**, 411 (1984); **23**, 420 (1984).
- ¹⁰D. M. Husband and F. Gadala-Maria, *J. Rheol.* **31**, 95 (1987).
- ¹¹For a recent review and further references on percolation theory, see D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1985).
- ¹²P. G. de Gennes, *J. Phys. (Paris)* **40**, 783 (1979).
- ¹³J. F. Brady and G. Bossis, *J. Chem. Phys.* **80**, 5141 (1984); *J. Fluid Mech.* **155**, 105 (1985); *Ann. Rev. Fluid. Mech.* **20**, 111 (1988).
- ¹⁴R. Blanc, M. Belzons, C. Camoin, and J. L. Bouillot, *Rheol. Acta* **22**, 505 (1983).
- ¹⁵R. Blanc and E. Guyon, in *Percolation Structures and Processes*, edited by G. Deutscher, R. Zallen, and J. Adler, *Annals of the Israel Physical Society* No. 5 (Hilger, Bristol, 1983).
- ¹⁶D. Quemada, *J. Mech. Theor. Appl. (France) Suppl.* 267 (1985); 289 (1985).
- ¹⁷J. Peyrelasse, M. Moha-Ouchane, and C. Boned, *Phys. Rev. A* **38**, 4155 (1988); J. Peyrelasse and C. Boned, *ibid.* **41**, 938 (1990).
- ¹⁸H. Goldsmith and S. Mason, in *Rheology*, edited by F. R. Eirich (Academic, New York, 1964), Vol. 4, p. 85.
- ¹⁹Obviously a more general expression $\eta_r \sim (1/q^N)^\alpha$ could be taken. Here, however, we choose the simplest mean-field-type expression with $\alpha = 1$.
- ²⁰G. Grinstein and D. Mukamel, *Phys. Rev. B* **27**, 4503 (1983).
- ²¹H. Scher and R. Zallen, *J. Chem. Phys.* **53**, 3759 (1970).
- ²²I. Webman, J. Jorther, and M. H. Cohen, *Phys. Rev. B* **11**, 2885 (1975).
- ²³T. B. Lewis and L. E. Nielsen, *Trans. Soc. Rheol.* **12**, 421 (1968).
- ²⁴R. Pätzold, *Rheol. Acta* **31**, 322 (1980).
- ²⁵In Ref. 24, Pätzold showed three experimental curves which were obtained with different rheometers. In Fig. 4 we used only the data set obtained by the special rheometer built by Pätzold. In connection with the other two data sets the criticism concerning the nonconvexity of $\eta(\phi)$ as discussed earlier applies again.