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Shear thickening as a consequence of an acoustic resonance in sheared colloidal crystals

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Synopsis

A model is presented that predicts the critical shear rate of shear thickening of soft sphere colloidal suspensions. It is based on the idea that shear in a colloidal crystal leads to a periodic variation of the elastic modulus with time. At a specific shear rate an acoustic resonance occurs which leads to an increase of the viscosity. Good agreement with experimental results could be obtained by fitting the single parameter of the model. © 1998 The Society of Rheology. [S0148-6055(98)01505-3]

I. INTRODUCTION

When imposing a simple shear flow to an equilibrium colloidal crystal composed of particles with a soft interaction potential, these particles may arrange themselves into a long-ranged structure of hexagonal layers sliding over each other. The existence of this ordered state will be the starting point of our treatment. Experimental investigations [Hoffman (1972); Ackerson and Clark (1981); Barnes (1989); Boersma *et al.* (1990, 1991)] indicate that this structure disappears with increasing shear rate. This disappearance is accompanied by a pronounced increase of the viscosity, denoted as shear thickening. We will develop a model based on the assumption that this destruction of the periodic structure is due to the occurrence of an acoustic resonance within the sheared lattice.

Damped acoustic shear waves travel through a viscoelastic continuum as shown first by Joanny (1979) and later by Pieranski (1983). Within a sheared crystal the elastic modulus in the shear gradient direction varies periodically. Harrowell and Fixman (1987) demonstrated that this periodic variation amplifies long-wavelength transverse modes. By using an extension of the Lindemann criterion [Lindemann (1910)] they could predict an instability of the sheared colloidal crystal due to an acoustic resonance mechanism. Ronis and Khan (1990) improved the approach of Harrowell and Fixman (1987). They analyzed the macroscopic equations of motion of a dilute colloidal crystal under shear and studied the dependence of the acoustic resonance on the system size.

In contrast to the previous authors, we will apply a “two-medium” model, in which both media are considered as infinite, viscoelastic continua that are coupled with each other. One medium is an elastic colloidal crystal of monodisperse solid particles dispersed in the other medium, the viscous medium. The shear is applied to the viscous solvent and is transmitted to the particles. In our approach we suppose that all viscous

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effects are taken into account by the viscous medium with viscosity η_1 . This includes the viscous solvent with a viscosity η_0 , all hydrodynamic interactions between the particles and the viscous damping of movements of the colloidal crystal. Similar models have been used by other investigators in concentrated polymer solutions and gels [Harden *et al.* (1991)] and in dilute colloidal crystals [Lindsay and Chaiken (1985)]. Taking into account the time-periodic variation of the elastic modulus in the sheared suspension, an acoustic resonance occurs. This phenomenon is accompanied by shear thickening. The model presented here will allow the calculation of the critical shear rate $\dot{\gamma}_c$ for the maximum increase of the viscosity. This shear rate will be compared with experimental results.

II. THEORY

A. The hydrodynamic model

The starting point of our model is the two-medium assumption according to which one medium can be treated as a Newtonian fluid with effective viscosity η_1 and density ρ_1 . The shear-induced colloidal crystal represents the other medium; it is an elastic continuum with density ρ_2 and elastic modulus E . The effective viscosity η_1 corresponds to that of the real suspension with a volume fraction Φ of the colloidal particles. This viscosity is due to the viscous solvent and to the hydrodynamic interactions between the particles, to the viscous medium. In our approach the related viscous damping of the colloidal particles is captured in the properties of the viscous medium. We will use a phenomenological equation based on percolation theory, which describes how the volume fraction influences the viscosity of a suspension consisting of hard spheres dispersed in a solvent with a viscosity η_0 .

Furthermore we assume that under the influence of a simple shear flow a spatial distribution of monodisperse particles in hexagonally close packed (hcp) layers occurs with the close packed array of particles pointed along e_x , the mean flow direction. The layers are orthogonal to and periodic in the e_z direction (shear gradient direction). The applied simple shear flow

$$\mathbf{v}_0 = \begin{bmatrix} 0 & 0 & \dot{\gamma}_0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} r \quad (1)$$

allows the hexagonal planes to slip freely over each other, as discussed, e.g., by Hoffman (1972) and Ackerson and Clark (1983). The motion of the colloidal particles causes the elastic properties of the sheared colloidal crystal in the e_z direction to vary periodically in time and space. The time periodicity is determined by the externally applied (macroscopic) shear rate $\dot{\gamma}_0$. We define a modulus $\mathbf{M}(t)$ of the sheared colloidal crystal as the tensor:

$$\mathbf{M}(t) = E \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 - \epsilon \cos(\Gamma \dot{\gamma}_0 t) \end{bmatrix}. \quad (2)$$

Here E is the isotropic elastic modulus (linear compression) of the undisturbed two-dimensional hcp crystal and ϵ is a small-valued parameter that describes the modulation of the elastic modulus. The value of the parameter Γ depends on the direction of the shear and the structure of the lattice [Ronis and Khan (1990)]. For a simple shear in an

orthorhombic lattice the value of Γ is given by $\Gamma = 2\pi g_z/g_x$, with the lattice constants g_x and g_z in the x and z directions. The shear rate can be scaled by

$$\dot{\gamma} = \dot{\gamma}_0 \Gamma. \quad (3)$$

The modulus of a crystal at rest, in principle being a tensor of fourth order, is simplified as being isotropic of second order. This assumption is made because the nondiagonal terms in simple shear cannot be defined well. Additionally our main interest is in local movements of the suspension in the z direction, which are being induced by the particles in xy planes that slide over each other.

In this work we are interested in the effects of deviations from affine, uniform shear field. Therefore, we introduce a displacement field $\delta \mathbf{u}$ for the position \mathbf{u} of the colloidal particles and a velocity deviation field $\delta \mathbf{v}$ for the velocity \mathbf{v} of the viscous medium:

$$\mathbf{u} = \mathbf{v}_0 t + \delta \mathbf{u} \quad (4)$$

and

$$\mathbf{v} = \mathbf{v}_0 + \delta \mathbf{v}. \quad (5)$$

The interaction between the elastic crystal and the viscous continuum is treated as an effective local friction force proportional to the local difference between velocities of the particles of the colloidal crystal and the viscous medium.

In our case of two infinite coupled media, these assumptions lead [see also Joanny (1979) and Lindsay and Chaikin (1985)] to a set of linearized coupled equations of motion. The equation for the viscous medium with a density $(1-\Phi)\rho_1$ is:

$$(1-\Phi)\rho_1 \frac{\partial \delta \mathbf{v}}{\partial t} = \mathbf{div} \boldsymbol{\sigma}^{(1)} - \boldsymbol{\Xi}(\delta \mathbf{v}, \delta \dot{\mathbf{u}}). \quad (6)$$

For the crystal continuum with a density $\Phi\rho_2$ we arrive at

$$\Phi\rho_2 \frac{\partial^2 \delta \mathbf{u}}{\partial t^2} = \mathbf{div} \boldsymbol{\sigma}^{(2)} + \boldsymbol{\Xi}(\delta \mathbf{v}, \delta \dot{\mathbf{u}}). \quad (7)$$

Here $\boldsymbol{\sigma}^{(1)}$ and $\boldsymbol{\sigma}^{(2)}$ are the stress tensors within the viscous medium and in the elastic crystal, respectively. The medium-crystal coupling vector $\boldsymbol{\Xi}$ takes care of the Stokesian friction between particles and liquid medium (“action is reaction”) and takes the form

$$\boldsymbol{\Xi} \propto \xi(\Phi)(\delta \dot{\mathbf{u}} - \delta \mathbf{v}) \quad (8)$$

while the hydrodynamic friction coefficient $\xi(\Phi)$ is an increasing function of the volume fraction.

On hydrodynamic length and time scales, i.e., neglecting the diffusive motion of the colloidal particles, the coupling between the velocities of the colloidal crystal and the solvent is very strong. Following Lindsay and Chaikin (1985) we confine our investigation to the limit of strong coupling. The essential physics of the strong coupling is when the solvent velocity approaches the velocity of the colloidal crystal

$$\delta \dot{\mathbf{u}} \approx \delta \mathbf{v}. \quad (9)$$

In this limit the coupled set of the equations of motion reduces to a single formula:

$$\rho \frac{\partial^2 \delta \mathbf{u}}{\partial t^2} = \mathbf{div} \boldsymbol{\sigma}, \quad (10)$$

with

$$\begin{aligned}\rho &= (1-\Phi)\rho_1 + \Phi\rho_2, \\ \boldsymbol{\sigma} &= \boldsymbol{\sigma}^{(1)} + \boldsymbol{\sigma}^{(2)}.\end{aligned}\quad (11)$$

The stress tensor term in Eq. (10) becomes

$$\mathbf{div}\boldsymbol{\sigma} = \mathbf{M}(t)\Delta\delta\mathbf{u} + \eta_1\Delta\delta\dot{\mathbf{u}}\quad (12)$$

while η_1 is the high shear viscosity of the suspension, corresponding to a layered hcp structure and Δ is the Laplace operator.

B. The acoustic resonance

In order to investigate Eq. (10) we introduce a spatial Fourier transform of the deformation field:

$$\mathbf{A}(\mathbf{k}, t) = \int \delta \mathbf{u}(\mathbf{r}, t) e^{-j\mathbf{k}\mathbf{r}} d^3r, \quad (13)$$

where $\mathbf{A}(\mathbf{k}, t)$ is the time and wave number dependent amplitude of local displacements of a volume element from its initial position. Inserting (13) in (10) we obtain

$$\rho \frac{\partial^2 \mathbf{A}(t)}{\partial t^2} + k^2 \eta_1 \frac{\partial \mathbf{A}(t)}{\partial t} + k^2 \mathbf{M}(t) \mathbf{A}(t) = 0. \quad (14)$$

According to Eq. (2) the modulus $\mathbf{M}(t)$ is periodic with time. Therefore Eq. (14) is a Mathieu equation [Mc Lachlan (1964)]. Equation (14) can be solved for small values of the parameter ϵ as a Taylor expansion of the amplitude in factors of ϵ :

$$\mathbf{A}(t) = \mathbf{A}^{(0)}(t) + \epsilon \mathbf{A}^{(1)}(t) + O(\epsilon^2). \quad (15)$$

Substituting this expansion in (14), the zero order in ϵ leads to a damped wave equation in the unsheared system:

$$\frac{\partial^2 \mathbf{A}^{(0)}(t)}{\partial t^2} + k^2 b \frac{\partial \mathbf{A}^{(0)}(t)}{\partial t} + k^2 c^2 \mathbf{A}^{(0)}(t) = 0, \quad (16)$$

where the coefficient b is given by

$$b = \frac{\eta_1}{\rho} \quad (17)$$

and the sound velocity c of the suspension is given by

$$c^2 = \frac{E}{\rho}. \quad (18)$$

Equation (16) can be solved by writing the zero-order amplitude as a damped wave:

$$\mathbf{A}^{(0)}(t) = \mathbf{A}^{(0)} e^{-pt}. \quad (19)$$

Substitution of Eq. (19) in (16) gives a dispersion relation in p

$$p^2 - bk^2 p + c^2 k^2 = 0. \quad (20)$$

Here p is either real, describing an overdamped creeping motion, with

$$p_{1,2} = \frac{bk^2}{2} \pm \sqrt{\frac{b^2k^4}{4} - c^2k^2} \quad (21)$$

or complex, related to damped propagating waves, with

$$p_{1,2} = \delta \pm j\omega \quad (22)$$

while

$$\delta = \frac{bk^2}{2}, \quad (23)$$

$$\omega = \sqrt{c^2k^2 - \frac{b^2k^4}{4}}.$$

Now we will investigate contributions to $\mathbf{A}(\mathbf{k}, t)$ originating from first order perturbations in ϵ . Because the E_x and E_y moduli are assumed to be constant, the transverse modes in e_x and e_y are always damped waves. However in Eq. (14) we get a contribution in the z direction from the first order in ϵ of the form

$$\frac{\partial^2 A_z^{(1)}(t)}{\partial t^2} + k^2 b \frac{\partial A_z^{(1)}(t)}{\partial t} + k^2 c^2 A_z^{(1)}(t) = c^2 k^2 A_z^{(0)}(e^{-p_1 t} + e^{-p_2 t}) \cos(\dot{\gamma} t), \quad (24)$$

where we have chosen a linear combination of (19) with the solutions (21) and (23). This formula can be solved by means of a Laplace transform as performed in Appendix A.

For damped propagating waves with $p_{1,2}$ given by (22) the amplitude of the first order becomes infinite at a specific, externally applied shear rate. For this instability the amplitudes in the e_z direction become

$$A_z^{(0)}(t, \omega) = 2A_z^{(0)} e^{-\delta t} \cos(\omega t), \quad (25)$$

$$A_z^{(1)}(t) = \frac{2A_z^{(0)} c^2 k^2 e^{-\delta t}}{(\delta^2 + \omega^2)(\dot{\gamma}^2 - 4\omega^2)} \{2\omega[\omega \cos(\omega t) + \delta \sin(\omega t)] \cos(\dot{\gamma} t) - \dot{\gamma}[\delta \cos(\omega t) - \omega \sin(\omega t)] \sin(\dot{\gamma} t)\}.$$

The first order amplitude has a singularity, as known from the theory of Mathieu equations [Mc Lachlan (1964)], at a critical value of the shear rate equal to 2ω with

$$\Gamma \dot{\gamma}_c(k) = 2\omega(k) = 2 \sqrt{c^2 k^2 - \frac{b^2 k^4}{4}} \quad (26)$$

for a wave with wave number k . The dependence of the scaled critical shear rate on k is displayed in Fig. 1, for a suspension of polyvinylchloride particles in dioctylphthalate (PVC/DOP) with $\Gamma = 1$ (this suspension will be discussed in more detail in Sec. III). For practical systems the range of possible values of wave number k is limited both by the system size and by the root in Eq. (26).

The singularity of the amplitude $A_z(k, t)$ describing propagating acoustic shear waves is essentially a resonance effect. At first sight it seems unclear which wave number k_0 from the range of possible wave numbers, k dominates this instability. However from dimension analysis of the argument under the root in (26) we know that the size of the wave vector can be written as

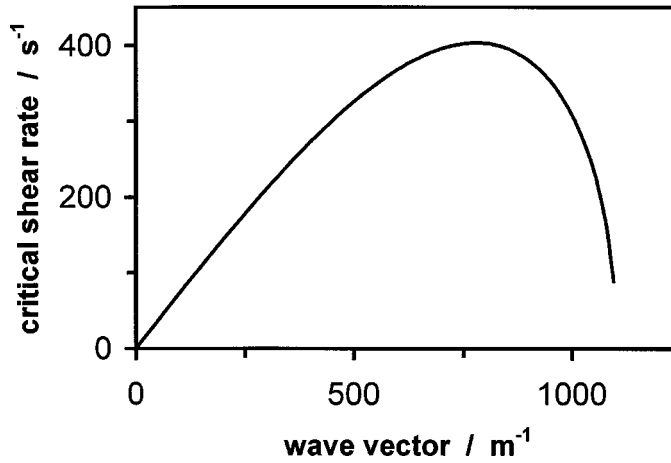


FIG. 1. The critical shear rate (at maximum η) as a function of the wave vector amplitude k for a PVC-DOP suspension ($\Phi = 0.45$).

$$|k_0| = a_0 \frac{c}{b} \quad (27)$$

while we interpret a_0 as a free, dimensionless parameter. Below we will estimate the value of this unknown parameter from experiments.

Using (27) and (3) the critical shear rate in Eq. (26) turns into

$$\dot{\gamma}_c = \frac{a_0}{\Gamma} \sqrt{4 - a_0^2} \frac{1}{\tau}, \quad (28)$$

where Γ and a_0 are dimensionless constants; the characteristic relaxation time τ is given by

$$\tau = \frac{b}{c^2} = \frac{\eta_1}{E}. \quad (29)$$

Note for a suspension with a constant elastic modulus the instability takes place at a constant critical shear stress:

$$\sigma^{(c)} = a_0 \sqrt{4 - a_0^2} \frac{E}{\Gamma}. \quad (30)$$

From dimensional analysis alone it would also have been possible to determine that any critical stress must scale with E . However, the extra of our theory is that: (i) it proposes an explicit mechanism for the critical behavior, (ii) it shows that at this condition the viscosity is at a maximum, and (iii) it indicates how the viscosity rises on approaching the critical criterion. In Sec. II C we will quantify this viscosity increase in the vicinity of the critical condition.

C. Excess dissipation

Here we will consider the relative increase in dissipation, due to an increase of the amplitude of the first order in ϵ . The average rate of energy dissipation W of a wave in the z direction, with amplitude A_z and with angular frequency ω , is given by [Landau and Lifshitz (1964)]

$$W^{\text{dis}}(\omega) = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} F^{\text{dis}}(t, \omega) \dot{A}_z(t, \omega) dt \quad (31)$$

in which the dissipative force density component

$$F^{\text{dis}} = k^2 \eta_1 \dot{A}_z(t, \omega) \quad (32)$$

is given by the second term of Eq. (14).

The relative increase of the dissipation, due to the contribution of the wave amplitude of the first order in ϵ , can in good approximation be evaluated from

$$\Delta W_{\text{rel}}^{\text{dis}}(\dot{\gamma}, \omega) \propto \frac{\int_0^{2\pi/\omega} \dot{A}_z^{(1)}(t, \dot{\gamma}, \omega)^2 dt}{\int_0^{2\pi/\omega} \dot{A}_z^{(0)}(t, \dot{\gamma}, \omega)^2 dt}. \quad (33)$$

The time derivatives of the amplitudes are

$$\begin{aligned} A_z^{(0)}(t, \omega) &= -2A_z^{(0)} e^{-\delta t} [\omega \sin(\omega t) + \delta \cos(\omega t)], \\ \dot{A}_z^{(1)}(t, \omega, \dot{\gamma}) &= -\frac{2A_z^{(0)} k^2 c^2 e^{-\delta t}}{(\dot{\gamma}^2 - 4\omega^2)(\delta^2 + \omega^2)} \{ [\delta \dot{\gamma}^2 \cos(\omega t) + \omega(2\delta^2 - \dot{\gamma}^2 + 2\omega^2) \sin(\omega t)] \cos(\dot{\gamma} t) \\ &\quad - \dot{\gamma} [(\delta^2 - \omega^2) \cos(\omega t) - 2\delta \omega \sin(\omega t)] \sin(\dot{\gamma} t) \}. \end{aligned} \quad (34)$$

Substituting the latter equations into (33) and using ω from (26) we arrive at

$$\Delta W_{\text{rel}}^{\text{dis}}(\dot{\gamma}, \dot{\gamma}_c) \propto \frac{1}{\Gamma^4(\dot{\gamma}_0^2 - \dot{\gamma}_c^2)^2}. \quad (35)$$

The extra dissipation will lead to an increase of the viscosity of the sheared system, which in turn has a maximum when the externally applied shear rate $\dot{\gamma}_0$ equals the critical shear rate $\dot{\gamma}_c$. Thus this acoustic-resonance instability is accompanied by an increase of the viscosity (shear thickening).

Note that the critical shear rate for shear thickening defined here differs from the one generally employed in discussions of the shear rate dependence of the viscosity. The latter critical shear rate is at the point where the viscosity starts to increase, whereas in the sense of a resonance the critical shear rate corresponds to the maximum of the viscosity.

D. Estimation of the free parameter

In order to estimate the free parameter a_0 of Eq. (27) we will study two experimental examples and predict the critical shear rates: (i) a suspension of PVC particles dispersed in DOP as investigated by Hoffman (1982), and (ii) a suspension of glass particles in glycerol/water as investigated by Boersma *et al.* (1990).

In order to evaluate the critical shear rate using (28) we have to determine the elastic modulus and the viscosity of the sheared suspension. We neglect, as a first order approximation, the shear rate dependence of E of the colloidal crystal, which leads to the assumption:

$$E(\dot{\gamma}) \approx E(\dot{\gamma} = 0). \quad (36)$$

We assume an ordering of the particles as in a two-dimensional hcp lattice. On closest passage two particles in successive layers have the same interparticle distance in the direction of the shear gradient as two adjacent particles have within a layer. The volume-fraction dependent elastic modulus E under shear can now be approximated from its value under equilibrium conditions. At rest the elastic modulus E is related to the equilibrium shear modulus G according to $E = 2G(1 + \rho)$, where ρ is the Poisson contraction ratio. Assuming a Poisson contraction ratio of ~ 0 , $E = 2G$. Buscall derived an expression for G of a two-dimensional hcp crystal [Buscall *et al.* (1982)]:

$$G(\Phi) = \frac{\pi N n(\Phi) x_e(\Phi)^2}{64} \left. \frac{\partial^2 U(x, \kappa)}{\partial x^2} \right|_{x=x_e}, \quad (37)$$

where x_e is the interparticle center to center distance scaled by $\sigma_0 = 2a$ and where a is the particle radius. Here the number N of nearest neighbors per unit cell is taken as $N = 8$. The number density n of the particles at volume fraction Φ obeys the formula

$$n(\Phi) = \frac{\Phi}{V_0} \quad (38)$$

while

$$V_0 = \frac{4}{3}\pi a^3 \quad (39)$$

is the volume of a particle. The distance h between the surfaces of two nearest neighbors in a hexagonally layered structure [Boersma (1990)] is

$$h(\Phi) = \left(\frac{8\pi a^3}{3\sqrt{3}\Phi} \right)^{1/3} - 2a. \quad (40)$$

The two-particle interaction potential is assumed to be given by the Poisson–Boltzmann theory as a screened Coulomb potential in the Derjaguin constant potential approximation [Russel *et al.* (1989)]:

$$U(x, \kappa) = \frac{\pi \epsilon_0 \epsilon_r \sigma_0}{z^2} \Psi_0^2 \ln(1 + e^{-\kappa(x-1)}). \quad (41)$$

Here we used a scaled Debye reciprocal length κ defined by $\kappa = \kappa_D \sigma_0$, where

$$\kappa_D = \sqrt{\frac{2N_a C_z^2 e^2}{\epsilon_0 \epsilon_r k_B T}}. \quad (42)$$

We will use the result from a phenomenological theory that describes the low shear viscosity η_{low} of a hard sphere suspension. The influence of the temporary formation of clusters of colloidal particles on the viscosity of the sheared colloidal suspension has been determined by Campbell and Forgacs (1990), applying a percolation theory. They established an equation for the low shear suspension viscosity η_{low} :

TABLE I. Physical parameters of the suspensions discussed.

Parameter	(i) PVC in DOP	(ii) Glass in glycerol/water
relative dielectric constant of the solvent ϵ_r	5.2	48.65
radius of the particles a	0.625×10^{-6} m	1.2×10^{-6} m
surface voltage of the particles Ψ_0	90×10^{-3} V	75×10^{-3} V
temperature, T	298 K	293 K
valency of the ions, z	1	1
density of the solvent ρ_0	981 kg/m ³	1000 kg/m ³
density of the particles ρ_1	1400 kg/m ³	2530 kg/m ³
solvent viscosity η_0	0.054 Pa s	0.14 Pa s
salt concentration, C	0.00167 mol/m ³	0.01 mol/m ³

$$\eta_{\text{low}}(\Phi) = \eta_0 \left[\exp\left(\frac{\Phi_{\text{hcp}} - \Phi_p}{\Phi_{\text{hcp}} - \Phi}\right) - 1 \right] \quad (43)$$

for volume fractions $\Phi > \Phi_p$. The parameter Φ_p is the percolation threshold, which is independent of the underlying structure ($\Phi_p = 0.16$), and $\Phi_{\text{hcp}} = \pi/3\sqrt{3} = 0.605$ is the maximum packing fraction of a hexagonally layered structure; η_0 is the viscosity of the solvent fluid.

In our analysis we need the viscosity η_1 of the suspension in the high shear rate limit, but undisturbed by the resonance. In order to obtain that viscosity η_1 we introduce an unknown coefficient ξ_0 which we assume to be independent of the volume fraction:

$$\eta_1(\Phi) = \eta_{\text{low}}(\Phi) \xi_0, \quad (44)$$

while η_{low} is given by Eq. (43). We can write Eq. (28) in the form

$$\dot{\gamma}_c = \xi \frac{E(\Phi)}{\eta_{\text{low}}(\Phi)} \quad (45)$$

while we have reduced all unknown parameters to a single fitting parameter ξ :

$$\xi = \frac{a_0}{\Gamma \xi_0} \sqrt{4 - a_0^2}. \quad (46)$$

With the equations given the theoretical and experimental values of the critical shear rate can be compared as a function of the volume fraction. We use the set of data [Hoffman (1982); Boersma *et al.* (1990)] as summarized in Table I. Note that the value for the salt concentration of the PVC in DOP suspension originates from an estimation using Fig. 9 of Hoffman (1974) for the used surface potential.

1. PVC in DOP

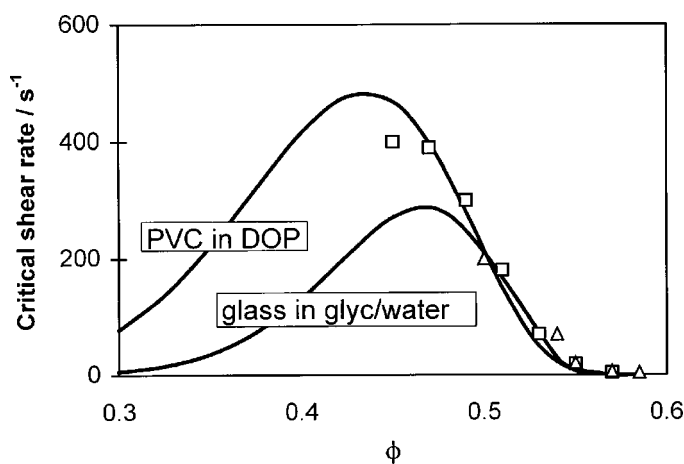
The shear rates at the maximums of the viscosity measurements (critical shear rates) with PVC latexes by Hoffman (1982) are summarized in Table II. By choosing the parameter $\xi = 20$ we fitted our model to the experimental values of the critical shear rate at the lower volume fractions (higher critical shear rates). In doing so the formula of Campbell and Forgacs was used without any modification. For the other volume fractions we obtain quite good agreement. Deviations occur especially for very high volume fractions. Here the critical shear rate is very small and the strong coupling limit may not be

TABLE II. Comparison of experimental and theoretical values of the critical shear rate for PVC/DOP suspensions.

Volume fraction Φ	Critical shear rate $\dot{\gamma}_c$ ($^{\circ}$ /s) theory		Critical shear rate $\dot{\gamma}_c$ ($^{\circ}$ /s), experiments [Hoffman (1982)]
	$\phi_{\max} = 0.605$ $\xi = 20$	$\phi_{\max} = 0.622$ $\xi = 13$	
0.45	523	409	400
0.47	447	376	390
0.49	316	297	300
0.51	170	193	180
0.53	57	92	70
0.55	7	24	18
0.57	0.1	3	≈ 4

perfectly valid. This is because the movement of the particles and the solvent may be different for small shear rates. The dependence of the critical shear rate on the volume fraction is shown in Fig. 2 for the used set of data (filled squares: experimental, open squares: theoretical). At small volume fractions the critical shear rate is small but it increases with increasing volume fraction. This originates from the fact that at small volume fractions the viscosity is almost constant when increasing Φ , while the elastic modulus increases appreciably, according to (37). Unfortunately the rise in viscosity due to shear thickening reduces with decreasing volume fraction. This appears to be the reason for not clearly finding this phenomenon at low values of ϕ . With increasing ϕ the critical shear rate reaches a maximum at Φ_m and thereafter decreases with increasing volume fraction, because in this region the viscosity increases faster than the elastic modulus does. The acoustic resonance can occur only for $\Phi < \Phi_{\text{hcp}}$, because the viscosity of the sheared hcp-layered structure becomes infinite at Φ_{hcp} .

Also indicated in Table I is a fit of our model to experimental data assuming that ϕ_{\max} may be optimized when the particles are not perfectly monodisperse. The combination

**FIG. 2.** Comparison of the theoretical and experimental critical shear rates (at maximum η) with PVC-DOP suspensions (\square), (\blacksquare) and glass-in-glycerol/water suspensions (\triangle), (\blacktriangle).

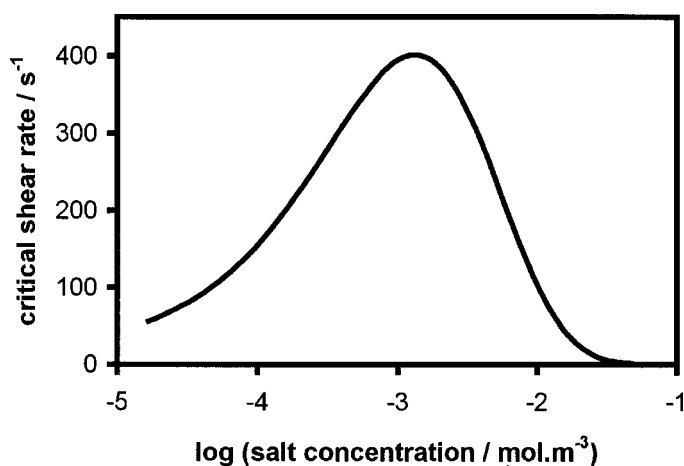


FIG. 3. Model prediction of the dependence of the critical shear rate (at maximum η) on the salt concentration, with $\Phi = 0.45$ and with the other system parameters equal to those used in Fig. 2.

$\phi_{\max} = 0.622$, $\xi = 13$ now gives considerable improvement in the comparison of calculated and measured critical shear rates. However we will not further elaborate on this.

Using the set of parameters employed before for monodisperse particles ($\phi_{\max} = 0.605$, $\xi = 20$), the dependence of the predicted critical shear rate has been determined as a function of the salt concentration at a constant volume fraction $\Phi = 0.45$. The result is shown in Fig. 3. As the viscosity was assumed to be independent of the salt concentration, the critical shear rate is now only influenced by the dependence of the elastic modulus on the salt concentration. At very high salt levels the double layer repulsion [$\sim \kappa^2 \exp(-\kappa x$, see Eqs. (37) and (41)] is effectively suppressed by compression of the double layers, resulting in a negligible modulus. On decreasing the salt level, double layers expand and repulsive interaction becomes appreciable leading to a noticeable modulus and an increasing critical shear rate. On further decreasing the salt level the double layers are so extended that the interaction energy becomes almost linear in the distance. According to Eq. (37) this results in a reduction of the modulus and thus of the critical shear rate.

Another characteristic of the critical shear rate is how it depends on the particle size. As can be seen from Fig. 4 the critical shear rate increases drastically on reducing the particle size at constant volume fraction $\Phi = 0.45$ and salt concentration $C = 0.00167$ mol/m³. This is due to the fact that with decreasing particle sizes at constant volume fraction and salt concentration the elastic modulus increases, because κ decreases in Eq. (42).

2. Glass in glycerol/water (86.1% mass/mass)

Applying the same formalism developed above, the critical shear rate can be evaluated while we again set the free parameter $\xi = 20$, again with $\phi_{\max} = 0.605$. The experimental values of the critical shear rate have been obtained from the maximum of the viscosity in Boersma *et al.* (1990). The results are summarized in Table III. The range of volume fractions is smaller than with Hoffman's experiments. The agreement between the experimental and theoretical data is reasonable. Note that the maximum of the viscosity versus shear rate curve was difficult to determine at the lower volume fractions, because the variations in the viscosity are rather small. The results are also plotted in Fig. 2 (solid

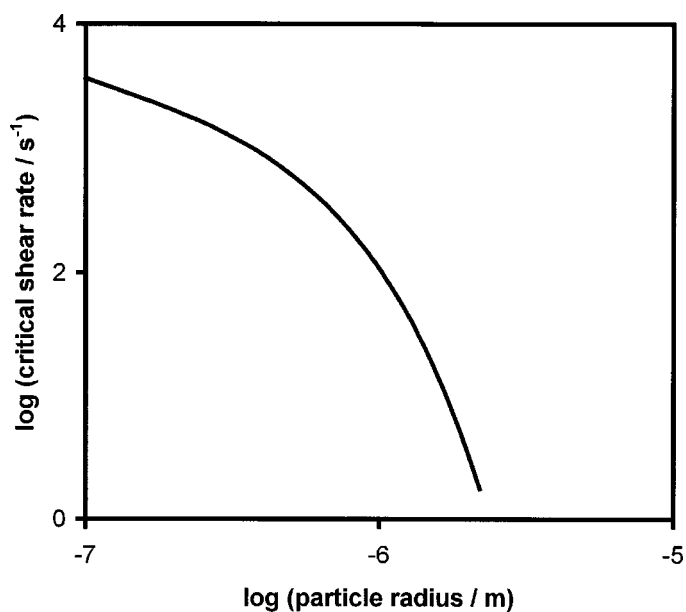


FIG. 4. Model prediction of the dependence of the critical shear rate (at maximum η) on the particle size, with $\Phi = 0.45$ and with the other system parameters equal to those used in Fig. 2.

triangles: measured, open triangles: theoretical). It is remarkable that Hoffman's and Boersma's results coincide at higher volume fractions, and so do the theoretical predictions using $\xi = 20$ in both cases. The theoretical predictions deviate at low volume fractions due to the fact that the double layer thickness is smaller in the case of glass suspension, leading to a faster drop in modulus when reducing the volume fraction.

As with the PVC/DOP suspension the critical shear rates deviate from the expected value for high values of the volume fraction, presumably because the strong coupling assumption is no longer justified. That the agreement between experiment and theory is slightly less than with the PVC/DOP system may also be due to the larger polydispersity in the size of the glass particles as compared with that of the PVC particles.

TABLE III. Comparison of experimental and theoretical values of the critical shear rate for glass in glycerol/water suspensions.

Volume fraction Φ	Critical shear rate $\dot{\gamma}_c$ (1/s) theory; $\phi_{\max} = 0.605$, $\xi = 20$	Critical shear rate $\dot{\gamma}_c$ (1/s) experiment [Boersma <i>et al.</i> (1990)]
0.5	233	≈ 200
0.54	32	70
0.55	10	14
0.57	0.1	6
0.585	9×10^{-6}	4

III. DISCUSSION

A. Comparison with experiments

The application of light, x-ray and neutron scattering techniques allows the simultaneous investigation of the microstructure and the transport properties, as first utilized by Hoffman (1972) with a PVC latex in DOP. He established the connection between an order–disorder transition and the variation of the transport properties. Ackerson found similar transitions in dilute dispersions [Ackerson and Clark (1983)]. Starting at high shear rates and going down to lower values he denoted the transition from a disordered structure into a sheared layer structure as transition I. Decreasing the shear rate further, a transition into a polycrystalline (disordered) structure occurs. Here the layered structure becomes unstable. He denoted this as transition II. In our interpretation the equilibrium state of a colloidal crystal is unstable against a shear perturbation and forms a disordered structure at a critical shear strain as discussed by Kaldasch (1996). On increasing the shear rate, a shear induced order transition takes place, which is similar to transition II as denoted by Ackerson, but passed in the opposite direction. Transition I, however, is the instability, where the hexagonal planes disappear due to an acoustic resonance.

When the relaxation time of the suspension in the equilibrium colloidal crystal is large at high volume fractions and high Péclet numbers, the nonequilibrium structure layered structure seems to be frozen when the perturbation starts with high shear rates as in an experiment carried out by Yan and Dhont (1993).

The shear thickening as well as the shear melting transition in colloidal suspension has been of interest to many authors. Before the work of Hoffman (1972) shear thickening was considered as a rheological phenomenon and mainly treated in a phenomenological manner as summarized in the review by Barnes (1989).

Experimentally shear thickening is found normally to be related to “dilatancy,” implying a “temptative” expansion of the suspension volume under a continuous shear deformation. In the present model such dilatancy is not accounted for explicitly, due to the assumption that the system is infinitely large. Due to these infinite distances any reduction in liquid pressure induced by the acoustic waves (not evaluated in our model) will not lead to a nonzero pressure gradient and no volumetric change is predicted. Experimentally this dilatancy effect is reflected in the often observed gradual descent in viscosity of a suspension under critical shear conditions due to migration of liquid from parts in the measuring cell where the shear rate is lower in areas where the critical condition is present.

An underlying assumption within the present model is that the time-averaged microstructure persists on both sides of the critical shear rate. In practice resonances may lead to imperfections in the ordering, which eventually may result in a shear-induced order–disorder transition. This may also explain why beyond the critical shear rate the predicted shear thinning is not found experimentally. For this reason our model is expected to have predictive capabilities only on the low shear rate side of the resonance state. Even if thermodynamically the favorite structure beyond the critical shear rate is an ordered one, disorder may persist due to disturbances continuously imposed by the flow which have extremely large relaxation times.

Decreasing the absolute value of the surface charge and the concentration of the counter ions by varying the pH value, Laun (1988) obtained the expected shift of the critical shear rate of dilatancy to lower values for decreasing repulsive forces (smaller elastic modulus) by investigating a concentrated polystyrene latex dispersion. In the same publication the temperature dependence of a suspension of polystyrene particles in diethyleneglycol/formamide has been studied. It was found that the critical shear rate

shifts to lower values for decreasing temperatures. A similar result has been obtained by Boersma *et al.* (1990) from a polystyrene in water/glycerol suspension. These results are in agreement with the model, since the increase of the viscosity with decreasing temperatures shifts [according to Eq. (28)] the critical shear rate to lower values. The critical shear stress is expected to be rather independent of the temperature according to Eq. (30) because the elastic modulus varies only slightly with the temperature.

With the same argument we can understand the effect of solvents of different viscosity on shear thickening. Figure 11 of Barnes (1989) and Fig. 9 of Boersma *et al.* (1990) confirm in Eq. (30) that for equal elastic moduli the transition takes place at a constant stress.

The increase of the critical shear rate for decreasing particle sizes, as shown by Barnes (1989), is partially due to the increase of the elastic modulus with decreasing particle diameter according to a decrease in the scaled Debye parameter κ in Eq. (42). Also the liquid viscosities of the suspensions with larger particles usually are larger. Note that our model is developed under the assumption of monodisperse particles. A polydisperse distribution has been found experimentally to correspond with a less pronounced increase of the viscosity. In the approach here a possible explanation for this phenomenon is that the density variations become less periodic in the sheared colloidal crystal and the resonance effects are reduced.

We also compare the theory with recent, well documented results by Chow and Zukowski (1995a,b) for suspensions with particle radii of 0.12–0.26 μm . For this purpose only those systems for which, apart from G_0 , also values of τ_c and $\dot{\gamma}_c$ are available, are useful to some extent, these systems having $0.525 < \Phi < 0.595$. Note that the index c indicates the shear condition where the viscosity signal just starts to exhibit slight noise that they interpret as an indication of the start of shear thickening. Consequently, η^c is the viscosity just before the onset of thickening. That definition, as also used by Hoffman and by Boersma *et al.*, deviates from our present criterion in that we consider the condition of maximum viscosity. Predicting $\dot{\gamma}_c$ by calculating G_0/η_c leads to an overestimation of $\dot{\gamma}_c$ by a factor 11 ± 4 (their Table 2). The amount of data by them do not allow drawing definite conclusions on the dependence of $\dot{\gamma}_c$ on Φ . However their results suggest that the maximum $\dot{\gamma}_c$ is at much larger Φ than with the results shown in Fig. 2. This can be well explained from our model when realizing that with small values of the electrical double layer thickness $d \ln(G_0)/d\Phi$ is much larger, which leads to much larger values of Φ at which the increase of η overrules the increase of G_0 .

The systems of Chow and Zukowski seem to behave differently from the systems of Hoffman and Boersma. First, their moduli are lower by a multiplication factor between 0.001 and 3 when compared with results assessed on the basis of the Derjaguin formula for electrostatic repulsive interactions (as no electrokinetic data are available we assumed $\psi_0 = -0.050$ V). The dependence of G_0 on Φ for Chow's systems suggests that the particles behave as constant charge particles rather than having constant potential. Moreover, theory predicts G_0 to scale approximately with a^{-2} while the experimental data indicate an a^{+3} scaling. Second, their values of η_{rel}^c vary between ~ 40 and ~ 90 , the lowest value occurring at the highest value of Φ : at 0.595. It is evident that on the basis of, for example, the theory of Campbell and Forgacs [our Eq. (43)] η^c should be much higher due to the divergence at $\Phi_{\text{hcp}} = 0.605$. This anomaly has already been noted by Chow and Zukowski in that they did not clearly find $\dot{\gamma}_c$ scaling with h/a . Only by deliberately setting the divergent condition at 0.68 can a reasonable consistency between the theoretical and experimental levels of η_{rel}^c be found (within $\sim 40\%$). In keeping with their results they found that $\dot{\gamma}_c \sim G_0/\eta_0$ where η_0 is the solvent viscosity. It is evident

that on the basis of those results we are not allowed to invalidate the previously reported scaling of $\dot{\gamma}_c$ with h/a by Boersma *et al.* (1990).

Experimental results on the system size dependence of the critical shear rate of shear thickening obtained by Chow and Zukoski (1995b) show that it is important especially at high volume fractions. They found that the critical shear rate decreases with decreasing system sizes. According to our model the system size becomes limiting when the corresponding wavelength k_{sys} is comparable or larger than the wavelength k_0 of the dominant deformation wave of the sheared suspension. The experimentally found dependence of $\dot{\gamma}_c$ on k is expected only to occur when k_s is on the right side of the maximum of the $\dot{\gamma}_c(k)$ dependence as shown in Fig. 1. However the experimental investigations by Chow and Zukoski (1995a) show that the critical shear rate is independent of the system size for practical systems (> 1 mm).

Finally we note that the model presented, being applied here to electrostatically stabilized suspensions, is expected to be also applicable to sterically stabilized colloidal suspensions, when using the appropriate formulas [Boersma *et al.* (1990)].

B. Comparison with other models

Other explanations for shear thickening in colloidal suspensions have been given by Hoffman (1974), Ackerson and Clark (1981), and Boersma *et al.* (1990). The basic idea of Hoffman is that a shear stress couple acting on a doublet of particles in a sheared crystal is the reason for the instability. In the model presented here the reason for the instability comes from the periodic modulation of the modulus in the flow gradient direction, leading to a resonance between the modulation frequency and the eigenfrequency of propagating acoustic shear waves.

An increase of the local oscillations coming from the acoustic resonance can lead to a structural transition with a formation of clusters (flow blockage), when the forces acting on a colloidal particle are of the order of the repulsive stabilization as assumed by Boersma *et al.* In this case the critical shear rate of shear thickening is ruled by Boersma's equation [Boersma (1990); Boersma *et al.* (1995)] with the critical shear rate

$$\dot{\gamma}_c = \frac{2\pi\epsilon_0\epsilon_r\Psi_0^2\kappa h}{6\pi\eta_0a^2} \frac{1}{2}. \quad (47)$$

Note that the acoustic resonance can be expected to cause instability even in very dilute suspensions accompanied by a global disordering and an alteration of the dynamic properties. Such phenomena have been observed by Lindsay and Chaikin (1985). The attempt by Chow and Zukoski (1995b) to expand Boersma's approach to dilute suspensions, by creating a maximum of the critical shear rates at a specific volume fraction Φ_{max} , evolves in the model presented here in a natural way (Fig. 3).

IV. CONCLUSIONS

The model presented here explains shear thickening of sheared colloidal suspensions as the occurrence of an acoustic resonance. The resonance is the result of the periodic modulation of the elastic modulus in a shear colloidal crystal structure. Applying the hydrodynamic equation of the colloidal suspension—the critical shear rate, where a maximum in the viscosity occurs, can be derived. A good agreement with experimental results for high critical shear rates could be found. For low critical shear rates the used approximations have to be improved.

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APPENDIX A

When using as initial conditions that both $A^{(1)} = 0$ and $dA^{(1)}/dt = 0$ at $t = 0$, then the standard Laplace transform of Eq. (24) becomes

$$A^{(1)}(s) = \frac{c^2 k^2 A^{(0)}}{s^2 - bk^2 s + c^2 k^2} \left(\frac{s+p_1}{(s+p_1)^2 + \dot{\gamma}^2} + \frac{s+p_2}{(s+p_2)^2 + \dot{\gamma}^2} \right). \quad (\text{A1})$$

The reverse Laplace transform of (A1) contains the sum of all residuals s_1 of $A^{(1)}(s_1)$ with $\text{Re}(s_1) < 0$. The poles s_1 of $A^{(1)}(s_1)$ are at

$$\begin{aligned} s_1 &= -p_1 - j\dot{\gamma}, & s_2 &= -p_1 + j\dot{\gamma}, \\ s_3 &= -p_2 - j\dot{\gamma}, & s_4 &= -p_2 + j\dot{\gamma}. \end{aligned} \quad (\text{A2})$$

The reverse Laplace transform of (A4) thus has the form

$$A^{(1)}(t) = c^2 k^2 A^{(0)} \sum_{l=1}^4 [(s+s_l)e^{st} A^{(1)}(s_l)]_{s=s_l}. \quad (\text{A3})$$

Using (A1) and (A2) in (A3) we obtain the time dependent first order amplitude:

$$A^{(1)}(t) = c^2 k^2 A^{(0)} \left(\frac{((p_1 - p_2)\cos(\dot{\gamma}t) - \dot{\gamma}\sin(\dot{\gamma}t))e^{-p_1 t}}{p_1[\dot{\gamma}^2 + (p_1 p_2)^2]} - \frac{[(p_1 - p_2)\cos(\dot{\gamma}t) + \dot{\gamma}\sin(\dot{\gamma}t)]e^{p_2 t}}{p_2[\dot{\gamma}^2 + (p_1 + p_2)^2]} \right). \quad (\text{A4})$$

In the case of damped propagating waves p_1 and p_2 are given by Eq. (22) and the amplitude turns into

$$\begin{aligned} A^{(1)}(t) &= \frac{2A^{(0)}c^2 k^2 e^{\delta t}}{(\delta^2 + \omega^2)(\dot{\gamma}^2 + 4\omega^2)} \{2\omega[\omega \cos(\omega t) + \delta \sin(\omega t)]\cos(\dot{\gamma}t) \\ &\quad - \dot{\gamma}[\delta \cos(\omega t) - \omega \sin(\omega t)]\sin(\dot{\gamma}t)\}. \end{aligned} \quad (\text{A5})$$

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