RHEOLOGY OF CONCENTRATED DISPERSIONS

R. Blanc

To cite this version:
R. Blanc. RHEOLOGY OF CONCENTRATED DISPERSIONS. Journal de Physique Colloques, 1986, 47 (C1), pp.C1-65-C1-71. <10.1051/jphyscol:1986110>. <jpa-00225494>

HAL Id: jpa-00225494
https://hal.archives-ouvertes.fr/jpa-00225494
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
RHEOLOGY OF CONCENTRATED DISPERSIONS

R. BLANC

Département de Physique des Systèmes Désordonnés, Université de Provence, UA 857 du C.N.R.S., F-13397 Marseille Cedex 13, France

RESUME—Cet article présente de manière succincte les principales grandeurs physiques qui doivent être prises en considération dans la rhéologie des suspensions concentrées. On donne ensuite les grandes lignes des problèmes actuels qui se posent dans l'étude de la viscosité des suspensions, leur vitesse de sédimentation et les processus d'agrégation. On met en particulier en avant le rôle joué par l'existence de structures ordonnées ou aléatoires.

ABSTRACT—In this paper we briefly present the main relevant physical quantities in the rheology of concentrated dispersions. Main lines of three topics (shear viscosity, sedimentation velocity and aggregation processes) are then given. The importance or ordered or random structures is emphasized.

Nature and industrial processes provide numerous examples of complex systems in which solid particles are dispersed in a fluid: slip used in the manufacture of ceramics, natural muds in rivers or estuaries, drilling and mining fluids, cellulosic fibers in paper pulp, pastries, blood, concrete and cements...

Such systems afford very various behaviours; their mechanical, physical or physicochemical properties are, at the present time, widely misunderstood. Such a lack of understanding is due to the complexity of these systems cumulating the difficulties of random heterogeneous media and that of hydrodynamic systems. Due allowance being made for their eminent importance in the industrial or natural processes, they have been the subject of numerous practical studies and a considerable knowledge has been cumulated. But there is not, at the present time, a complete theoretical corpus allowing a deep understanding of these systems.

When one considers the case of one isolated particle in a fluid, some simple situations as, for instance, the sedimentation in a quiescent fluid or the behaviour of the particle in a sheared fluid may be exactly (or with a very good approximation) solved if:

i) the fluid is unbounded

ii) the viscous forces prevail over the inertial ones (low Reynolds' number regime)

iii) the particle's shape is simple enough (sphere /1/, cylinder /2/, ellipsoid /3/).

As soon as one of these three conditions is not fulfilled one does not know the solution except in few situations. Among unsolved problems, some concern a single sphere either in fast sedimentation in an unbounded fluid /4/ or in slow sedimentation inside a cylindrical tube /5/. So it is not very surprising that more complex situations and especially those related to concentrated dispersions have not yet been solved. I propose in this paper to isolate the main parameters relevant to the properties of these systems and to put forward some aspects of the rheology of dispersions closely related to the science of ceramics.
Let us first consider, in a container, a dispersion of identical spheres in a fluid. We suppose that, due to a suitable stirring, the dispersion is homogeneous: except the statistical fluctuations the number of particles by unit volume is the same everywhere in the system. Let us apply to this two phase medium an external field as, for instance, gravity. Then, the spheres go down or up depending on their buoyancy-corrected weight. The path followed by a given particle depends on the net result of forces and torques exerted on it by the fluid, the external field and the other particles.

A part of the force and torque exerted by the fluid is due to its molecular nature and corresponds to the translational and rotational Brownian motions. Another part is due to the convective motion of the fluid regarded as a continuous medium. The deterministic stresses exerted on the particle result from the flow of the fluid due to the motion of that particle and of all the others. Each particle sediments in a fluid perturbed by the fall of the others. This indirect interaction between spheres strongly depends on the volume fraction in the dispersion. It is called the hydrodynamic interaction. The relative importance of the Brownian and convective effects (Peclet's number), essentially depends on the size of the particle. In ordinary conditions, the Peclet's number is about one for spheres when the radius is approximately equal to one micron. Brownian motion can, in general, be neglected for particles larger than few microns (large Peclet's number regime).

When the size of the suspended particles is in the colloidal range (1-1000nm) there is a competition between the sedimentation of the particle and their Brownian diffusion: a concentration profile takes place in the dispersion.

Such a concentration profile is stable unless an aggregation process takes place in the suspension: if two particles can come very close each other due to their Brownian motion or the flow of the suspending fluid, they can aggregate under the action of Van der Waals interaction /6/ so that the size of the "particles" increases and the dispersion flocculates. Very often, the particles get a surface charge in the fluid due to an unequal distribution of charge between its surface and the fluid. Then, a cloud of ions, called the double-layer, surrounds the particle and screens its charge. The repulsive forces between two particles are reduced when they are far from each other, but when they are close the overlap of the clouds presents the formation of aggregates and stabilizes the dispersion. Nevertheless the addition of an electrolyte which increases the ionic concentration and reduces the extent of the cloud may greatly modify the repulsive forces leading to an aggregation of particles. So, an important parameter to take into account is the ionic concentration in the fluid and more generally the physico-chemical properties of the fluid, reason why one can add polymer or other ingredients in the system in order to avoid or to assist the flocculation.

Let us suppose now that the weight of the particles is exactly compensated by the buoyancy force. If one imposes known stresses or known motions to the different parts of the boundaries delimiting the dispersion a velocity field and a stress field take place in the system. Clearly, the behaviour of the dispersion does not depend only on the nature of the particles and the fluid on the interactions between particles, but also on the nature of the stresses or the imposed motion. In an homogeneous and Newtonian fluid, two parallel planes moving parallel to themselves with opposite velocities induce a simple shearing motion: the velocity field in the fluid is linear. From the measurements of the tangential stresses on one of the planes, one can calculate the viscosity of the fluid. If the fluid between the planes is a concentrated dispersion, the velocity profile is not linear and measurements of tangential stresses give access only to an effective viscosity which would be that of an homogeneous fluid which submitted to the same solicitation would develop the same stresses on a plane delimiting the dispersion. Moreover one observes normal stresses characteristic of a non-Newtonian behaviour. If the same dispersion is submitted to a Poiseuille flow in a tube, the velocity profile is not the well-known parabolic one and the effective viscosity computed from the pressure drop, the flux and the geometry of the tube has, in general, a value different from that obtained in the simple shearing motion. So the viscosity is not a characteristic of the dispersion but depends on the type of the imposed flow.
Another parameter to take into account is the shape of the particles. A sphere suspended in a fluid in a simple shearing motion rotates with an angular velocity which is equal to \(1/2 \ G\), where \(G\) is the shear rate. In the same velocity field, an ellipsoidal particle rotates with a non constant angular velocity /3/. If the particle is prolate (cigar-like) it spends more time with its axis of revolution parallel to the stream lines than perpendicular. The viscosity of dispersion of prolate ellipsoids is greater than that of a dispersion of spheres with the same volume fraction.

II- VISCOSITY OF CONCENTRATED DISPERSIONS

In the first years of this century, Einstein, in his work on brownian movement, computed the viscosity \(\eta\) of a dilute dispersion of spheres and obtained the well known relation:

\[
\eta = \eta_0 \left(1 + \frac{5}{2} \ \phi \right)
\]

(1)

where \(\eta_0\) is the viscosity of the suspending fluid and \(\phi\) is the volume fraction /7/. This law is correct only when the volume fraction is very weak: a few percent /8/. Due to hydrodynamic interaction between spheres not take into account by Einstein, the viscosity increases more rapidly than predicted from the relation (1). Considering interactions between two spheres, Batchelor /9/ has obtained a relation up to the second order in \(\phi\):

\[
\eta = \eta_0 \left(1 + \frac{5}{2} \ \phi \ + K \ \phi^2 \right)
\]

(2)

where \(K\) is a numerical coefficient which depends on the type of flow and on the importance of brownian motion (low/high Peclet's number regimes). Such a relation applies for volume fraction up to 10 - 15 % for spheres with hydrodynamic interactions only. For larger values of \(\phi\), there is a wide diversity of phenomenological, semi-empirical or empirical relations /10/.

For suspensions of particles in the colloidal range, the viscosity is increased by the repulsion between the overlapping clouds (cf. I) and the resistance of these clouds to deformation. As the forces between particles are greatly affected by the variations in ionic concentration, one observes very important effects on the viscosity /11/.

For large values of \(\phi (45 - 60 \%)\), ordered structures can appear in dispersion of spheres, as observed by Hoffman /12/ or Patzold /13/. The Hoffman's experiments, performed in a simple shear, show an organization of spheres in parallel planes in which there is an hexagonal ordering of spheres observed by light diffraction. Such a structure results from the competition between repulsives forces on the one hand and Van der Waals interaction and shear induced stresses on the other hand. Above a critical shear rate, this structure is destabilized: the diffraction pattern characteristic of hexagonal order disappears and the viscosity increases by one or two orders of magnitude. The Patzold's experiments show that the existence of such a structure is closely related to the simple shearing motion. In an extensionnal flow there is no regular structure in the suspension and the viscosity for large (- 60 %) values of volume fraction is higher in this type of flow than in simple shearing motion.

In the intermediate range of concentration (20-50 %), shear induced structures appear in suspensions of spheres /14/, /15/. One observes the existence of dynamical clusters of particles even in the case where the only relevant interaction between spheres is the hydrodynamic one. These clusters are observed as well in real experiment /16/ as in computer simulations /17/ on two-dimensional dispersion /18/. By analogy with the percolation theory /19/, de Gennes suggested a rheological model of suspensions /20/ in which above a critical value \(\phi^*\) of the volume fraction one has a two phase system: an infinite cluster on the one hand and fluid and finite clusters on the other. The rheological properties of such a system are not, at the present time, fully
understood: studies on intra-clusters and inter-clusters contributions to the viscosity, elastic and viscoelastic properties of clusters are now in progress.

III - SEDIMENTATION

It is well known that an isolated sphere of radius \( a \) settles in an unbounded fluid with the Stokes' velocity \( U_0 \)

\[
U_0 = \frac{F}{6 \pi a \eta}
\]  

(3)

where \( F \) is the buoyancy-corrected weight of the sphere and \( \eta \) the viscosity of the fluid. When one considers a suspension, the average settling velocity of spheres is lower than that given by (3), even for volume fraction as low as 1 \%. This phenomenon, due to interactions between spheres, can be represented by an hindered settling function \( f(\phi) \) so that the average settling velocity is given by

\[
U = U_0 f(\phi)
\]  

(4)

For large spheres with only hydrodynamic interactions, Batchelor /21/, computed the \( f \) function:

\[
f(\phi) = 1 - 6.55 \phi
\]  

(5)

The experiments of Buscall et coll. /22/ on micron-sized spheres show that the \( f \) function is linear in \( \phi \) (with a coefficient of the order of 5 rather than 6.55) up to 10%.

The theoretical analysis has to take into account the multiparticle interaction and the spatial distribution of the sedimenting particles which is not known a priori. Being itself a part of the problem. So the Batchelor's result (5) assumes that, for low values of \( \phi \), the first correction to Stokes's law results for pairwise interactions in a random distribution. Non hydrodynamic interactions between particles as Van der Waals attractive forces can cause a non-random distribution with an excess of close pairs of spheres /23/. As for the viscosity, one of the question to be solved, is the existence of a microscale structure in a sedimenting suspension due to multiparticle hydrodynamic and/or non hydrodynamic interactions.

Assuming that \( f(\phi) \) depends only on the volume fraction and monotonically decreases with \( \phi \), Kynch /24/ used kinematic-wave theory to describe the shifting of \( \phi \)-discontinuities between the suspensions and the clear fluid at the top on the one hand and between suspensions and the sediment layer at the bottom, on the other hand. The velocity of the upper discontinuity is used in measurements of the average settling velocity /22/, /25/ from which it is possible to propose empirical expressions of the \( f \) function. The above-mentioned points together with sedimentation in inclined vessel, polydisperse suspensions, and lateral segregation are the subjects of an excellent review by Davis and Acrivos /26/.

IV- AGGREGATION PROCESSES

As mentioned in I, aggregation process can occur in a suspension. When the system is macroscopically at rest the brownian motion may bring together two particles which may stick under the action of attractive interaction. The rate of formation of pairs of particles and more the growth of clusters of particles has been studied first by Smoluchowski /27/. Recent computer simulations, initiated by the work of Witten and Sander /28/, showed that, in this diffusion-limited aggregation (D.L.A.), the clusters are not very compact. Their dendritic shapes present self-similar properties which can be expressed by a fractal dimension \( d_F \) related to the Euclidian dimension \( d \) (the dimension of the space in which the clusters growth) by the approximate relation /29/.

\[
d_F \sim \frac{5}{6} d \quad (d = 2, \ldots, 6)
\]  

(6)
Diffusion-limited cluster-cluster aggregation /30/, chemically-controlled cluster-cluster aggregation /31/ have been recently studied as well from geometrical (fractal dimensions) viewpoint as from temporal evolution (time-dependant cluster-size distribution). Real experiments on aggregation in a system at rest have been recently performed on aggregating proteins /32/, gold colloids /33/ or macroscopic spheres /34/.

When the dispersion is submitted to a shear, the convection motion of the suspending fluids plays an important role in the aggregation processes. Two limiting regimes appear: the previous one (diffusion-limited) where the aggregation is solely due to brownian motion (perikinetic aggregation) and, at the opposite, the orthokinetic aggregation solely due to shear. In this last case the hydrodynamic forces and torques action on the spheres control, together with the other interactions (Van der Waals, double-layer), the growth of aggregates. The effect of the shear is double. On the one hand, the collision frequency and hence the possible building of a doublet varies linearly with the shear rate G, but on the other hand the mean life-time of a doublet of close spheres for which attractive forces can play a role varies like $G^{-\beta}$. Then the rate of formation of pairs may be expressed /20-b/ by:

$$\rho = G \alpha$$  \hspace{1cm} (7)

where $\alpha$ is a sticking probability related to the shear rate and to a characteristic time $\tau$ of attractive forces by

$$\alpha = (G \tau)^{-m}$$  \hspace{1cm} (8)

Values 0.5 and 0.18 of the $m$ exponent have been respectively obtained by de Gennes /20-b/ and Van de Ven and Mason /35/. From (7) and (8), one can see that the rate of association is an increasing function of $G$.

V- CONCLUSION

In this paper, we have put forward the main physical quantities relevant to the properties of concentrated suspensions the importance of which is considerable in natural and industrial processes. When the volume fraction in the suspension is large, the interactions between particles play an important role in the rheological properties of the system. Depending on the type of flow, regular or random structures can appear in the suspension. Such structures clearly appear in aggregation processes and are suspected in sedimenting dispersion. The influence of these structures on the rheological properties is undoubtless important but, up to now, largely misunderstood.

REFERENCES

/1/ LANDAU L. et LIFCHITZ E. - Mécanique des Fluides ed. Mir Moscou 1971
BATCHelor G.K. - An Introduction to fluid dynamics - Cambridge University Press (1967)

/2/ BATCHelor G.K., GREEN J.T. - J. Fluid Mech. 56, 375 (1972)

ANczurowski E., Mason S.G. - Trans. Soc. Rheol. 12, 109 (1968)


ANSELMET M.C. - These de 3ème cycle - Université de Provence - Marseille (1984)

/7/ EINSTEIN A; - Ann. Physik 19, 289 (1906) with corrections in Ann. Physik 34, 591 (1911)

/8/ VAND V. - J. Phys. Colloid Chem. 52, 277, 300 and 314 (1948)


/10/ see f.i. QUEMADA D. - Rheol. Acta. 16, 82 (1977)

/11/ PRLYNG C.F. - J. Colloid Sci. 16, 713 (1963)


/14/ KARNIS A., GOLDSMITH H.L. and MASON S.G. - J. Colloid Sci. 22, 531 (1966)


/22/ DE Gennes P.G. - J. Physique, 40, 783 (1979)


/28/ Von SMULICHOWSKI M. - Physik Z., 17, 585 (1916)

/29/ Z. Phys. Chem. 92, 129 (1918)
/31/ FAMILY F., MEAKIN P. and VICSEK J.- preprint