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The change of viscosity with concentration of suspended particles and a new concept of gelation

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Abstract. The change in viscosity of a liquid with different concentrations (volume fractions) of suspended particles has been measured using a differential viscometer. The results support the recently introduced concept of gelation, in that the viscosity first diverges when the concentration of suspended particles reaches a critical value, and ‘gelation’ comes after that.

1. Introduction

The common conception of *gelation* is the immobilization of a fluid, though it is not the only mechanism causing fluid immobility. Usually gelation is associated with clusters spanning the entire fluid (divergence in cluster size), and it usually occurs when the clustering probability [1] exceeds a threshold which is usually known as the *gel point*. On the gel point being approached, the viscosity of the fluid is observed to increase. It is understood that the intrinsic viscosity (the intrinsic viscosity is the logarithmic derivative of the dynamic viscosity with respect to the concentration of the suspension in the zero-concentration limit) varies with the volume of the suspended particles, and diverges as the size of the suspended particles diverges. This leads one to believe that the viscosity diverges due to divergence in the size of the suspended particles. However, a careful observation of this phenomenon indicates that as the cluster sizes become larger, it is associated with the development of shear elasticity, and hence such a model always ‘expects’ a fluid to be viscoelastic close to the gel point. Experiments in recent years [2, 3] have shown that the viscosity of the gelling fluid can increase to large values without any measurable shear elasticity developing. The observed results indicate departure from the conventional school of thought and, therefore, require a new interpretation.

Another cause of immobility in fluids is the freezing of the fluid (with dense suspension) to a colloidal crystal (the glass transition) [4] due to mutual interaction between the suspended particles. For suspended particles with hard-sphere interactions this transition is known to occur at a volume fraction of 0.494, and is associated with microscopic density fluctuations. A recent experiment [4] to demonstrate such a transition has been performed by Segrè *et al* using viscometry and dynamic light scattering on colloidal solutions with different volume fractions.

In this article we present a new concept of gelation on the basis of the hydrodynamic interactions between the suspended particles which is capable of explaining the observed phenomenon. In other words we differentiate two types of gels: one is the *inelastic* gel which does not have a shear elasticity but is immobile due to the largeness of the viscosity, and the other is the conventional *elastic* gel. We also present here our experimental observations

of the variation of the viscosity of fluids containing dense suspensions. Here, unlike in our earlier experiments on γ -irradiated polydimethyl siloxane (PDMS), the concentration of suspended particles is measurable and hence provides a more direct test of our model of viscosity divergence presented earlier [3]. The paper is organized to present the experiments, observations and proposed model in different sections below.

2. Experiments with suspended particles

Finely powdered silicon of an irregular shape, obtained from British Drug House Ltd, UK, of an average particle size of less than $1 \mu\text{m}$, is used as the suspended particles in this experiment. The density of silicon was noted to be 2.3 g cm^{-3} . The liquid in which the silicon powder is to be mixed is polydimethyl siloxane (PDMS) of two different viscosities. One of the reasons for choosing PDMS is its unusual property of having a viscosity that is almost independent of the temperature. The viscosities of these liquids are measured by Stokes's method and found to be 21.21 and 32.47 P (where P is the symbol for poise). The difference of the viscosity of PDMS containing suspended silicon powder is measured with respect to that of pure PDMS using a differential viscometer [5]. The viscosity of PDMS containing different volume fractions of suspended silicon dust starting from very small volume fractions and going to volume fractions where the viscosity suddenly increases severalfold, to about fifty times the original viscosity (viscosity divergence), are measured. Care is taken to produce a dense, homogeneous mixture without creating any air bubbles and to transfer a measured amount of the mixture to the viscometer.

To measure the difference in viscosity using the Couette-type differential viscometer, the angular deflection of the inner cylinder is plotted as a function of the angular velocity of the outer cylinder. A straight-line plot indicates that the viscosity of the suspension is independent of the shear rate. It is also observed that if the shear rate is suddenly reduced to zero (zero angular velocity of the outer cylinder) the deflection gradually settles back to zero. This indicates that the fluid has not developed any shear elasticity due to the addition of the suspension. Both of these observations indicate that the PDMS containing suspended particles is Newtonian even close to the viscosity divergence point. To extend the range of the viscometer to very high viscosities, low shear rates are sometimes used. Care is taken to prevent large twists of the suspension wire to avoid loss of calibration and nonlinearities of the twist-torque curve.

The same experiments were repeated with powdered glass (of irregular shape) as suspended particles. Vacuum-dried, powdered glass of average particle size $14 \mu\text{m}$ (major axis) were added to 21.21 and 32.47 P grades of PDMS and the same experiments were repeated. The density of glass was measured to be 2.51 g cm^{-3} .

3. Observations

The variations of the scaled viscosities (η/η_0) of the 21.21 and 32.47 P grades of PDMS containing powdered silicon and glass suspended particles plotted as functions of the volume fraction are shown in figures 1 and 2. All four sets of data fit excellently with our [6] earlier result on the viscosity variation as a function of the concentration (here the volume fraction is ϕ) of suspended particles obtained using the random-resistance-network model [7]:

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_0}\right)^{-\gamma} \quad (1)$$

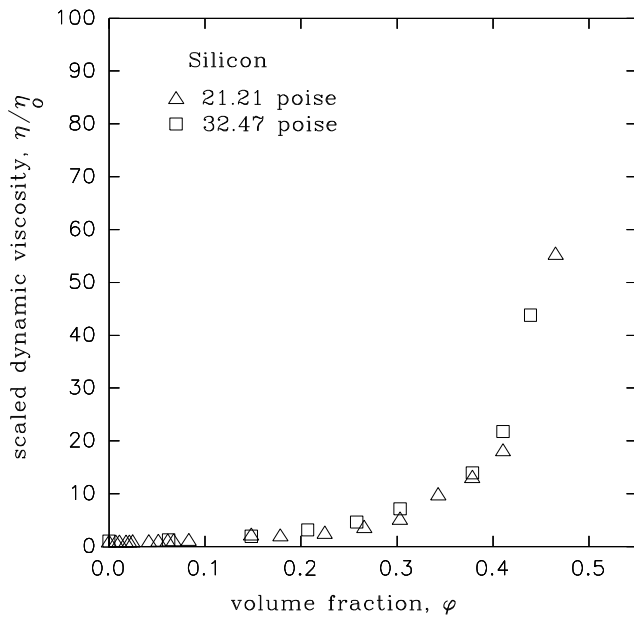


Figure 1. The observed scaled viscosity (η/η_0) with different volume fractions (ϕ) of silicon powder for two different liquids (21.21 P and 32.47 P) fall on the same curve, indicating the lack of dependence on η_0 as expected.

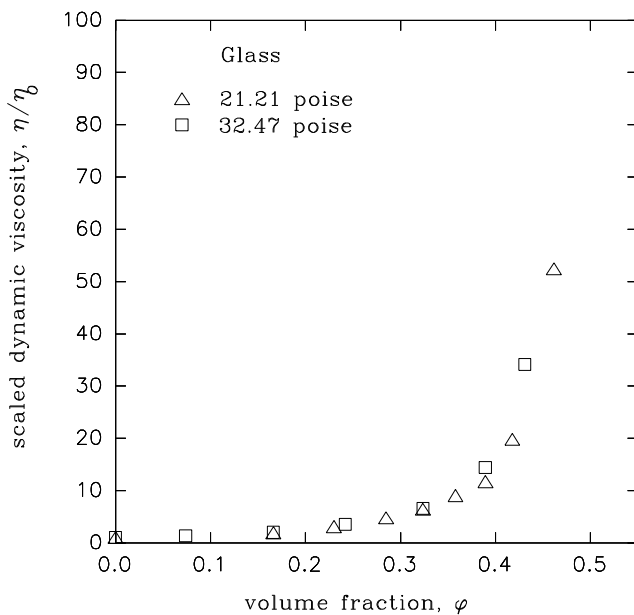


Figure 2. The observed scaled viscosity (η/η_0) with different volume fractions (ϕ) of glass powder for two different liquids (21.21 P and 32.47 P) fall on the same curve, indicating the lack of dependence on η_0 as expected.

where η_0 is the viscosity of the pure PDMS liquid. The values of ϕ and γ obtained by least-squares fitting are presented in table 1.

Table 1. Threshold volume fractions (ϕ_0) and viscosity exponents (γ) obtained by least-squares fitting the variation in viscosity of 21.21 and 32.47 P PDMS, containing silicon or glass powders, to equation (1).

Powder	PDMS grade	Viscosity	ϕ_0	γ
	(cS)	(P)		
Silicon	2000	21.21	0.56 ± 0.01	2.21 ± 0.01
	3000	32.47	0.52 ± 0.01	2.01 ± 0.01
Glass	2000	21.21	0.53 ± 0.01	1.93 ± 0.01
	3000	32.47	0.51 ± 0.01	1.86 ± 0.01

4. The model

A solid particle moving in a fluid creates a velocity field inside the fluid. This velocity field creates an additional drag force on neighbouring particles. This process is bidirectional in the sense that each particle in the fluid affects all other particles in the fluid and is also affected by each of them. This occurs even when the fluid is quite viscous, when the inertial term ($\rho \mathbf{u} \cdot \nabla \mathbf{u}$) of the Navier–Stokes equation

$$\rho \dot{\mathbf{u}} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u} \quad (2)$$

which relates the fluid velocity (\mathbf{u}) to the pressure (p) may be neglected in comparison with the viscous term ($\eta \nabla^2 \mathbf{u}$). This is what we refer to as the *hydrodynamic interaction* between the particles, and it is responsible for the divergence in viscosity for dense suspensions. One may note here that the volume density of the drag force is *not* simply the volume density of the particles multiplied by the drag force per particle—that is true only in the dilute suspension limit. This difference is due to the fact that in the dynamical case the particles are mobile, and hence the velocity field (even in the absence of the nonlinear term) is no longer a simple superposition of the velocity fields of individual particles. This is in turn due to the fact that the variation of the velocity of a test particle affects all of the other particles, which in their turn affect the test particle. Here the test particle is hydrodynamically linked to all other particles in the fluid and it loses its ability to respond individually. This mechanism may in some cases totally arrest the flow and is understood as viscosity divergence.

Cross linking of gamma-irradiated polydimethyl siloxane gives rise to larger and less mobile clusters. Cross linking is caused by recombination of radicals, or monomers with unpaired electrons, caused by the breakage of side-chain bonds. Since the irradiation rate is low, the volume density of radicals with one unpaired electron is small. The density of radicals with more than one unpaired electron is expected to be much smaller than that of those with one unpaired electron. Hence dimers are expected to be the dominant form of recombined polymers. Dimers (and other recombined polymers), being less mobile, play the role of suspended particles. Hydrodynamic interaction between the dimers causes the viscosity to diverge at a critical concentration. The dose corresponding to the critical concentration of dimers is known as the *threshold dose* and the liquid is considered to have reached the *gel point*.

One may note that at this gel point the flow is arrested by the hydrodynamic interaction of the suspended particles. These particles are neither in contact with one another nor are they bonded to one another at this gel point. Hence at this gel point the liquid does not develop any shear elasticity, and hence the liquid is not a viscoelastic gel. Further irradiation of this inelastic gel generates larger cross-linked clusters, thereby causing the

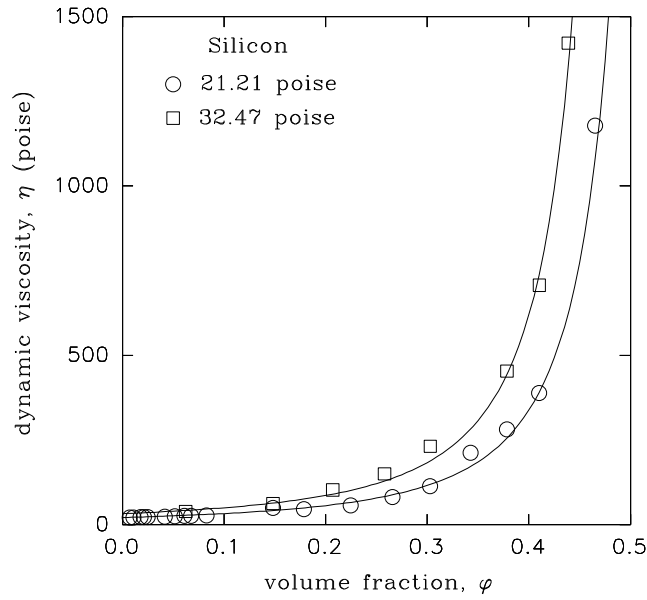


Figure 3. The observed viscosities (η) with different volume fractions (ϕ) of silicon powder for two different liquids (21.21 P and 32.47 P). The solid lines represent fits of equation (1) to the data.

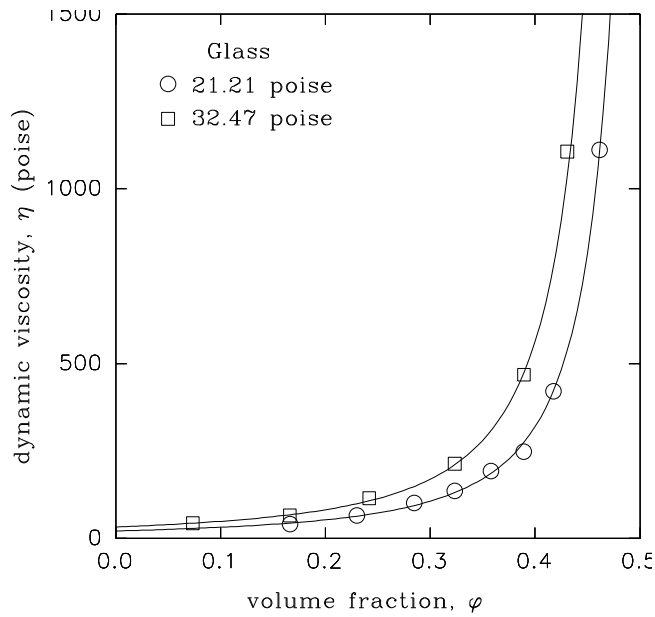


Figure 4. The observed viscosities (η) with different volume fractions (ϕ) of glass powder for two different liquids (21.21 P and 32.47 P). The solid lines represent fits of equation (1) to the data.

liquid to become viscoelastic. This process of cross linking subsequently proceeds until the entire liquid is spanned by one large cluster. The shear elasticity continues to increase with

the density of cross links until one gets a rigid solid.

We observe from figures 1 and 2 that the scaled viscosities of the 21.21 P and the 32.47 P samples of polydimethyl siloxane have identical dependences on the volume fraction of the suspended particles and do not depend on the nature of the liquid. The data were also separately fitted with equation (1), and the least-squares-fitted data are presented in figures 3 and 4 with the fitting parameters presented in table 1. A close examination of table 1 shows that the threshold volume fractions for viscosity divergence (ϕ_0) for silicon and glass are similar, and the fluid is immobilized at a volume fraction of about 0.53. However, we find that the viscosity exponent (γ) of silicon is significantly different from that of glass powder. This probably indicates that γ depends on the shape and size of the suspended particles.

5. Conclusion

The excellent agreement of the data on the variation of the viscosity of PDMS with the volume fraction of suspended particles with our theoretical model [3] implies that the viscosity divergence of γ -irradiated PDMS is due to the concentration of cross-linked clusters exceeding a threshold. This also suggests that the viscosity divergence of γ -irradiated PDMS is not synonymous with *gelation*. This inelastic gel is the manifestation of the hydrodynamic interactions between the suspended particles (so is a glass transition), and occurs at volume fractions in the range 0.5 to 0.6 as has been found experimentally [4, 8]. Gelation occurs only after the viscosity has diverged when the liquid is effectively immobile. Hence this work indicates that the conventional concept of gelation needs further thought. More work is also needed beyond the region of *viscosity divergence* up to the formation of a *viscoelastic gel*.

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