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Explanations for the cause of shear thickening in concentrated colloidal suspensions

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Synopsis

In contrast to recent publications suggesting that particle cluster formation alone can play an important role in the shear thickening flow behavior of concentrated colloidal suspensions, we believe that there is little if any substantive evidence to prove it. To support this view, we use data from various studies, including data from studies concluding that layered flow is not involved. One reason for the confusion seems to center around the inability of various light-scattering and neutron-scattering techniques to show particle layering before shear thickening when the layers are not well defined. In this regard, one should understand that layered flow can occur without rigorous ordering of particles within the layers, and as the flowing suspension approaches the point of instability, the hydrodynamic forces driving for the instability will jostle the particles within the layers sufficiently to make it even harder to see the layering and any ordering, if it exists, within the layers. Having these views, we argue that the process described by Hoffman (1972, 1974) for shear thickening is still applicable with refinements. The major refinement is the idea that, after the hydrodynamic forces cause the instability which breaks up the layered flow, particle jamming probably involves cluster formation both with and without particle contact. Particle roughness and angularity will facilitate the contact. Finally, we agree with various authors who argue that the best chance of finding shear thickening in concentrated colloidal suspensions without layer formation lies in Brownian hard-sphere suspensions, but the evidence given for it so far is not definitive. © 1998 The Society of Rheology. [S0148-6055(98)00501-X]

I. INTRODUCTION

Shear thickening implies that the viscosity of a fluid increases with increasing rates of shear, and although it can be gradual, in the extreme, this phenomenon leads to a discontinuous jump in viscosity. Fascinating as this may be to a scientist, this response is unacceptable, for instance, to a production engineer who may be confronted with extreme shear thickening when he or she attempts to increase productivity by increasing line speed in a coating operation which applies a shear thickening suspension to a substrate. Given the right circumstances, all kinds of suspensions of solid particles in a fluid show this phenomenon, and the impact on industrial processes such as mixing, coating, milling, and spraying is considered a severe problem [Barnes (1989)]. In part, because of its negative impact on industrial processes, shear thickening has been extensively studied over the last three decades, and a considerable body of knowledge has developed, which improves our understanding of the phenomenon. There are, however, some important aspects of the process, which are not yet understood. A review of some parts of this developing body of knowledge gives perspective to the problems addressed in this paper.

Early on, shear thickening was generally depicted as a “well-behaved” rise in viscosity with increasing shear until Hoffman (1972) reported that highly concentrated suspensions of monodisperse particles actually exhibit a discontinuous jump in viscosity at some critical rate of shear. Hoffman (1972, 1991) also observed that monodisperse suspensions under shear exhibit diffraction patterns, which change with the onset of shear thickening. Using these patterns, he was able to show that layers of particles, packed in a two-dimensional hexagonal packing at low rates of shear, break up into less ordered arrays in the region of shear thickening. In most viscometric flows, each layer of particles is parallel to surfaces of constant shear, and one axis of the packing always points in the direction of flow. These results led Hoffman to suggest that a flow instability caused the particles to break out of their ordered layers at some critical level of shear stress and jam into one another, thereby causing the rise in viscosity. Based on these ideas, Hoffman (1974) developed a mathematical model to predict the critical shear stress at the onset of shear thickening, but the model was never rigorously tested.

Reasoning that the flow instability is controlled principally by a balance between the stabilizing forces of repulsion between particles and hydrodynamic forces in concentrated colloidal dispersions, Hoffman (1983, 1992) as well as Boersma *et al.* (1990) suggested that dimensionless groups governing the onset of the instability would include $\mu \dot{\gamma} a^2 / \epsilon \Psi_0^2$ when particles are stabilized by charge, and $\mu \dot{\gamma} a^2 V_s / (0.5 - \chi) \Delta^2 k T$ when particles are stabilized by steric stabilization. In these equations, μ is the viscosity of the suspending fluid, $\dot{\gamma}$ is the shear rate, a is the particle radius, ϵ is the dielectric constant of the fluid, Ψ_0 is the surface potential of the particles, V_s is the volume of the solvent molecule, χ is the Flory–Huggins parameter, Δ is the thickness of the layer yielding steric repulsion, k is Boltzmann’s constant, and T is the absolute temperature. Other dimensionless groups that are known or expected to govern shear thickening include the volume fraction of the particles in the suspension, and the ratio of some characteristic dimension, such as the average distance between particles, h , to the Debye length, $1/\kappa = (\epsilon k T / e^2 I)^{1/2}$ in charge stabilized systems. In the equation for the Debye length, e is the electronic charge and I the ionic strength. If the dispersion is not unimodal, one might also expect to need some dimensionless ratio characterizing the size distribution of particles in the sample.

Taking a different tack, Brady and co-workers began simulating the flow behavior of concentrated suspensions by Stokesian dynamics. Investigating moderate density charge stabilized suspensions by this approach, Brady and Bossis (1985, 1988), found that the model predicts shear thickening without layering, and the cause of shear thickening appears to be cluster formation. These clusters are composed of compact groups of particles formed when shear forces drive particles nearly into contact. Under these conditions, short range lubrication forces cause the increase in viscosity with increasing shear as the clusters become larger and larger. This explanation for shear thickening dates back at least to Krut (1952). Bossis and Brady (1989) and Phung and Brady (1992) obtained similar results when modeling the behavior of hard-sphere suspensions. Using a similar approach to simulate suspensions in narrow gaps, Brady and Bossis (1988) predicted the formation of gap spanning clusters. Chow and Zukoski (1995a) believe that clusters of this sort are responsible for shear thickening in very dense, charge and sterically stabilized suspensions. D’Haene and co-workers (1993) offer evidence for a similar conclusion. More recently, Boersma *et al.* (1995) used Stokesian dynamics to predict the response of suspensions in which significant attractive and repulsive forces occur between monodisperse particles. In agreement with experimental data, they predict that shear thickening is associated with a microstructural transition from ordered layers to an amorphous state with cluster formation. Contrasting the two mechanisms proposed to

explain the cause of shear thickening, Bender and Wagner (1995, 1996) suggested that flow dichroism measurements and the colloidal stress-optical relationship could be used to differentiate between the two. In their words (1995),

“... clusters are composed of compact groups of particles formed when shear forces drive particles into contact, such that particle motion is dominated by lubrication forces. ... Hoffman’s (alternate theory) suggests that shear thickening is a consequence of an order-to-disorder transition, where the shear-thickened state is more fluid-like. The former mechanism would lead to large hydrodynamic stresses upon shear thickening, but, by our stress-optical relation, would leave the 45° dichroism essentially unchanged. The latter ... suggests increases in the stresses due to thermodynamic forces dominating the shear-thickened suspension. Thus, one would expect a direct correspondence between the shear stress and measured dichroism in the shear-thickened suspension.”

Using this approach with model colloidal suspensions of silica that exhibited near hard-sphere behavior, they concluded that cluster formation was the cause of shear thickening in their suspensions, and they suggested that the order–disorder mechanism was not involved. See Bender and Wagner (1995), page 180. It is not clear, however, why they concluded that the order-to-disorder transition theory leads to a more “fluidlike” state when shear thickening occurs. Hoffman’s (1972, 1974) original hypothesis was that particles order into layers at low rates of shear, but at some critical point an instability develops, which causes them to break out of their layers and jam into one another. Although Hoffman originally viewed this jamming process as one involving physical contact between particles, it is reasonable to assume that the jamming process may involve both cluster formation without physical contact and (cluster formation with) physical contact. Surface roughness on the particles and particle angularity will facilitate the contact. In support of these possibilities, cluster formation is predicted by the Stokesian dynamics studies of Dratler *et al.* (1997) and Boersma *et al.* (1995), once the transition from ordered-to-disordered flow occurs in stabilized suspension systems, and Ball and Melrose (1995) predict particle contact that leads to shear thickening as a result of “lubrication breakdown” between the particles. Assuming that cluster formation and particle contact occur, one can reason that lubrication forces and the resistance caused by friction will lead to shear thickening. When one understands these concepts, it seems evident that Bender and Wagner’s data showing cluster formation does not rule out the involvement of an order-to-disorder transition in the shear-thickening process.

Bender and Wagner later deduced (1996), from the results of small-angle neutron-scattering measurements, that shear thickening occurs in their suspensions without any shear-induced transition from layered-to-unlayered flow. Laun *et al.* (1992), Chow and Zukoski (1995a, 1995b) and Fagan and Zukoski (1997) made similar observations. Although that could be true, one cannot rely on light diffraction or small-angle neutron-scattering measurements to prove it, as all the afore-mentioned authors attempted to do. The reason for this is, in the strictest sense, the order–disorder mechanism only requires that particles move over one another in layers, and these layers may be poorly defined, especially as one approaches the instability point. Rigorous ordering of particles within the layers is not required as part of the order–disorder mechanism, although it routinely happens when there are sufficient forces of repulsion between monodisperse particles as shown by the work of Hoffman (1972, 1991), Laun *et al.* (1992), and Chow and Zukoski (1995b).

A number of things can compromise the rigorous ordering required for measurement by light diffraction or small-angle neutron-scattering such as weak (or no) forces of repulsion between the particles, variations in particle size, low particle volume fraction,

and random motion of particles within their “cells” in the ordered packing during flow. Random motion of the particles within their “cells” results from perturbations generated during flow, especially as one approaches the point of instability. Interestingly enough, it is under conditions such as these where we find reports of shear thickening caused by particle clustering without layering. See for example, Laun *et al.* (1992), Chow and Zukoski (1995a, 1995b), Bender and Wagner (1996), and Fagan and Zukoski (1997). This being the case, it is important to evaluate the results of these and other studies carefully to see if the conclusions drawn are really valid.

In the text that follows, we present the results of approaches we have taken to make these evaluations. These approaches include an examination of the appropriate dimensionless groups associated with the two mechanisms being considered; the idea is to look for the dimensionless group(s) most nearly having some characteristic value that predicts the onset of shear thickening at some fixed concentration of particles. We also look at the value of Peclet numbers, Pe , at the point where shear thickening occurs to see if it lies in the right range for Brownian diffusion to be a significant but diminishing factor as required by the clustering mechanism. Then, we review data on the effect of particle size, because particle clustering without the order–disorder transition predicts that the onset of shear thickening should be inversely proportional to a^3 while the order–disorder theory predicts that shear thickening is inversely proportional to a^2 . Finally, we discuss reasons for a difference in many cases between the point at which shear thickening is initiated and the point at which the shear ordering of particles begins to degrade.

II. APPLICABLE DIMENSIONLESS GROUPS

When several different mechanisms are proposed to explain some process of interest, dimensionless groups can often be used to judge which mechanism is correct. The key lies in the fact that dimensionless groups define the interrelationships of controlling parameters for each mechanism, and some characteristic value should be realized, from a number of different experiments, for the group that truly applies. So it follows, in the case of shear thickening, that we should be able to find one characteristic value for the appropriate dimensionless group which consistently heralds the onset of shear thickening at some given concentration of particles. Analysis of the order–disorder mechanism tells us that the instability should be controlled by $\mu \dot{\gamma} a^2 / \epsilon \Psi_0^2$ when particles are stabilized by charge, and $\mu \dot{\gamma} a^2 V_s / (0.5 - \chi) \Delta^2 kT$ when particles are stabilized by steric stabilization. For the particle clustering mechanism without layering, the dimensionless group of interest is the Peclet number. In conventional form, it is $6\pi\mu\dot{\gamma}a^3/kT$, although Bender and Wagner (1996) have proposed another form, $\sigma_c a^3/kT$, in which σ_c is the shear stress measured at the onset of shear thickening.

For the purposes of comparing values of these dimensionless groups at the onset of shear thickening in stabilized suspensions, a collection of data on colloidal suspensions of monodisperse as well as polydisperse particles from various studies is tabulated in Table I. The sources of the data are listed under “Reference” in column 1, and the particles and fluids used are listed in column 2. The meaning of the acronyms listed in that column are the following: PSEA is styrene ethylacrylate copolymer, PVC is polyvinyl chloride, PMMA is polymethylmethacrylate, PS is polystyrene, EtGly is ethylene glycol, DOP is dioctyl phthalate or 2-ethylhexyl phthalate, and THFA is tetrahydrofurfural alcohol. The third column labeled “Repulsion” indicates the way in which the suspensions were stabilized, and ϕ in the fifth column indicates the volume fraction of particles in the suspensions. Variations in ϕ were kept within a narrow range from 0.57 to 0.60 so that the known effect of ϕ on the onset of shear thickening could be suppressed. The M or P

TABLE I. Values of $\sigma_c a^3/kT$, $Pe_c = 6\pi\mu\dot{\gamma}_c a^3/kT$ and $\mu\dot{\gamma}_c a^2 \times 10^2$ at the onset of shear thickening from various literature studies along with parameters used to calculate them.

Reference	Particles/fluid	Repulsion	Temp. (K)	ϕ	μ (Pa s)	$\dot{\gamma}_c$ (1/s)	σ_c (Pa)	a (μm)	$\sigma_c a^3/kT$	$6\pi\mu\dot{\gamma}_c a^3/kT$	$\mu\dot{\gamma}_c a^2 \times 10^2$ (Pa μm^2)
Laun <i>et al.</i> (1992)	PSEA/EtGly	Charge	291	0.587	0.021	10	25	0.148 P	20.2	3.20	0.460
Bender and Wagner (1996)	Silica/THFA	...	298	0.59	0.005	40	4	0.165 M	4.37	4.11	0.545
D'Haene thesis (1992)	PMMA/decalin	Steric	298?	0.59	0.00255	84	30	0.345 M	300	40.3	2.55
Hoffman (1987)	PVC/DOP	Steric	298	0.57	0.054	4	120	0.625 M	7130	241	8.44
Boersma thesis (1990)	PVC/DOP	Steric	298	0.60	0.054	5	18.9	0.70 P	1580	426	13.2
Boersma <i>et al.</i> (1990)	PS/water	Charge	293	0.575	0.001	400	80	0.805 M	10320	973	25.9
Boersma thesis (1990)	PS/water	Charge	293	0.584	0.001	107	11.8	1.3 M	6415	1097	18.1
Max/Min =									2362	343	56

listed next to the size of the particles in the ninth column of Table I indicates whether the particles were monodisperse or polydisperse.

Values for the two different forms of the Peclet number at the onset of shear thickening are given in the next to the last two columns in the chart. In these numbers, σ_c and $\dot{\gamma}_c$ indicate the shear stress and shear rate, respectively, at which shear thickening is initiated. One of these two Peclet numbers should remain relatively constant if particle clustering without layering is the cause of shear thickening. From the data in these two columns, it is evident that neither is even close to being constant, although the traditional form of the Peclet number shows the least variation. Measured in terms of the ratio of the largest to the smallest value for each dimensionless group, the variation in $\sigma_c a^3/kT$ is 2362 while the variation in $6\pi\mu\dot{\gamma}_c a^3/kT$ is 343. In contrast to this, the known portion of the dimensionless groups that apply for the order-disorder mechanism only varies by a factor of 56 from the largest to the smallest value, and the variation in these values correlates with expected changes in the force of repulsion between the particles. Evidence for this correlation is given by the values of $6\pi\mu\dot{\gamma}_c a^3/kT$ at which the onset of shear thickening occurs. Increasing values of this parameter are most likely telling us that the onset of shear thickening is being suppressed by ever stronger forces of repulsion between the layers. So, we anticipate that the increasing values of $\mu\dot{\gamma}_c a^2$, which are evident as we proceed down the last column, could be balanced off by increasing values of the repulsive term in the denominator of the dimensionless groups for charge and sterically stabilized suspensions. Thus, it is quite possible that variations in the full dimensionless groups, i.e., $\mu\dot{\gamma}_c a^2/\epsilon\Psi_0^2$ for charge stabilized suspensions or $\mu\dot{\gamma}_c a^2 V_s/(0.5-\chi)\Delta^2 kT$ for sterically stabilized suspensions, will be even less than the value of 56 given in the chart for $\mu\dot{\gamma}_c a^2$. The ultimate test will be to include the rest of the parameters in the appropriate dimensionless groups for suspensions stabilized by charge or steric effects, but the required data are not available from most of these studies. This being so, we can only say that these data on the stabilized suspensions appear to support the concepts of the order-disorder theory better than the cluster formation theory. Further information is required to fully evaluate this conclusion. It is evident, however, that the data in Table I *do not* support the idea of cluster formation without layering as the cause of shear thickening since the Peclet numbers vary so widely. And, the values of Pe_c in all the studies, except those by Bender and Wagner (1996), Laun *et al.* (1992), and D'Haene (1992) are large enough to exclude Brownian diffusion as a significant factor in the shear-thickening process represented by these data. In this regard, de Kruif *et al.* (1985) calculate that Brownian motion becomes insignificant at $Pe \cong 100$ in hard-sphere suspensions. As repulsive forces build between particles, the value should be even lower.

Backing away from the whole set of data in Table I, one might argue that clustering without layering could be the mechanism for shear thickening in just the first three studies, for it was in those studies that the authors observed shear thickening without evidence of ordered layers. To us, the mechanism of clustering without layering still seems suspect since Laun and D'Haene both report strong hysteresis at the onset of shear thickening, which depends on whether one approaches the region with increasing or decreasing stress, and van der Werff and de Kruif (1989) report evidence of particle ordering in silica suspensions quite similar to those studied by Bender and Wagner. Hysteresis is easily understood with the order-disorder mechanism, but it seems unlikely if clustering without layering is the cause of shear thickening. With the order-disorder transition, particles in highly concentrated suspensions will have trouble breaking up the ordered layer structure because of space constraints as one increases stress, and con-

versely, once particles are in disarray, they will have trouble getting back into organized layers as one approaches the transition point from higher stress levels.

Since the data in Table I appear to support the concepts of the order–disorder transition with layering, it is logical to ask what the layers might look like in the suspensions that contain polydisperse particles. In our view, the thickness of these layers is probably linked to the relative amounts of the various sizes, and it is conceivable that the layers could be thicker than the largest particles, especially at high particle loading levels. Within thick layers, particles will be able to accommodate more efficient packing so that the movement of layers over one another is still possible when the volume fraction of particles exceeds 0.60. Even with unimodal distributions, flow will be possible when the particles exceed 60% of the volume, if thick layers form with interlocking particles within these layers. Through possibilities such as these, one can rationalize ways for monodisperse suspension to flow when the particles exceed 60% of the volume in the manner observed by Williams *et al.* (1979), D’Haene *et al.* (1993), Bender and Wagner (1996), and Frith *et al.* (1996).

Flow in layers at levels above 60% by volume have been a matter of concern in the past, because layers, one particle thick, of monosized particles packed in a two-dimensional hexagonal packing can only move past one another freely at levels up to 60% by volume. Above that level, interpenetration of the layers is required, and particles in one layer would have to move down the grooves of the next. This seem very unlikely because of dislocations in the packing and the constraints on particle movement in these highly loaded systems.

III. EFFECTS OF PARTICLE SIZE

One important difference between the dimensionless group associated with cluster formation and the two dimensionless groups associated with the order–disorder transition is the dependence on particles size. If the onset of shear thickening is controlled by the order–disorder transition, then the onset should correlate with a^2 , whereas it should correlate with a^3 if particle clustering initiates shear thickening without an order–disorder transition. Looking first to the extensive collection of data accumulated on shear-thickening systems in a literature review by Barnes (1989), we find a plot that correlates the onset of shear thickening with particle size for systems in which the particle phase volume is nominally 50%. This plot has been reproduced with changes as Fig. 1 in this paper. For the purposes of this discussion, we have only included sizes in the colloidal range, which run from 0.03 to 3 μm . Also, data were only included for suspensions made with fluids ranging in viscosity from 1 to 18 mPa s, so that the effects of the suspending fluid viscosity are somewhat suppressed. Finally, some corrections were made in the values listed in the table given by Barnes.

After doing this, linear regression was used to establish the best line through the data, and the results were statistically analyzed to establish levels of confidence. The slope of the line through the data provides the value of the exponent for the particle radius, which scales with the onset of shear thickening. The results of this analysis indicate that the best line through the data has a slope of -2.06 , and the slope lies within the bounds of -1.45 and -2.67 at the 99% confidence level. Since a slope of -2 is required for the order–disorder mechanism, while a slope of -3 is required for the clustering mechanism, we can conclude, with a high level of confidence, that the clustering mechanism is excluded as a means for explaining these data.

As a means for looking at data on a much more uniform set of samples, we also plotted separately in Fig. 2 the data of Wagstaff and Chaffey (1977) on suspensions of

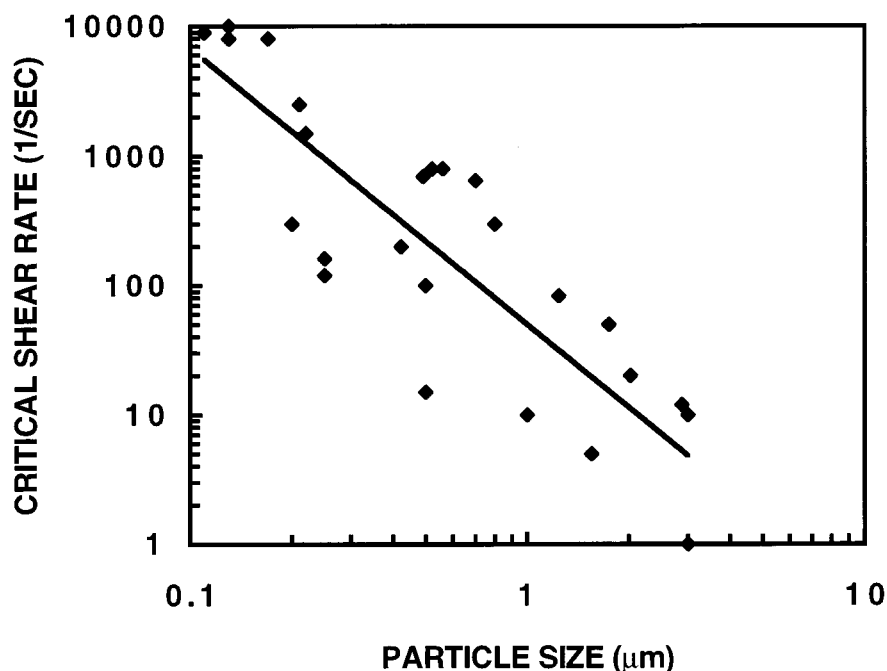


FIG. 1. Effect of particle size on the critical shear rate at which shear thickening is initiated. Data were taken principally from a tabulation by Barnes (1989). The fluids used to prepare these suspensions varied in viscosity from 1 to 18 mPa s. The line through the data, obtained by linear regression analysis, has a slope of -2.06 .

polymethylmethacrylate and PMMA/ethyl acrylate copolymer particles stabilized with poly(12 hydroxysteric) acid. These particles were dispersed in a high-boiling aliphatic hydrocarbon. The size of the particles prepared by Wagstaff and Chaffey ranged from 0.042 to 2.02 μm in diameter and the viscosity of the suspending fluid was 2.1 mPa s. Noting that the volume fractions listed by Wagstaff and Chaffey in their Table I are for the cores of the particles only without the shell of the stabilizer, we computed the concentration of the entire particles (core and shell) in the suspensions using a value of 6.2 nm, which they gave as the thickness of the stabilizer shell. The numbers obtained are listed in Table II. Plotting the critical shear rate for the onset of shear thickening as a function of particle size for suspension containing particles at a level of 0.45–0.53 as shown in Fig. 2, we find by regression analysis that the best line through the data has a slope of -2.03 . Statistical analysis of the data predicts that the slope of the line lies within the bounds of -1.64 and -2.41 at the 99% confidence level. Since a slope of -2 is required for the order-disorder mechanism, while a slope of -3 is required for the clustering mechanism, we conclude as before, with a high level of confidence, that the clustering mechanism is excluded as a means for explaining the data.

As an aside, it is relevant to note that the particles in the suspensions studied by Wagstaff and Chaffey are essentially the same as those studied more recently by D'Haene and others. See D'Haene (1992), D'Haene *et al.* (1993), Frith *et al.* (1996). Although Frith *et al.* most recently suggested that the mechanism causing shear thickening with their suspensions could depend on the suspending fluid, the evidence seems weak. If the particles were moving in layers as they suggest in decalin, but not in dioctyl phthalate or di-dodecyl phthalate, then the high shear plateau relative viscosity for the decalin suspensions should be noticeably lower than the others. This is not the case, as

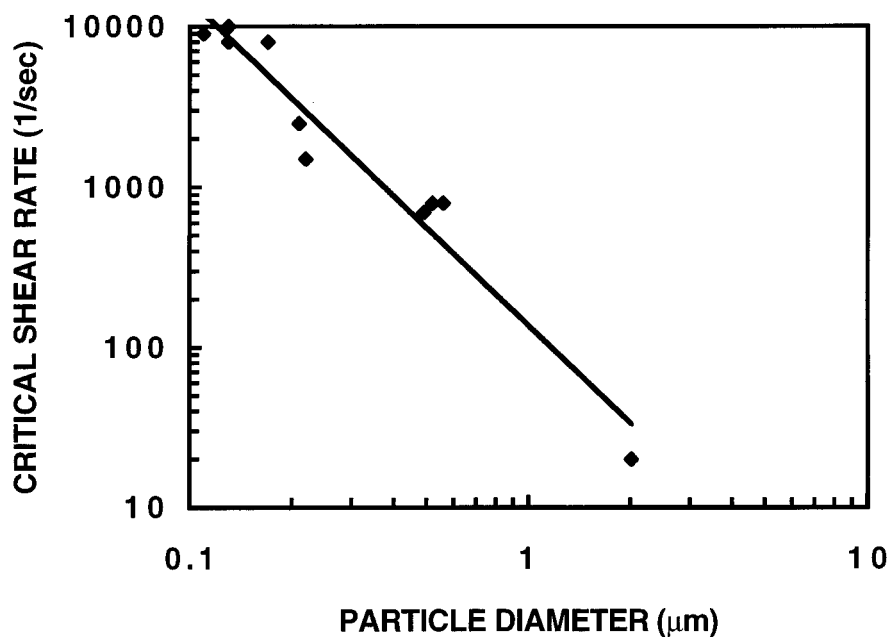


FIG. 2. Effect of particle size on the critical shear rate at which shear thickening is initiated in suspensions of PMMA and PMMA/ethyl acrylate copolymer particles dispersed in a high-boiling aliphatic hydrocarbon. The particles were sterically stabilized with poly(12 hydroxyteric) acid. The data used for this plot were published by Wagstaff and Chaffey (1977). The line through the data, obtained by linear regression analysis, has a slope of -2.03 .

shown in their Figs. 2 and 3. We think it is likely that the conclusions drawn from Wagstaff and Chaffey's data apply to the suspensions studied by D'Haene *et al.* also. That is, the instability driving the order-disorder transition determines the onset of shear thickening in their suspensions also.

Since some of the data in Figs. 1 and 2 were obtained on monodisperse suspensions, while other data were obtained on polydisperse systems, we also have evidence support-

TABLE II. Data from Wagstaff and Chaffey (1977) along with calculated values of ϕ_T , the volume fraction of the particles, vs ϕ_C , the volume fraction of the particle cores.

Sample	a (nm)	D_p (nm)	ϕ_T/ϕ_C	ϕ_C	ϕ_T	$\dot{\gamma}_c$ (1/s)	ϕ_C	ϕ_T	$\dot{\gamma}_c$ (1/s)	ϕ_C	ϕ_T	$\dot{\gamma}_c$ (1/s)
a	21	42	2.173	0.30	0.65	...	0.27	0.59	...	0.25	0.54	$> 10^4$
b	55	110	1.398	0.50	0.70	1500	0.42	0.59	3500	0.34	0.48	9000
c	105	210	1.188	0.52	0.62	85	0.49	0.58	1800	0.43	0.51	2500
d	260	520	1.073	0.54	0.58	85	0.50	0.54	800	0.44	0.47	800
e	1010	2020	1.019	0.44	0.45	20
f	65	130	1.314	0.51	0.67	700	0.45	0.59	8000	0.39	0.51	10000
g	110	220	1.179	0.56	0.66	1300	0.48	0.57	3000	0.44	0.52	1500
h	280	560	1.068	0.57	0.61	85	0.52	0.56	700	0.44	0.47	800
i	85	170	1.235	0.52	0.64	2000	0.44	0.54	8000	0.40	0.49	8000
j	245	490	1.078	0.54	0.58	800	0.50	0.54	700	0.44	0.47	700
k	65	130	1.314	0.49	0.64	...	0.43	0.57	8000	0.40	0.53	8000

ing the idea that particles move in layers before shear thickening occurs regardless of the narrowness of the distribution. We know in the case of polydisperse suspensions, however, that rigorous ordering of particles in a two-dimensional hexagonal packing within each layer will be prevented by variations in the size of the particles. As a result, light diffraction and small-angle neutron scattering will fail to detect the layering via diffraction patterns from ordered layers, but this result does *not* exclude the possibility that layered flow is occurring.

Knowing this, it is helpful for us to review the work of Laun and co-workers (1991, 1992), which has been cited as casting doubts about the necessity of a shear-induced order–disorder transition being required to induce shear thickening. The experiments in question involved two charge stabilized dispersions, both of which showed shear thinning followed by extreme shear thickening. They are referred to as dispersions A5G and C5G5 by Laun *et al.* (1992). Following changes in structure versus the rate of shear with small-angle neutron scattering, they found distinct maxima indicating shear-induced long-range particle structures in dispersion A5G in the shear-thinning regime, but not in dispersion C5G5. This result led Laun and others to question whether an order–disorder transition is required for shear thickening to occur. As Laun and co-workers observed, the particles in A5G were relatively monodisperse, while the particles in C5G5 had a broad distribution. This being the case, one can expect dispersion A5G to be ordered rigorously enough to show particles packed in a hexagonal packing as Laun and co-workers observed. On the other hand, dispersion C5G5 had a broad enough particle size distribution (0.150–0.400 μm) to prevent the rigorous ordering required to give the diffraction phenomenon they were looking for. We must emphasize once again that the lack of diffraction patterns in a situation like this does not show that the particles were randomly ordered in the shear-thinning region of flow. Some other test is required to determine whether polydisperse systems order into layers at levels below the critical shear stress for shear thickening.

Having arrived at these conclusions, one can suggest that the plots given in Figs. 1 and 2 may not contain data on systems governed only by clustering, or alternatively one could argue that they might contain data on these systems, but not over a wide enough size range to show the effect of size in suspensions where clustering occurs. That, in fact, could be true. The obvious solution is to identify a system where the clustering mechanism is said to prevail, and then generate the needed data to get the plot. Attempts of this sort, documented in the recent literature, have failed because the authors did not appreciate the range of sizes that must be covered to override the scatter in the data.

IV. OTHER REPORTS SUPPORTING THE PARTICLE CLUSTERING THEORY

Without belaboring the point, it seems prudent to give careful consideration to two recent studies by Zukoski and co-workers. In the most recent one, Fagan and Zukoski (1997) report on the flow behavior of concentrated suspensions of 0.497 μm silica particles in water as well as in a glycerin–water mixture containing roughly 95% glycerin. Results with the aqueous suspensions led them to conclude that shear thickening in the water systems was governed by the order–disorder transition from layered-to-unlayered flow. On the other hand, suspensions in the glycerin–water mixture shear thickened without any evidence of ordering from light diffraction, and this result led them to conclude that hydrodynamic clustering alone was the cause of shear thickening in the near pure glycerin. To test this view, we took the data given for the suspensions in the near pure glycerin, and calculated the value of the Peclet number at the point where shear thickening first appeared. A representative value obtained for one of the suspensions

containing particles at a level of 46% by volume was 669. As discussed in previous text, this value is large enough to exclude Brownian effects, and thus, the clustering mechanism as the explanation for shear thickening in these suspensions.

Earlier on, Chow and Zukoski (1995b) provided a detailed study of microstructure along with shear-thickening data on concentrated suspensions of charge stabilized polystyrene in water. The results of particular interest to us now are the relationships between shear thickening and the state of shear ordering in these suspensions. At a particle level close to 60% by volume, shear melting occurred quickly and the onset of shear thickening coincided with that event. Proceeding to lower particle levels, however, they found a divergence in which shear melting began before the onset of shear thickening. To explain these results, they concluded that the layered structure “melted” before hydrodynamic forces were sufficient to cause shear thickening by clustering, and shear thickening was delayed until particles were driven to cluster at higher levels of shear.

We offer an alternate explanation. At the level near 0.60, particles are crowded so close together within and between the layers that there is essentially no room for them to jostle about as the flow rates approach the point of instability. As a result, the ordering does not degrade until the layered flow goes fully unstable, so shear thickening and shear melting coincide as observed. At lower levels of particles, however, the particles gain more room to jostle about as hydrodynamic forces approach the point of instability. This jostling process causes some apparent degradation of the ordered structure, which they observed as shear melting before shear thickening. Increasing divergence between the onset of shear melting and shear thickening, which occurred as the amount of particles was reduced, is simply the result of more space between particles, and with more space, less force to hold them in place. This allows the jostling to start sooner. Having this explanation for their results, one does not need to invoke two mechanisms for shear thickening to explain what they observed. In our view, it is less likely that a complex intermeshing of two different mechanisms is a valid explanation for shear thickening when one mechanism can be used to explain all the experimental observations.

V. CONCLUSIONS

After evaluating key data available in the literature on shear thickening in concentrated suspensions, we conclude that substantive evidence for hydrodynamic clustering as the sole cause of shear thickening is not evident, although it is conceivable that this mechanism could prevail in Brownian hard-sphere suspensions. Presently, the following model appears adequate to explain shear thickening in concentrated colloidal suspensions. Before shear thickening occurs, particles move in layers, but they do not have to be rigorously ordered in these layers, and the layers can have a thickness ranging from one particle diameter (with unimodal distributions) to some multiple of the average particle diameter. Then, at the onset of shear thickening, a hydrodynamic instability acts to drive particles out of these layers. When this happens, the particles interact through clustering and/or through physical contact. Lubrication forces and frictional forces are most likely involved in this shear thickening process in one case or another. Colloidal stability is generally required for shear thickening to occur although it may be possible to have shear thickening in the limiting case of no particle attraction or repulsion. Dimensionless groups that should control the onset of shear thickening in concentrated colloidal dispersions involve a balance between hydrodynamic forces, which drive the instability, and forces of repulsion between the particles that tend to suppress it.

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