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Computer simulations of shear thickening of concentrated dispersions

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Synopsis

Stokesian dynamics computer simulations were performed on monolayers of equally sized spheres. The influence of repulsive and attractive forces on the rheological behavior and on the microstructure were studied. Under specific conditions shear thickening could be observed in the simulations, usually together with a change in the microstructure from ordered layers to a state with large clusters. These clusters are responsible for the high viscosities in shear thickening conditions. The shear thickening results show qualitative agreement with the theoretically expected behavior and with experiments. Van der Waals forces are found to sharpen the shear thickening transitions by inducing even stronger clusters and thus higher viscosities. © 1995 Society of Rheology.

I. INTRODUCTION

Shear thickening in concentrated dispersions has received increasing attention in the last two decades (e.g., Hoffman, 1972; Laun, 1984, 1988; Barnes, 1989; Boersma *et al.*, 1990). This is partly because shear thickening is a problem in industrial processing of concentrated suspensions and partly because shear thickening dispersions can exhibit very strong rheological effects, which are probably related to changes in the microstructure of the dispersion. If it would be possible to observe these changes in the microstructure and to relate them to changes in the viscosity of the dispersion this would give valuable insight into the processes that determine suspension rheology. In the past several attempts have been made to study the microstructure of concentrated dispersions with light or neutron scattering techniques (e.g., Hoffman, 1972; Tomita and van der Ven, 1984; Ackerson, 1990; D'Haene *et al.*, 1993; Chow and Zukoski, 1995a, b). Among these authors only Hoffman and Chow and Zukoski studied the changes in microstructure due to shear thickening. Hoffman found that the origin of the dramatically discontinuous shear thickening in his experiments was due to a transition from an ordered, easy flowing, state of the dispersion to a completely disordered state. Nowadays it is quite generally accepted that some sort of an order-disorder transition is responsible for shear thickening in most dispersions (Barnes, 1989). At shear rates below the shear thickening transition repulsive interparticle forces keep the particles separated and smoothly flowing strings or layers of particles produce an ordered structure with a relatively low viscosity. As the shear rate increases the hydrodynamic forces start to dominate the repulsive interparticle

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forces leading to the destruction of the order in the suspension and to the generation of clusters. These clusters grow larger and larger and eventually may obtain a size comparable to the measuring device, producing, e.g., gap-spanning clusters in a Couette system (Boersma *et al.*, 1991).

More recently, another method of studying the influence of the microstructure on the rheological behavior of dispersions has become available. This is the technique of computer simulations. Especially, the Stokesian dynamics (SD) method, in which hydrodynamic, Brownian, and interparticle forces can be included, has yielded some very good results (Brady and Bossis, 1988). More specifically, with the SD method it was shown that dispersions of particles with a repulsive potential (but with no Brownian forces working on them) exhibit shear thickening, and that this is indeed due to an order-disorder transition (Brady and Bossis, 1985). Shear thickening was also found in Brownian dispersions, even without repulsive interparticle forces (Brady and Bossis, 1988; Phung and Brady, 1992; Bossis *et al.*, 1993). It seems that in these simulations at low shear rates the Brownian forces serve as the repulsive forces, and that, as the shear rate is increased, the hydrodynamic forces become more important, finally leading to clusters and an increased viscosity. Although shear thickening has also been observed in molecular dynamics simulations (Heyes, 1986; Barnes *et al.*, 1987), none of these simulations have provided the quantitative agreement with experiments that SD simulations have done.

In this work we will present Stokesian dynamics simulations of monolayers of equally sized spherical particles. We will show that the shear thickening transition can be observed in the simulations and we will study the dependence of this transition on several parameters. The simulations are in good qualitative agreement with experimental results and with a criterion for the shear rate at which shear thickening starts (Boersma *et al.*, 1990). An order-disorder transition was observed which was accompanied by a variety of structure changes eventually leading to cluster formation. This cluster formation is even more pronounced if Van der Waals forces are included. It should be noted that these simulations are different from Stokesian dynamics simulations on Brownian particles (Phung and Brady, 1992). While both simulations show shear thickening the current simulations do not include Brownian forces, but do include electrostatic and van der Waals forces. It will be shown that these forces can radically dominate the rheological dispersion behavior.

II. SIMULATION TECHNIQUE

A. The Stokesian dynamics method

The principles of the method used here have been explained extensively elsewhere (Durlinsky *et al.*, 1987), and therefore only the most important aspects will be mentioned here. The starting point of the method is the coupled N -body Langevin equation:

$$\mathbf{M} \cdot \frac{d\mathbf{U}}{dt} = \mathbf{F}^H + \mathbf{F}^P + \mathbf{F}^B. \quad (1)$$

Here $\mathbf{M}$ is a generalized mass/moment-of-inertia matrix of dimension $3N \times 3N$ in the two-dimensional case, $\mathbf{U}$ is the particle translational/rotational vector of dimension $3N$ in the two-dimensional case (v_x, v_y, ω_z) considered here, and the $3N$ force/torque vectors $\mathbf{F}$ represent the hydrodynamic forces $\mathbf{F}^H$, the interparticle forces $\mathbf{F}^P$ ($\mathbf{F}^P$ also includes the external forces, if present), and the Brownian forces $\mathbf{F}^B$.

If external and Brownian forces are excluded (as in our simulations) and if the particle Reynolds number $\text{Re} = \rho \dot{\gamma} a^2 / \eta_0$ is small ($\ll 1$), the Langevin equation becomes

$$\mathbf{F}^H + \mathbf{F}^P = 0. \quad (2)$$

The exclusion of Brownian forces requires that the Péclet number $Pe = \dot{\gamma} a^2 / D = 6\pi\eta_0 a^3 \dot{\gamma} / k_B T$ is large ($\gg 1$). Here ρ is the density of the medium, $\dot{\gamma}$ is the shear rate, a is the particle radius, η_0 is the medium viscosity, D is the diffusion coefficient of a single, isolated particle, and $k_B T$ is the thermal energy.

The hydrodynamic forces on the particles in a dispersion undergoing a bulk linear shear flow are (Brenner and O'Neill, 1972)

$$\mathbf{F}^H = -\mathbf{R}^{FU} \cdot (\mathbf{U} - \mathbf{U}^\infty) + \mathbf{R}^{FE} : \mathbf{E}^\infty, \quad (3)$$

where $\mathbf{U}^\infty$ is the velocity of the bulk shear flow evaluated at the particle center, $\mathbf{E}^\infty$ is the bulk rate of strain tensor, and $\mathbf{R}^{FU}(\mathbf{x})$ and $\mathbf{R}^{FE}(\mathbf{x})$ are the configuration dependent resistance matrices that give the hydrodynamic forces/torques on the particles due to their motions relative to the fluid ($\mathbf{R}^{FU}$) and due to the imposed shear flow ($\mathbf{R}^{FE}$). $\mathbf{x}$ is the generalized configuration vector specifying the location (in two dimensions: the x and y position) and orientation (in two dimensions: the z angular position) of all N particles. The interparticle forces $\mathbf{F}^P$ in this study will be DLVO-electrostatic repulsion forces and Van der Waals attraction forces (see below). If $\mathbf{R}^{FU}$ and $\mathbf{R}^{FE}$ are known and if $\mathbf{E}^\infty$ and $\mathbf{F}^P$ are given as well, by combination of Eqs. (2) and (3) the velocities of the particles $\mathbf{U} - \mathbf{U}^\infty$ can be calculated. The change in configuration over a small time step is calculated after which the configuration is updated. With the new configuration, the process can then be repeated, thus allowing one to follow the dynamic evolution of the particle configuration.

For calculating the viscosity the bulk stress $\langle \Sigma \rangle$ is needed. This is defined as an average over the volume V containing the N particles (remember that we are discussing a monolayer here, with a thickness of one particle diameter) and is given by

$$\langle \Sigma \rangle = IT + 2\eta_0 \mathbf{E}^\infty - \frac{N}{V} \{ \langle \mathbf{S}^H \rangle + \langle \mathbf{S}^P \rangle \}. \quad (4)$$

Here IT stands for an isotropic term of no interest for the incompressible dispersion and the particle contributions to the bulk stress are given by

$$\langle \mathbf{S}^H \rangle = -\langle \mathbf{R}^{SU} \cdot (\mathbf{U} - \mathbf{U}^\infty) - \mathbf{R}^{SE} : \mathbf{E}^\infty \rangle, \quad (5)$$

$$\langle \mathbf{S}^P \rangle = -\langle \mathbf{x} \mathbf{F}^P \rangle. \quad (6)$$

$\mathbf{R}^{SU}(\mathbf{x})$ and $\mathbf{R}^{SE}(\mathbf{x})$ are again configuration dependent resistance matrices relating the particle "stresslets" $\mathbf{S}$ to the particle velocities, as calculated before, and to the imposed rate of strain.

In the Stokesian Dynamics method, first the far-field approximation to the grand mobility matrix, $\mathbf{M}^\infty$, relating the particle velocities (translational and rotational) and rate of strain to the forces, torques, and stresslets is filled with the appropriate interaction functions (given in Durlofsky *et al.*, 1987, Appendix A). Then this matrix is inverted giving the far-field approximation to the resistance matrix, $\mathbf{R}^\infty$. To include lubrication interactions into this resistance matrix they are added pairwise, while taking care not to include the far-field parts of the lubrication, as they are already contained in $\mathbf{R}^\infty$. This leads to the final grand resistance matrix $\mathbf{R}$, given by

$$\mathbf{R} = (\mathbf{M}^\infty)^{-1} + \mathbf{R}^{2B} - \mathbf{R}^{2B, \infty}. \quad (7)$$

$\mathbf{R}^{2B}$ is formed with the use of the two sphere resistance functions given in the literature (Kim and Karrila, 1991). $\mathbf{R}^{2B, \infty}$ is formed by simply inverting $\mathbf{M}^{2B, \infty}$, a two-body mobility matrix containing terms to the same order in $1/r$ as $\mathbf{M}^\infty$ (r is the characteristic

interparticle spacing). Once $\mathbf{R}$ has been evaluated for a given configuration, its components $\mathbf{R}^{FU}$, $\mathbf{R}^{FE}$, $\mathbf{R}^{SU}$, and $\mathbf{R}^{SE}$ are known, giving the possibility to calculate the evolution of a configuration and of the viscosity. To obtain the viscosity of a specific dispersion under shear one has to take the time average of the viscosity once a steady state has been reached.

B. Interparticle forces

In these simulations we used two types of interparticle forces: electrostatic, DLVO-type, repulsion forces and Van der Waals attraction forces. The repulsive forces are given by (Verwey and Overbeek, 1948):

$$F_R = 2\pi\epsilon_0\epsilon_r s_0^2 \left(\frac{\kappa a \exp(-\kappa a h/a)}{1 \pm \exp(-\kappa a h/a)} \right), \quad (8)$$

where ϵ_0 is the permittivity of vacuum, ϵ_r is the relative dielectric constant, $1/\kappa$ is the Debye double layer thickness, and a the particle radius, and h is the distance between the particle surfaces. The $+$ and $-$ in Eq. (8) correspond to the assumption of a constant surface potential s_0 (where s_0 is often approximated by the ζ potential) and of a constant surface charge density of the spheres (where s_0 is now the surface potential at $h = \infty$).

The Van der Waals forces, including retardation effects, are given by (Schenkel and Kitchener, 1960)

$$F_A = -\frac{Aa}{12h^2} \left(\frac{1+3.54p}{(1+1.77p)^2} \right) \quad p < 1, \quad (9)$$

$$F_A = -\frac{Aa}{12h^2} \left(\frac{0.98}{p} - \frac{0.434}{p^2} + \frac{0.0674}{p^3} \right) \quad p > 1,$$

where A is the Hamaker constant and $p = 2\pi h/\lambda$, with λ the London wavelength.

C. Computational aspects

For the computer simulations, all variables and equations were nondimensionalized, as indicated in Table I. The scalings of angular velocity Ω (the third component of $\mathbf{U}_i$) and rate of strain tensor $\mathbf{E}$ follow from combination of the scaling factors for length and velocity.

If we now define a dimensionless shear rate $\dot{\gamma}^*$:

$$\dot{\gamma}^* = \frac{6\pi\eta_0 a^2 \dot{\gamma}}{2\pi\epsilon_0\epsilon_r s_0^2}, \quad (10)$$

and a balance between the two colloidal forces F_{AR}^* :

$$F_{AR}^* = \frac{A}{24\pi\epsilon_0\epsilon_r s_0^2 a}, \quad (11)$$

then we get, in the case of $\dot{\gamma}^* < 1$:

$$-\tilde{\mathbf{R}}^{FU} \cdot (\tilde{\mathbf{U}} - \tilde{\mathbf{U}}^\infty) + \dot{\gamma}^* \tilde{\mathbf{R}}^{FE} : \tilde{\mathbf{E}}^\infty + \tilde{\mathbf{F}}_R + F_{AR}^* \tilde{\mathbf{F}}_A = 0. \quad (12)$$

From this equation the velocities can be solved giving the particle velocities as

$$\tilde{\mathbf{U}} = (\tilde{\mathbf{U}} - \tilde{\mathbf{U}}^\infty) + \dot{\gamma}^* \tilde{\mathbf{x}}_y,$$

TABLE I. Dimensionless quantities used in the simulations.

Quantity	Dimension ^a	Symbol	Dim. less symbol	Quantity
				Dim. less quantity
Position	L	x	$\tilde{x}$	a
Force (repulsive)	$M^2 L/T^2$	F_R	$\tilde{F}_R$	$ F_{R,0} = 2\pi\epsilon_0\epsilon_r\epsilon_0^2$
Force (attractive)	$M^2 L/T^2$	F_A	$\tilde{F}_A$	$ F_{A,0} = A/12a$
Velocity	L/T	U	$\tilde{U}$	$ F_{R,0} /6\pi\eta_0 a$ ($\dot{\gamma}^* < 1$) $\dot{\gamma}a$ ($\dot{\gamma}^* > 1$)
Grand resist. matrix element	ML^n^{-1}/T	R_{ij}^{AB}	$\tilde{R}_{ij}^{AB}$	$6\pi\eta_0 a^n$ ^b
Time	T	t	$\tilde{t}$	$1/\dot{\gamma}$

^a L = length; M = mass; T = time.^b n = 1,2,3 depending on the specific element of the resistance matrix.

$$\tilde{\Omega} = (\tilde{\Omega} - \tilde{\Omega}^\infty) - 0.5\dot{\gamma}^*, \quad (13)$$

where x_y is the y component of the particle position and where the translational and rotational components of the velocity vector U are now written separately as $\tilde{U}$ and $\tilde{\Omega}$.

If $\dot{\gamma}^* > 1$, we get

$$-\tilde{R}^{FU} \cdot (\tilde{U} - \tilde{U}^\infty) + \tilde{R}^{FE} : \tilde{E}^\infty + (1/\dot{\gamma}^*)\tilde{F}_R + (F_{AR}^*/\dot{\gamma}^*)\tilde{F}_A = 0, \quad (14)$$

and the particle velocities can now be found as

$$\tilde{U} = (\tilde{U} - \tilde{U}^\infty) + \tilde{x}_y,$$

$$\tilde{\Omega} = (\tilde{\Omega} - \tilde{\Omega}^\infty) - 0.5. \quad (15)$$

For the calculation of the viscosities a similar nondimensionalization is used, giving similar results. Equations (12) and (13) are used at relatively low values of $\dot{\gamma}^*$ (≤ 1), while Eqs. (14) and (15) are used at values of $\dot{\gamma}^* > 1$, because in the latter case the contributions from the forces “drop out,” finally giving the hydrodynamic limit.

Using these nondimensionalizations, the input parameters for the simulations are the length of the square cell used in the simulations, the areal fraction, defined as $\varphi_A \equiv N\pi a^2/L^2$, $\dot{\gamma}^*$, F_{AR}^* , λ , and κa . An additional input parameter is the number of time steps after which a new mobility matrix has to be formed and inverted. Since the mobility matrix changes only significantly when the particle configuration changes significantly, the filling and inverting do not have to be performed at every time step, thus saving computation time. In these simulations the mobility matrix was inverted every ten steps. It was checked that this resulted in no significant differences with simulations in which the mobility matrix was inverted every time step.

The parameters of the dispersion used in these simulations were taken from the literature (Boersma *et al.*, 1990; Takamura *et al.*, 1981) and are given in Table II. These are parameters for a dispersion of polystyrene in water. Use of these values resulted in a value of F_{AR}^* of 4.54×10^{-5} , while the value of $\dot{\gamma}^*$ becomes $\dot{\gamma} \cdot (0.002 \text{ s})$. Variation of $\dot{\gamma}^*$ is thus equivalent to variation of $\dot{\gamma}$.

For the time stepping a fourth-order Adams–Bashford scheme was used. Other methods as, e.g., the Gear algorithm were also tried but no differences were found. For inverting the grand mobility matrix and solving Eqs. (12) or (14), Cholesky methods were used as can be found in any standard library (e.g., Linpack). The use of this method

TABLE II. Parameters of the dispersions used in the simulations.

Name	Symbol	Value
Medium viscosity	η_0	0.001 Pa s
Particle radius	a	0.805×10^{-6} m
Hamaker constant	A	2.7×10^{-21} J
Relative dielectric constant	ϵ_r	80.37
Permittivity of vacuum	ϵ_0	8.9×10^{-12} F/m
London wavelength	λ	2×10^{-7} m
Surface potential	ζ_0	37×10^{-3} V

is possible because the grand mobility and the resistance matrix are both symmetrical and positive definite, due to the dissipative nature of the system. In the simulations a square unit cell was used and periodic boundary conditions were applied (Bossis and Brady, 1984). The particle motions were followed in time until a stationary state was reached. This was determined by plotting the development of the relative viscosity. When the average viscosity did not change significantly anymore over approximately 5000 time steps this viscosity was used as the relative dispersion viscosity for that simulation. Runs were performed on three different computers: a VAX/VMS 8530 computer, an Alliant concentrix F-2800 computer, and a NEC SX-2 supercomputer. A typical run of 25 particles and 30 000 time steps took approximately 9 min on the NEC SX-2. This was 50 times as fast as the VAX and 12 times as fast as the Alliant. For 49 particles the 30 000 time steps on the NEC SX-2 took approximately 30 min, showing that due to vectorization the expected increase in computer time of $O(N^3)$ (with N being the number of particles, see also Durlofsky *et al.*, 1987) could be drastically reduced.

III. RESULTS AND DISCUSSION

A. General considerations

First the proper functioning of the computer programs was checked by reproducing open and closed two-sphere trajectories, as computed by Batchelor and Green (1972). Agreement was found to be excellent. Also some hard sphere simulations were performed, and compared with the monolayer simulations of Brady and Bossis (1985) and with experimental results (Pätzold, 1980; van der Werff and de Kruijff, 1989). Areal fractions in the simulations were related to volume fractions by scaling both with their fraction at maximum packing. As maximum volume fraction for the experiments 0.605 (freely sliding hexagonally packed layers) was chosen, the maximum areal fraction was set at 0.785. Agreement was found to be very good. Only at the higher areal fractions ($\varphi_A > 0.5$) was there some discrepancy (30%). This is probably due to the slow convergence of the mobility interactions. To avoid this problem alternative techniques like the Ewald summation (Brady and Durlofsky, 1988) should be used. But since in this study we were mainly interested in the influence of interparticle forces and in the structural changes in the dispersion this was not necessary here. Snap shots of the hard sphere simulations showed that, as expected, indeed cluster formation takes place. As the volume fraction becomes higher, the clusters become larger and more dense. Sometimes even a cell spanning cluster could be observed, resulting in temporarily very high viscosities.

Starting configurations were generated by a Monte Carlo procedure for placing disks in a plane with their centers in a rectangular area, avoiding overlapping. The influence of

FIG. 1. Equilibrium configuration resulting from a monolayer simulation at zero shear rate and without Van der Waals forces. $\kappa a = 10$.

the starting configuration on the final microstructure and viscosity was checked. It was found to be of almost no influence on the microstructure and to produce only a small statistical spread in the viscosity results (approximately 4% spread).

Without shear some particle configurations were left to relax from a starting configuration to an equilibrium configuration. A typical result is given in Fig. 1 for a value of $\kappa a = 10$, without Van der Waals forces. It can be seen that all particles are at a certain distance from each other but that no obvious ordered structure exists. When this configuration was used as starting configuration for dynamic simulations again no marked influence of starting configuration was detected.

Since we performed simulations on a monolayer of particles the convergence problems associated with the long-range hydrodynamic interactions are less important than in the three-dimensional case (Bossis and Brady, 1989). Thus no methods to improve convergence, like the previously mentioned Ewald sum, are needed. It is, however, important to check for the influence of the number of particles. It was found that especially for well-stabilized dispersions at low shear rates, the number of particles is unimportant down to 25 particles (lower numbers were not checked). For higher shear rates and for hard sphere interactions at higher volume fractions this is not always the case, as will be discussed below. A number of particles of 49 was found, however, to be high enough to avoid convergence problems in these simulations. Convergence problems and influence of number of particles showed mostly in differences in the calculated relative viscosity or in the nonpositive definiteness of the mobility matrix, halting the simulations.

In most cases the dimensional time step was of the order of $10^{-3}\dot{\gamma}^*/\dot{\gamma}$ for $\dot{\gamma}^* \leq 1$ and $10^{-3}/\dot{\gamma}$ for $\dot{\gamma}^* > 1$. In Tables III–V (see below) the characteristics for the different simulations are given, together with the dimensionless time step, the number of steps, and the number of particles used in the specific simulations. When runs were performed several times from different starting configurations, this is indicated also by, e.g., a “2×” placed behind the number of steps. Averaging for the viscosity was done usually with the last 5000 steps. With the time steps used sometimes overlap of particles was seen. This overlap could be avoided by using a smaller time step. To avoid excessive computing times, however, a small amount of overlap (maximally 1% of the particle radius) was

TABLE III. Simulation characteristics for electrostatically stabilized dispersions without Van der Waals attraction, $\varphi_A = 0.5454$.

Run	N	Δt	N_{steps}	$\dot{\gamma}^*$	κa	η_r
ES1	25	10^{-2}	20 000	0.1	10	2.33
ES2	25	2×10^{-3}	30 000	0.5	10	2.16
ES3	49,25	10^{-3}	30 000(3 $\times$)	1.0	10	2.59
ES4	25	10^{-3}	30 000	2.0	10	3.35
ES5	25	10^{-3}	30 000	2.5	10	4.3
ES6	49,25	5×10^{-4}	60 000(2 $\times$)	5.0	10	5.71
ES7	25	10^{-3}	30 000	8.0	10	7.45
ES8	49,25	10^{-3}	30 000(3 $\times$)	10.0	10	9.67
ES9	49	10^{-3}	30 000	100.0	10	14.3
ES10	49	10^{-2}	60 000	0.01	1	4.89
ES11	25	10^{-2}	30 000	0.1	1	4.93
ES12	25	10^{-3}	20 000	1.0	1	9.23
ES13	49	10^{-3}	30 000	10.0	1	15.7
ES14	25	10^{-2}	200 000	0.01	100	3.01
ES15	49	10^{-2}	20 000	0.1	100	3.17
ES16	49	10^{-3}	20 000	1.0	100	3.26
ES17	49	10^{-3}	40 000	10.0	100	3.28
ES18	49	10^{-3}	35 000	25.0	100	4.87
ES19	49	10^{-3}	30 000	100.0	100	12.34

TABLE IV. Simulation characteristics for electrostatically stabilized dispersions with Van der Waals attraction, $\varphi_A = 0.5454$, $\kappa a = 10$.

Run	N	Δt	N_{steps}	$\dot{\gamma}^*$	F_{AR}^*	η_r
VW1	25	10^{-2}	20 000	0.1	4.54×10^{-25}	2.38
VW2	25	10^{-3}	20 000(2 $\times$)	1.0	4.54×10^{-25}	3.24
VW3	25	10^{-3}	20 000	2.5	4.54×10^{-25}	4.51
VW4	25	10^{-3}	20 000(2 $\times$)	5.0	4.54×10^{-25}	8.01
VW5	25	10^{-3}	20 000(2 $\times$)	10.0	4.54×10^{-25}	13.5
VW6	49	10^{-3}	30 000	100.0	4.54×10^{-25}	29.2
VW7	49	10^{-3}	40 000(2 $\times$)	1.0	4.54×10^{-5}	2.93
VW8	49	10^{-3}	20 000	2.0	4.54×10^{-5}	18.3
VW9	49	10^{-3}	20 000(2 $\times$)	5.0	4.54×10^{-5}	48

TABLE V. Simulation characteristics for electrostatically stabilized dispersions without Van der Waals attraction, $\varphi_A = 0.4647$, $\kappa a = 10$.

Run	N	Δt	N_{steps}	$\dot{\gamma}^*$	η_r
LV1	25	10^{-2}	30 000	0.01	1.98
LV2	25,49	10^{-2}	20 000(2 $\times$)	0.1	2.12
LV3	25,49	10^{-3}	30 000(2 $\times$)	1.0	2.27
LV4	49	10^{-3}	30 000	5.0	2.71
LV5	49	10^{-3}	40 000	10.0	3.79
LV6	49	10^{-3}	40 000	25.0	3.95

FIG. 2. Relative viscosities of sheared monolayers plotted against dimensionless shear rate for different values of κa . No Van der Waals forces were present and $\phi_A = 0.5454$. (▼) $\kappa a = 1$; (+) $\kappa a = 10$; (●) $\kappa a = 100$.

allowed. In case of overlapping particles, for the computation of their velocities these particles were considered to be separated by a gap of 10^{-8} times the particle radius. With simulations with a smaller time step it was checked that this procedure had no noticeable influence on particle configuration and dispersion viscosity.

B. Simulations of the flow of repulsive particles without Van der Waals forces at a fixed volume fraction

In Table III we give the parameters for the simulations at different values of κa and $\dot{\gamma}^*$, and the corresponding values of the relative viscosities. In Fig. 2, these viscosities (which are the total viscosities, i.e., the sum of all the contributions to the viscosity) are plotted as a function of $\dot{\gamma}^*$. In all these flow simulations the areal fraction was 0.5454 and Van der Waals attraction was ignored. For the electrostatic repulsion the constant surface potential assumption was used (Boersma *et al.*, 1990).

The evolution of the microstructure was observed visually in all cases. It appeared possible to distinguish different types of microstructures which developed during the shearing process. The main types found were crystal-like (A), layered structures (B), imperfect layered structures (C), more random structures in which strings of particles were visible (D), and situations in which clusters of particles occurred (E). These observations are summarized in Fig. 3. The evolution of a crystal-like structure or of a layered structure proceeded rapidly, typically after one deformation unit. On the other hand it often required ten or more deformation units before it became clear which of the other structures (imperfect layers, strings, clusters) would prevail. In cases where no single structure type could be defined this may be due to the limited length of the flow simulation (typically 10–20 deformation units). It may be that in such cases a more extended simulation would have led to a single flow structure.

All dispersions investigated show shear thickening. At very high shear rates with all double layer thicknesses, the viscosities approach the corresponding value of a hard sphere dispersion ($\eta_r = 14.9$) as found in a separate simulation.

FIG. 3. Structures in shear flow simulations of dispersions in monolayers, in the absence of Van der Waals forces, for various values of κa and $\dot{\gamma}^*$. *A* = crystal-like structure; *B* = layered structure; *C* = imperfect-layer structure; *D* = structure with strings; *E* = cluster structure. *D/E* [or *D(E)*] indicates that structures *D* and *E* could be noticed with no [or some] preference for *D*. The dashed line marks the border between the areas with and without shear thickening. The drawn lines connect different points with the same structure.

First we will discuss the dispersion with $\kappa a = 10$. At very low $\dot{\gamma}^*$ the particles are arranged in a crystal-like structure (see Fig. 3) in which the crystal(s) tumble(s) due to the deformation imposed. A typical arrangement is shown in Fig. 4(a).

At higher shear rates the particle arrangement is in layers parallel to the flow direction. As an example a snapshot is shown in Fig. 4(b). In some cases one can observe temporary columns of particles directed approximately in the shear gradient direction [Fig. 4(c)]. This apparently is due to the fact that when particles in adjacent layers pass each other, the local flow resistance increases. This leads to stagnancy in a number of layers which now slide over each other only very slowly. Temporarily the shear is concentrated in one or two other layers until the blockage in the previously mentioned layers is broken up.

With again higher shear rates the layered structure is still preserved but the distance between the layers decreases. As an example in Fig. 4(d) a snapshot of this arrangement is given: in simulations with 49 particles the arrangement within the central flow cell of 49 particles changes from seven layers of seven particles into eight layers with five, six, or seven particles. The layers with five (six) particles look like layers containing seven particles but with two (one) particles missing; we denote these as "imperfect layers."

When comparing these observations with the experimental observations of Tomita and van de Ven (1984) using diffraction techniques it is remarkable that they observed an increase in distance between the layers with increasing shear rate, while in our simulations a decrease is seen. A possible explanation for this discrepancy is the two-dimensional nature of our simulations. One could easily imagine that these rather subtle changes in particle configuration can be severely influenced by the imposed two-dimensional flow. To study this phenomenon more closely three-dimensional simulations are necessary and no firm conclusions can be drawn at this point.

FIG. 4. Visual assessment of the microstructures in shear flow of monolayers with $\kappa a = 10$. (a) crystal-like structure at $\dot{\gamma}^* = 10^{-2}$; (b) layered structure at $\dot{\gamma}^* = 0.5$; (c) occurrence of columns of particles for a layered structure at $\dot{\gamma}^* = 0.5$; (d) imperfect layers at $\dot{\gamma}^* = 1$; (e) arrangement with strings at $\dot{\gamma}^* = 2.5$; (f) clusters at $\dot{\gamma}^* = 10$.

FIG. 5. Projected densities around a central particle for a dispersion in a monolayer under shear, for various values of κa and $\dot{\gamma}^*$, in the absence of Van der Waals forces.

FIG. 6. Influence of Van der Waals attraction on the relative viscosity of sheared monolayers. (+) no Van der Waals attraction; (▲) $F_{AR}^* = 4.54 \times 10^{-25}$; (◆) $F_{AR}^* = 4.54 \times 10^{-5}$.

At still higher shear rates the layered structure is unstable, particles of adjacent layers “collide” and form strings of particles [as an example see Fig. 4(e)]. The strings are often curved; their orientation is random as judged visually. These strings are rather persistent; they rotate and do not easily break up if they become oriented in the extensional direction of the shear.

At the highest shear rates investigated here, two-dimensional clusters are formed [see Fig. 4(f)]. These clusters are rather persistent but occasionally break up and form new clusters. The transition between strings and clusters is a smooth one.

With $\kappa a = 1$, similar phenomena as with $\kappa a = 10$ can be seen, except for two aspects. The first difference is that the transitions between the different types of microstruc-

FIG. 7. Snap shot of a highly clustered state in a sheared monolayer simulation, due to van der Waals attraction. Note the relatively open structure.

FIG. 8. Influence of the areal fraction on the flow curve of a sheared monolayer. ($\blacksquare$) $\varphi_A = 0.4647$; (+) $\varphi_A = 0.5454$, $\kappa a = 10$, no Van der Waals attraction.

tures take place at dimensionless shear rates that are now lower by a factor of ten. The second difference is that the hexagonal, crystal-like structure with $\kappa a = 1$ is less stable than that with $\kappa a = 10$.

With $\kappa a = 100$ neither crystal-like nor layered structures could be observed. Over an extended range of shear rates the type of arrangement of particles was between imperfect layers and strings: repeatedly an imperfect layer structure could be noticed which after some time disappeared due to strings that became visible for some time. At higher shear rates the cluster type was visible. These clusters, however, appeared to be less compact and less tightly bound together, presumably due to the relatively high repulsion forces at small distances (the repulsive force at small distances increases with decreasing double layer thickness, if the surface potential is kept constant).

The microstructures for the different conditions have also been analyzed in terms of the time-averaged projected densities around a central particle. In Fig. 5 a collection of such projected density surfaces is given.

With $\kappa a = 1$ as well as with $\kappa a = 10$ at the lowest shear rates the value of the viscosity becomes dominated by the ever increasing contributions of the interparticle forces. When Eq. (6) is written out in nondimensional form for the monolayer simulations the contribution to the total relative viscosity η_r due to the interparticle forces becomes (Brady and Bossis, 1985)

$$\eta_{r,F} = -\frac{3\varphi_A}{\dot{\gamma}^*} \frac{1}{N} \sum_{\alpha=2}^N \sum_{\beta < \alpha} \hat{r}^{\alpha\beta} \hat{F}_r^{\alpha\beta} \frac{\sin 2\psi_{\alpha\beta}}{2}, \quad (16)$$

where $\psi_{\alpha\beta}$ is the angle between particles α and β measured relative to the x axis with particle α at the origin. The caret denotes nondimensionalization. As can be seen $\eta_{r,F}$ scales with $1/\dot{\gamma}^*$, so when $\dot{\gamma}^*$ becomes very small, for the same configuration, $\eta_{r,F}$ becomes very large. In the trace of viscosity as a function of time this results in large oscillations, making the viscosity value difficult to analyze. Therefore these values have not been plotted in Fig. 2 [note that such oscillations have been found experimentally (Boersma *et al.*, 1991)]. The averaged viscosity at low shear rates seems, however, to be much higher than the one at high shear rates. This indicates that there might be a yield stress due to the interparticle forces. This is supported by the microstructure observed

under these conditions. The particles are arranged in a regular packing (especially with $\kappa a = 10$), whose orientation and persistence length are variable due to the imposed shear. We denote these as "liquid crystals." As Brownian motion was not taken into account the particles in this crystal have a zero self-diffusion coefficient. The stronger repulsive interparticle forces at $\kappa a = 1$ are also responsible for the higher viscosity value at low shear rates as compared with the $\kappa a = 10$ simulations. The higher values for the $\kappa a = 100$ simulations are due to the absence of a layered structure.

Finally, it can be seen that the shear rate at which shear thickening starts shifts to higher values of $\dot{\gamma}^*$ as the value of κa increases. The onset of shear thickening coincides with the occurrence of strings. String formation is prevented as long as the repulsion between two touching particles is strong enough. It is evident that at a constant surface potential the repulsive force at zero distance increases with increasing κa . The observed loss of order prior to shear thickening is in agreement with the light-scattering results of Chow and Zukoski (1995b).

C. Influence of Van der Waals attraction

Table IV lists the characteristics of the runs which included Van der Waals attraction. All runs were again performed at an areal fraction of 0.5454, while the value of κa was 10. The value of λ was chosen to be 2×10^{-7} m (see Table II), giving a value of $\lambda/a = 0.2484$. For the Van der Waals forces two different levels were studied. First of all, a realistic level, using the data in Table II, giving a value of F_{AR}^* [Eq. (11)] of 4.54×10^{-5} , and second, a value of F_{AR}^* of 4.54×10^{-25} . This second level was used to check the influence of a very small attractive force.

In Fig. 6 the results for the relative viscosity are shown as a function of dimensionless shear rate. It can be seen that up to the shear rate at which shear thickening starts there is no difference. Only at shear rates above $\dot{\gamma}_s^*$ the Van der Waals attraction results in a large increase of the viscosity. Even the very weak attraction already gives a viscosity increase of a factor of 3. The explanation of these high viscosity values lies in the fact that, when the cluster formation due to hydrodynamic forces takes place, the repulsive barrier is overcome and the attractive forces then keep the particles very strongly together. The highly connected, cell spanning clusters created in this way give rise to very large viscosities and also very high peaks are visible in traces of viscosity versus time. The clusters formed are much more open than the clusters formed with the hard sphere dispersions. They are, however, cell spanning and the connection between the particles in the clusters is much stronger. In Fig. 7 an example of a snap shot of such a highly clustered dispersion is shown.

In this context it is important to note that when the realistic values for the Van der Waals attraction were used the simulations started to show severe particle overlap, causing the calculations to halt. Also the simulations became very sensitive to the magnitude of the time step, indicating that they lost their quantitative value. It seems, however, that attractive forces can very well be held responsible for the very strong increase in viscosity found in experiments on shear thickening dispersions (Barnes, 1989; Hoffman, 1972; Boersma *et al.*, 1990).

D. Influence of the areal fraction

In Table V and Fig. 8 the characteristics and results of simulations with a different areal fraction are shown. For comparison in Fig. 8 the results for the higher areal fraction are also plotted. Although it is difficult to judge it seems that the shear thickening

FIG. 9. Comparison of rescaled viscosities from simulations of sheared monolayers with a typical experimental result for shear thickening in a 3D system. (▲) experiment; (▼) $\kappa a = 1$; (+) $\kappa a = 10$; (●) $\kappa a = 100$.

transition occurs at a higher shear rate for the less concentrated dispersion. Also the whole viscosity level is lower, and the high shear limit is again in accordance with the hard sphere viscosity.

At this lower areal fraction layer formation is very pronounced at the lower shear rates. Just as with the higher areal fraction at the values of $\kappa a = 1$ and $\kappa a = 10$, a transition from closely packed layers ($\dot{\gamma}^* = 0.01$), via less closely packed layers ($\dot{\gamma}^* = 0.1$), to strings ($\dot{\gamma}^* = 1; 5$), and clusters ($\dot{\gamma}^* = 10; 25$) could be observed.

E. Comparison with experimental results

It is interesting to compare these simulation results with experiments. Recently it was shown (Boersma *et al.*, 1990) that when performing experiments on electrostatically stabilized dispersions the shear rate for the shear thickening transition could be predicted from a force balance between stabilizing electrostatic and destabilizing hydrodynamic forces. When using the asymptotic formulas for these forces the shear rate at which shear thickening starts could be given as

$$\dot{\gamma}_s = \frac{2\pi\epsilon_0\epsilon_r s_0^2 \kappa h}{6\pi\eta_0 a^2} \frac{\kappa h}{2}, \quad (17)$$

where h , the distance between the spherical particles in a hexagonally close-packed arrangement, can be related to the volume fraction by

$$\frac{h}{a} = \left(\frac{8\pi}{3\sqrt{3}\phi} \right)^{1/3} - 2. \quad (18)$$

Here it was assumed that the particles are ordered in layers and that the distance between the layers is the same as the distance between the particles in a layer. The maximum volume fraction for such a flowing dispersion is 0.605. This analysis by Boersma *et al.* (1990) was restricted to very high volume fractions for which $\exp(-\kappa h)$ in the equation for the repulsive force could be approximated by unity.

From the simulations we learn that shear thickening is not related to the destruction of layers (as supposed by Boersma *et al.*, 1990), but primarily to the generation of strings

and/or clusters. Although both phenomena may be closely related (at $\kappa a = 1$ and $\kappa a = 10$), this is not always the case. Based on these observations in what follows we will develop a model in which we balance the hydrodynamic force on a particle joining a string with the electrostatic force on this particle.

We start with stating that shear thickening occurs when the electrical repulsive forces no longer suppress the formation of strings and/or clusters. Thus the criterion for shear thickening becomes that the electrical repulsive force at $h \rightarrow 0$ is of the order of the hydrodynamic force between two colliding particles (A and B). The evaluation of the latter force seems to be difficult due to the fact that the relative velocity $v_A - v_B$ of two colliding particles is unknown. However, both particles are in a shear flow and surrounded by other particles (e.g., particles $C, D, E, \dots$). The average distance between either of the two colliding particles (e.g., A) and the nearest surrounding particle (particle C) is of the order of h . The order of magnitude of the corresponding hydrodynamic force F_{AC} will be $6\pi\eta_0 a^3 \dot{\gamma} / h$ (see Boersma *et al.*, 1990). This force will be of the same order of magnitude as F_{AB} , because the total sum of forces on particle A has to be zero. That force (F_{AB}) should, in the framework of our model, be compared with $F(h \rightarrow 0)_{\text{repulsive}} = \pi\epsilon_0\epsilon_r \kappa a$. This leads to precisely the previously derived Eq. (17). But contrary to the previous model, it now appears that this equation also holds for the lower volume fractions as investigated in the simulations.

For a monolayer Eq. (18) becomes

$$h/a = \left(\frac{\pi}{\varphi_A} \right)^{1/2} - 2 \quad (19)$$

with an implicit maximum areal fraction of 0.785. We can rewrite Eq. (17) in terms of the dimensionless shear rate $\dot{\gamma}^*$; thus the critical dimensionless shear rate $\dot{\gamma}_s^*$ at which shear thickening starts becomes

$$\dot{\gamma}_s^* = \frac{\kappa a}{2} \frac{h}{a}, \quad (20)$$

where h/a is given by Eq. (19). For our simulations κa equals 1, 10, and 100 and, in case of $\varphi_A = 0.5454$, $h/a = 0.400$. This gives values for $\dot{\gamma}_s^*$ of, respectively, 0.2, 2, and 20. As can be seen in Fig. 2 this compares very well with the simulations, indicating a good agreement between experiment, theory, and simulations for the value of the shear rate at which shear thickening starts.

It is possible to rescale simulations and experiments on electrostatically stabilized, shear thickening dispersions against $N_d = 2\dot{\gamma}_s^* a / (\kappa a h)$. Shear thickening should then take place when N_d becomes larger than unity. In Fig. 9 the results for the different simulations are plotted against N_d . Also an experimental result of a polystyrene dispersion in glycerol/water (Boersma *et al.*, 1990) is plotted. Although the volume fraction of the experiment is much higher than the volume fraction corresponding to the simulations, resulting in very different quantitative values for the relative viscosities, it can be concluded that both simulation and experiment show the same qualitative behavior and that shear thickening can be scaled very well with N_d .

IV. CONCLUSIONS

It has been shown that with the Stokesian Dynamics method simulations can be performed of which the trends in the results compare qualitatively well with trends in experiments. Insight can be obtained in the mechanisms determining the shear thickening

transition with electrostatically stabilized dispersions and it can be concluded that the expected order-disorder transition is visible in the simulations. Above the shear rate at which shear thickening occurs hydrodynamic forces induce cluster formation and these clusters give rise to the high viscosities. These high viscosities compare very well with experimental results on the high shear limit of hard sphere dispersions. When Van der Waals attraction forces are present the clusters are more open but even more strongly connected and the resulting viscosities increase in magnitude. Van der Waals forces sharpen the shear thickening transitions.

The simulations indicate that the dependence of shear thickening on volume fraction, and double layer thickness is as expected from the theoretical predictions, and that the predictive equation for shear thickening also holds for lower volume (or areal) fractions. Also its dependence on particle size, medium viscosity, and ζ potential follows naturally from the simulations and is in accordance with the expected results. Furthermore the simulations indicate that shortly before the shear thickening transition the distance between the layers decreases. This is in contradiction with experimental results. A possible explanation is the two-dimensional nature of these monolayer simulations.

Finally it can be said that these simulations have proven to be a powerful tool in obtaining insight into the evolution of the dispersion structure and in determining the influence of the different parameters. Comparison of simulation trends with experimental trends is remarkably good, especially when taking into account the fact that only monolayers were simulated. With the availability of even faster computers three-dimensional simulations become possible and it can be expected that the quantitative agreement in the relative viscosity will become higher.

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