Research Article

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Stochastic transient Liquid-Solid Phase Separation reveals multi-level Dispersion States of Particles in Suspension

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Abstract: Wall slip or, more usually, liquid-solid phase separation at the boundary wall when measuring the rheological properties of particulate suspensions is normally considered an undesirable source of error. However, exclusion of a structure consisting of multiple particulates at a planar boundary can, in turn, reveal the nature of that structure and the way it interacts with other elements in the dispersion. Using a system of surface-treated ground calcite particles, designed to control lyophilicity, dispersed, respectively, in two comparative liquids, hexadecane (dispersive surface tension component only) and linseed oil (both dispersive and polar surface tension components), the relative wettability of the particulate surface can be studied. The static state is viscoelastic, with the elastic component reflecting the network of interacting forces acting to structure the particles together and/or to trap liquid within the long-range particle-particle matrix. As strain is applied under plate-plate geometry, selected aggregate structures become size-excluded at the wall, leading to a loss of shear coupling with the bulk polydisperse suspension. At high strain, given optimal solids content, this results in a stochastic transition between two discrete stress data sets, *i.e.* that with full shear coupling and that with only partial coupling. Stress recovery is subsequently monitored as strain is step-wise reduced, and the progress

toward loss of the stochastic transient phenomenon, together with its parallel change in magnitude, is used to describe the re-formation of primary agglomerates. Cessation of the phase separation indicates re-build of the close-to-static structure. Under certain conditions it is observed that the cessation may be accompanied by a secondary relaxation of state, indicating the build of a secondary but weaker structure, likened to the well-known dual-level flocculation in aqueous colloidal suspension. Rheo-optical observations using small angle light scattering illumination (SALS) are used to confirm a structure model switching from static (uncoupled with shear) to rotating (fully coupled to the boundary-defined shear) and finally uniformly sheared.

Keywords: liquid-solid phase separation, particulate structures in suspension, dispersibility of particles in liquids, colloidal structure formation, stochastic structures, rheology of suspensions, surface wettability in dispersed systems, rheo-optical structure analysis

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1 Introduction

The study of suspension rheology is full of examples where experimental measures are taken to ensure accurate, reproducible equilibrium rheometrical conditions. The behaviour of suspensions differs from that of homogeneous liquids. Stable colloidal dispersions, in which the particles are steric or charge stabilised, such that they remain discrete, and the liquid phase is free of other additives, so they can flow according to Stokesian dynamics, display effects dependent strongly on the solid phase particle concentration [1, 2]. More complex colloidal systems, however, display properties of particle-particle and particle-liquid interaction, to include flocculation and shear-induced aggregation, and apparent wall-slip [3–5]. Similarities are often falsely drawn, however, with the breakdown of the zero-velocity differential contact, *i.e.* contact discontinuity,

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at the sample-boundary wall interface shown by polymer melts, the latter being genuine wall-slip [6, 7]. The phenomenon seen in flocculated and structured colloidal suspension systems is more generally that of solids depletion by size or structure exclusion at the wall, resulting in an enrichment of the liquid phase and depletion of the solid phase, with the result that the observer measures the rheology of the thin liquid-rich layer, which either matches that of the liquid alone, usually Newtonian, or that of the liquid containing fine colloidal particles that have not been size excluded, usually thixotropic [8, 9]. In each case, the coupling of shear with the bulk suspension is either lost by potential shear banding or compromised by coupling via a progressive increase in polydispersity (inclusion of coarse component) as a function of distance from the wall; topics, which have been discussed widely in the scientific literature and reviewed by Divoux *et al.* 2016 [8].

In all cases of discontinuity or phase separation at a boundary, the system generally becomes unstable, except where the sample-wall separation is totally complete or that only the single phase is present in contact with the wall. The dynamic state at the sample-wall boundary is dependent on particle diffusion within the sample and/or the discontinuous or varying application of shear strain, and, hence, depending on timescale, either rotational coupling with asymmetric agglomerates or, if locally turbulent, non-uniform streamlines will lead to stochastic ingress of particles into the boundary layer. When this happens, stress coupling to within the bulk sample is momentarily restored. Under such circumstance, statistically random observations between these two states of solids depletion and solids coupling will occur. We propose, however, rather than discarding such a random two-state observation, to use this phenomenon of stochastic exclusion of a large structure consisting of multiple particulates at a planar boundary to reveal the nature of that structure and the way it interacts with other structural elements in the dispersion.

Our study generates the conditions of solids depletion at the wall by considering the effects of surface wettability of suspended particles by the host liquid in a particulate suspension. Using a system of variously surface treated ground calcite polydisperse particles, to control hydro- and oleophilicity, and so lyophilicity when dispersed, respectively, suspended in two comparative liquids, hexadecane (a pure alkane with dispersive surface energy component only) and linseed oil (vegetable derived, displaying both dispersive and polar surface energy components), the relative impact of wettability of the particulate surface by the suspending liquid can be studied rheometrically, in respect to particle-particle and particle-liquid interactions.

Depending on the aggregation state of the dry powder material prior to dispersing, applying shear to the suspension acts to a varying degree to separate particles into a dispersed or semi-dispersed state. In addition, arising from the various degrees of wettability, contrasting particle-particle structures are formed ranging from strongly aggregated material in the case of poor wettability of the surface, through a state of various levels of agglomeration, including both strongly and weakly attracting forces, to virtually complete particle-particle separation. Rheometric conditions are chosen to produce transient stochastic solids depletion at the wall under smooth plate-plate geometry. Monitoring the occurrence of this phenomenon we propose a particulate model to account for the behaviour, likened to the well-known dual-level flocculation in aqueous colloidal suspension (DLVO description) [9–11]. Rheo-optical observations, employing small angle light scattering illumination (SALS), are used to confirm the structure model response under shear.

2 Materials and methods

Two organic suspending liquids were chosen having contrasting properties of surface tension, in respect to both polarity and dispersivity and viscosity, to provide a range of conditions for exploring the wettability and subsequent dispersibility of polydisperse ground calcium carbonate particles (GCC), either in their natural open environment aged surface state or having been surface treated by adsorbed fatty acid under controlled environmental conditions of low humidity and elevated temperature.

The chosen liquids were (i) n-hexadecane (pure alkane), displaying a completely dispersive surface tension ($29.32 \text{ mN}\cdot\text{m}^{-1}$ at room temperature) and low viscosity (2.4 mPas), and (ii) linseed oil (vegetable oil, also known as flaxseed oil or flax oil), a colourless to pale yellow oil obtained from the seeds of the flax plant, displaying both significant dispersive and small retained polar components of surface tension ($23.2 \text{ mN}\cdot\text{m}^{-1}$) [12]. Linseed oil is a multicomponent oil consisting of triglycerides, acting like fats together with fatty acids, Table 1, as reported by Vereshagin and Novitskaya 1965 [13].

Calcium carbonate, being naturally an alkaline material, which, in water, buffers to pH 8.5–9.0, reacts at the particle surface in the presence of traces of moisture with molten fatty acids, such as palmitic and stearic acid, to form a complex coating layer consisting of calcium fatty acid salt and unreacted wax-like acid, *i.e.* partially chemisorbed and partially physisorbed [14]. This coating

Table 1: n-hexadecane and linseed oil typical composition and properties [12, 13]

n-hexadecane		Viscosity, η / mPas 2.4	Surface tension (liquid-vapour) / mN·m ⁻¹				
			dispersive 29.3		polar 0		
linseed oil		Viscosity, η / mPas	Surface tension (liquid-vapour) at 20°C / mN·m ⁻¹				
Component	Content /%		dispersive		polar acid-base* (Lewis acid)		
			total, σ_{LV}	Lifshitz van der Waals, σ_{LV}^{LW}	σ_{LV}^{AB}	components	
						acid, σ_{LV}^{+}	base σ_{LV}^{-}
doubly unsaturated linoleic acid	14.2-17.0	25.4	23.2	21.2	2.1	0.1	16.8
triply unsaturated α -linoleic acid	51.9-55.2						
monounsaturated oleic acid	18.5-22.6						

$\sigma_{LV}^{AB} = 2\sqrt{(\sigma_{LV}^{+} \cdot \sigma_{LV}^{-})}$: experimental surface tension data rounded to 1 decimal place [23]

renders the otherwise moisture attracting calcium carbonate surface hydrophobic, and thus, given the nature of the coating, lyophilic. Interestingly, the surface coverage of the chemisorbed stearate in the presence of excess water, determined by Shi *et al.* 2010 [15] using differential scanning calorimetry, is about 3.25 w/w%, much lower than the theoretical full monolayer coverage (4.17 w/w%), and confirmed using surfactant sorption and gas chromatography for the set of particles they studied. This was explained as being due to micelle formation of the fatty acid in water prior to adsorption, considered to differ from the case of adsorption from the melt state under essentially dry conditions, as used in the case studied here [16–19]. However, for chemisorption to occur the surface must at some stage become ionised, and it is hypothesised that this can only occur in the presence of, albeit minute, traces of moisture, such that, if this is the case, there remains a duality of surface behaviour between incomplete hydrophobicity and the coating-induced lyophilicity. Comparing the dispersibility of such particles in contrasting organic liquids can, therefore, reveal particle-particle interactions competing to destabilise the dispersion depending on the nature of the liquid.

The totally dispersive nature of the surface tension of hexadecane, therefore, will be compatible with the fully lyophilised surface regions on the GCC particles, whereas the mix of high dispersive surface tension component and the significant Lewis base (anionic equivalent) component in the polar part of the linseed oil surface tension (about 10% of the total) will exhibit a tendency toward amphiphilic behaviour. Furthermore, in this respect, when suspending uncoated calcium carbonate in linseed oil (pH ~6-8) some degree of selective carboxylic group adsorption via calcium chelation can be expected.

The GCC used in this study was sourced from Omya International AG. The raw marble from Italy was wet ground chemical-free and subsequently dried. The material particle size was analysed using two distinct methods: (i) providing an equivalent spherical hydrodynamic particle diameter under sedimentation dispersed in water (sodium polyphosphate used as dispersant) using Stokes' law (Sedigraph®, Micromeritics, Norcross, GA, USA), expressing the size distribution in terms of weight per cent finer than, and (ii) by determining the volume defined time-averaged laser light scattering cross-section in powder form (Malvern 2000, Malvern Panalytical Ltd, Enigma Business Park, Malvern, U.K.). In each case, two values were extracted from the size distribution and reported in Table 2, namely, the largest representative size as the diameter d_{98} at which (i) 98 w/w%, (ii) 98 v/v%, of the particles are finer than this value, and the (i) weight median d_{50} , (ii) volume median, size at which 50 w/w%, respectively v/v%, of the particles are finer than this value. For particulate samples that display the same density throughout the size distribution, the units w/w% and v/v% are naturally equivalent.

Surface treatment was made under controlled laboratory conditions, starting by pre-conditioning the GCC for 10 min at an elevated temperature of 120°C to provide a hot surface. Molten fatty acid 1 (1:1 mixture of palmitic and stearic acid) was applied to the particles under vigorous mixing (1 000 min⁻¹ (rpm)) using a Somakon MP-LB high shear unit (Somakon Verfahrenstechnik UG, Moltkestraße 11, 44536 Lünen, Germany), fitted with a scraper rotating counter to the mixing element to prevent build-up of agglomerates on the mixer walls. The machine settings quote mixer and scraper speeds (1 000 min⁻¹ and 40 min⁻¹ (rpm) in this case, respectively – see Table 2). Fatty acid

Table 2: Properties of the GCC filler prior to and after surface treatment, including conditioning and moisture pick-up.

Sample preparation conditions		
Pretreatment conditioning	conditioning time / min	10
	conditioning temperature T / °C	120
	mixer speed / scraper speed /min ⁻¹ (rpm)	1 000 / 40
Treatment step	Sample naming	(untreated) UT GCC
	treatment time / min	-
	mixer speed / scraper speed /min ⁻¹ (rpm)	1 000 / 40
	treatment agent	-
	treatment level / w/w%	0 (untreated)
Analysis		
	PSD* (Sedigraph [®])	
	$d_{50}/\mu\text{m}$	2.06
	$d_{98}/\mu\text{m}$	7.00
PSD* (Malvern 3000 [®]) (4 bar)	$d_{50}/\mu\text{m}$	2.03
	$d_{98}/\mu\text{m}$	8.50
	BET / m ² g ⁻¹	3.2
	water pick-up / mg·g ⁻¹ (single measurement)	1.51
Specific surface area, SSA	moisture at 105 °C / w/w%	0.05
	weight loss 105 to 400 °C / w/w%	0.09
	free (non-adsorbed) treatment agent / w/w%	not relevant
Water pick-up		
TGA		
Treatment analysis		

*PSD = particle size distribution as weight[®] / volume[®]%

(fatty acid treated – surface adsorbed) SA GCC 15 1 000 / 40

Fatty acid mixture (1:1 palmitic:stearic acid) 1.00

dose was calculated in respect to specific surface area (SSA) as measured using nitrogen gas adsorption (BET method) [20], with a target coverage of 100%. The residual non-chemisorbed fatty acid was determined using non-aqueous titration on the treated sample with an ethanolic KOH solution (concentration $0.1 \text{ mol} \cdot \text{dm}^{-3}$). The total amount of fatty acid was recorded by thermogravimetric analysis (TGA), and the difference between total amount of fatty acid and “free” fatty acid assumed to be chemisorbed fatty acid. In addition, moisture loss was recorded as a function of temperature, again using TGA, and the moisture pick-up from bone dry under controlled humidity conditions determined using a Gintronic Gravitest 6300 device recording the weight increase in $\text{mg} \cdot \text{g}^{-1}$ when changing from a 10% RH controlled atmosphere to 85% RH, all at 23°C .

To evaluate a potential effect arising from the likely species adsorption via Lewis acid-base interaction in the case of untreated GCC suspended in linseed oil, a sample of untreated GCC was paste mixed with linseed oil and baked in an oven at 60°C for 48 h. The particles, which effectively became dry varnished, were then ground in a stone pestle and mortar to break up agglomerates glued by the hardened oil.

2.1 Rheometrical analysis

Three regimes of rheological analysis of particle-in-liquid dispersions were applied using an MCR 300 rheometer (Anton Paar GmbH, Graz, Austria), at controlled solids levels. In all cases, parallel plate geometry with upper plate radius 25 mm and gap of 0.3 mm was used, the latter due to the micro (nano)scale of the suspended particles.

The response to shear of the dispersions was recorded as dynamic viscosity, η , plotted as a function of shear rate, $\dot{\gamma}$, ranging logarithmically from $0.01 - 1\,000 \text{ s}^{-1}$. The viscoelastic behaviour, expressed as the elastic storage, G' , and viscous loss, G'' , components of the complex modulus, $\mathbf{G} = G' + jG''$, where $j = \sqrt{-1}$, was investigated applying oscillatory strain, γ (ranging $0.01 - 1\,000\%$), at constant angular frequency, $\omega = 0.1 \text{ s}^{-1} (\text{rad} \cdot \text{s}^{-1})$. The viscoelastic region was determined with amplitude sweep measurements to generate a controlled stress response. Lastly, the stress-induced structure breakdown and recovery response to static strain was investigated using a strain “ramp-up” “ramp-down” sequence $\gamma = 0.1\% \Rightarrow 1\,000\% \Rightarrow 0.1\%$. It is under the latter condition that the stochastic two-state behaviour of the geometric boundary wall-sample solids depletion (apparent slip) and wall-sample

coupling (non-slip) is observed, hypothesised to reveal the state of inhomogeneous dispersion.

The model hypothesis of using random changes of shear state, according to boundary wall depletion or coupling, respectively, to reveal the particle-particle structural interplay with the state of flow, was further tested employing a rheo-optical technique. The aim was to reflect, and so confirm, the mechanistic state of motion of the particulate structural component in the suspension as a function of applied shear [21–23]. Small angle light scattering (SALS) experiments were made on an Anton Paar MCR302 equipped with two transparent parallel glass plates. A laser beam with a wavelength of 658 nm emitted from a diode point source located above the upper moving plate and was shone vertically down through the sheared sample (gap = 0.3 mm) using crossed polarisers, offset from the rotation axis by $\sim 1 \text{ cm}$. Scattering patterns were captured using a CCD camera located underneath the lower static glass plate. SALS causes the light to be scattered coherently by the particles, which is recorded whilst the rotating plate applies shear. Should a structural alignment occur under shear, for example a liquid crystal-like mesophase transition is induced, by applying a light polarising element along the incident light path an inverted polarisation by the sample generates a directed intensity pattern which will appear in the detector related to the collective interparticle and inter-alignment dimensions distributed in space. If, however, the material remains static, then a speckle pattern is observed, and if an isotropic homogeneous particle motion is induced by the shear the light intensity is recorded as being diffuse and evenly distributed over the complete sample.

Under the SALS conditions described above, a shear ramp, $\dot{\gamma} = 0 \text{ s}^{-1} \Rightarrow 500 \text{ s}^{-1} \Rightarrow 0 \text{ s}^{-1}$, enables the observer to determine the shear conditions under which the particulates are either in homogeneous motion in response to the shear or remain static due to boundary depletion (apparent slip) and/or shear banding. At low shear rates, the viscoelastic structure can also either be distorted under the strain, or remain solid whilst the boundary undergoes solids depletion, effectively causing apparent slip whilst retaining the initial static state structure in the bulk. Return to low shear, then reveals the degree of recovery of the structure, which, as we shall see in this case, is incomplete, exhibiting hysteresis throughout, or develops via an intermediary unstable secondary state of structuration. To achieve satisfactory light transmission, low solids suspensions must be used, and so the static viscoelastic structural state at the shear boundary is readily broken down at the start of shear, and apparent slip can readily occur.

3 Results and discussion

The results are reported firstly in respect to contrasting effects between the untreated and treated particle samples in each of the two different suspending liquids separately, and then in terms of the stress-strain response, including structure formation and breakdown, and the relationship between structure and solids depletion at the rheometric boundary providing information on the state of particle-particle aggregation. Example optical microscopy images are presented illustrating the structure relationship in respect to particle surface treatment and wettability in the purely non-polar dispersive liquid, hexadecane. Finally, observations from rheo-optical SALS analysis are discussed in the light of the proposed structural hypotheses.

3.1 Suspension behaviour in dispersive, non-polar, low viscosity hexadecane

The dynamic viscosity of the GCC samples suspended in the pure alkane (hexadecane), η , as a function of shear rate, $\dot{\gamma}$, is shown in Figure 1. It can readily be seen that the treated particles (SA GCC) display a significantly lower viscosity than the untreated (UT GCC), and are thus considerably better dispersed in the non-polar solvent. As solids content of the suspension is increased from 20 w/w% to 80 w/w%, it is also noticeable how both systems increase in their viscosity remaining separated by a decade until the very highest solids content when they cross over at the highest shear rate. Interestingly, this suggests that the untreated (UT GCC) sample does not initially undergo any further aggregation/flocculation as a function of solids content before or during the first stages of shear. However, the data for the UT GCC subsequently begin to show a secondary feature following the initial shear thinning at higher shear rates and higher solids content, indicating that a shear-induced aggregation at higher solids, leading to increased physical interaction, is likely occurring prior to a collective flow phenomenon. The aggregation, so induced, is then seen to support a collective flow behaviour, leading to a re-establishment of shear thinning as shear increases further. That this secondary induced structuration occurs at similar shear over the higher solids content range suggests that structures impacting on each other during flow leads to a dynamic equilibrium between aggregate formation and physical breakdown until the shear energy input starts to exceed that of breakdown to the point where cooperative flow begins, *i.e.* finally, yet higher shear con-

ditions reduce the system energy via collective shear thinning flow. Such features of flow for particles in suspension under shear were modelled by Toivakka 1997 for charge stabilised particles in water, in which the characteristic shear thinning, followed by a region of shear thickening and then further shear thinning under collective flow, as reproduced in the system studied here, was elucidated [24].

In contrast, also Figure 1, the surface treated sample (SA GCC) at the lowest and medium solids content shows a degree of resistance to breakdown of the static structure, and this occurs in two steps. The stability of the dispersion, though greater in comparison to the untreated UT GCC, displays nonetheless significant particle-particle interaction, which is only overcome by running at high solids content such that the shear flow can couple strongly with the particles and force them to flow independently. This contrasts strongly from the behaviour of the untreated UT GCC, in that virtually no secondary structure features are observable once the flow coupling is strong enough at high solids content. Such observations suggest that to achieve good dispersion of even the more compatible SA GCC in the non-polar solvent requires sufficient energy input to establish and maintain stability against particle-particle attraction/interaction. Interestingly, in Figure 1(d) the higher shear viscosity of the untreated (UT GCC) falls below that of the treated sample (SA GCC). Since no material was ejected, this finding indicates the advantage of cooperative flow supported by the somewhat larger aggregates in respect to energy loss, but not, of course, for achieving single particle dispersion, *i.e.* simply applying high shear is a not a successful processing method for dispersing in such a suspension.

Further information on these interactions can be gained from studying the viscoelastic response under oscillation, Figure 2.

Confirming the concept of the need for coupling between the sheared liquid phase medium and the solid phase particles to break the particle-particle cluster interactions, strong in the case of the untreated UT GCC in hexadecane versus weaker between treated (SA GCC) particles, Figure 2 illustrates that at lower solids content, 20 w/w%, the structure of the untreated sample (UT GCC) leads to a short but significant linear elastic region, matched by an increase in the viscous component as the strain induces stress which becomes relieved by viscous loss, manifest as a maximum in the G'' curve. Once the solids content is raised, this effect reduces as particle-particle volume occupancy increases, provided coupling between particles which aids the structure breakdown. The treated sample (SA GCC), therefore, shows this slightly longer region of almost linear elasticity before slowly transferring to viscous

Figure 1: Dynamic viscosity of untreated and surface treated GCC suspensions in hexadecane at increasing solids content: (a) 20 w/w%, (b) 30 w/w%, (c) 50 w/w%, (d) 80 w/w%, and linseed oil e) to h).

flow, although, as was hypothesised from the dynamic viscosity data, there remains a weak stabilising interaction between the particles which progressively yields to allow separate particle motion.

3.2 Suspension behaviour in weakly polar high viscosity linseed oil

Given the higher viscosity of the linseed oil-based dispersions, the dynamic viscosity reveals less readily the state

Figure 2: Viscoelastic properties, G' storage and G'' loss moduli, under strain, $\gamma = 0.01 - 1\,000\%$ at constant angular frequency, $\omega = 0.1\,\text{s}^{-1}$ ($\text{rad}\cdot\text{s}^{-1}$): (a) 20 w/w%, and (b) 40 w/w% and 50 w/w% solids content.

of the particle-particle interactions, and so we concentrate here on the viscoelastic properties under oscillatory strain, under the same rheometric conditions as in Figure 2. The first thing to notice in Figure 3 is that the sample compatibility reverses, *i.e.* the untreated (UT GCC) displays a significantly lower elastic component compared with the fatty acid treated (SA GCC) sample.

At the lowest tested solids, 20 w/w%, the viscous component in Figure 3(a) is mostly defined by the linseed oil itself and so is similarly high in both dispersions, but the elastic component, mostly related to particle-particle interactions, distinctly shows the difference between the untreated and treated samples in this medium. Nonetheless, as mentioned above, the loss modulus remains high in the case of linseed oil because the oil itself is highly

Figure 3: Viscoelastic properties of sample suspensions in linseed oil under oscillatory strain at constant angular frequency, $\omega = 0.1\,\text{s}^{-1}$ ($\text{rad}\cdot\text{s}^{-1}$): (a) 20 w/w%, (b) 50 w/w%, and (c) 80 w/w% solids content.

viscous and so the rheological data reflect more strongly the liquid phase viscosity. Furthermore, the high viscosity of the linseed oil provides more stable coupling with the suspended particle system and so the stochastic boundary condition behaviour is lost, or, perhaps more correctly said, viscous dampened. Higher solids levels, however, draw the response closer to the domination of the particle-particle interactions and so the moduli become more distinctly paired according to sample type. These findings support the hypothesis that compatibility between the particle surface and the liquid medium is still given by the closeness of surface energy match. There is very probably weak adsorption of the acidic polar components and so the Lewis base σ^- polar component is outermost on the

Figure 4: Schematic representation of the transitions occurring under increasing strain/shear for the two sample types in the two contrasting liquids.

particle surface and thus remains compatible (wetttable) within the linseed oil medium, resulting in the lower moduli values in contrast to the treated purely dispersive surface energy which is not fully compatible with the slightly polar medium. The role of acid-base interactions in respect to dispersibility within an albeit weakly polar medium is, therefore confirmed to be dominant [25].

At this preliminary stage, we offer a schematic representation of the structure state as described under dynamic shear and oscillatory strain, as shown in Figure 4.

The particle-particle interactions related to incomplete dispersion can still be present in the linseed oil medium but the high viscosity of the linseed oil masks the effects of these interactions on the boundary conditions, and so they are not separable/distinguishable in the data. This lack of detection of unstable boundary conditions in linseed oil-based dispersion is therefore a function of viscous dampening.

3.3 Viscoelastic hysteresis under strain

For the measurement of dynamic viscosity and response to constant stress under oscillatory strain, it is normally

assumed that the boundary between the sample and the rheometer geometry surface is fixed and the sample under shear consists of a homogeneous representative solids concentration dispersion. Concepts of various levels of coupling between the medium and the particles have been expressed to offer explanation for the various changes of particle-particle structure state within the suspension. We now go on to seek an understanding of the added likelihood of boundary solids depletion, leading to an inconsistent drop in viscosity as the boundary strain-inducing motion acts only on the liquid phase with minimal coupling to the bulk suspension. This depletion is most likely to occur when particles are large, due to boundary exclusion, and, in the case being considered, the largest particles are agglomerates of smaller particles. Thus, there is a strong possibility of boundary solids depletion under conditions of incomplete dispersion of the particles.

In this section, data are reported which were collected under a condition of strain ramp-up and ramp-down ($\gamma = 0.1\% \Rightarrow 1\,000\% \Rightarrow 0.1\%$) in logarithmic magnitude steps linearly over time, t , under oscillation once again at constant angular frequency $\omega = 0.1\text{ s}^{-1}$. The expected elastic modulus response to this regime in which there are no boundary, banding or failure to couple effects, is shown

Figure 5: The classically expected response of a viscoelastic suspension showing particle-particle structure interaction, breakdown and recovery, which can be partial only, over time.

schematically in Figure 5, in which the sample becomes distorted, the structure breaks down (often incompletely) until a minimum is reached under maximum strain, and then, as strain is ramped down, the structure eventually rebuilds over time, at first rapidly and then more slowly and, finally, imperceptibly slowly reaching the starting state or revealing an irreversible state of structure breakdown/change or dispersion, in which case the slow rate or lack of recovery is an indication of hysteresis.

Viewing Figure 6, in which raw data are shown without any additional data smoothing, a striking effect can be observed at the lowest solids concentration of 20 w/w% in the low viscosity hexadecane medium. Once the partial breakdown of the structure at maximum strain has resulted in a minimum value for the moduli, structure recovery at first, as expected, starts to occur rapidly as the strain is progressively reduced. Almost instantaneously as this recovery starts there appears a dual set of data; one set at significantly lower values, whilst the other follows the similar trend but at much higher levels, between which two states the system undergoes chaotic (stochastic) transition. This is proposed to be interpreted as an effective slip-stick like behaviour, caused not by true slip but by boundary solids depletion in the case of the lower moduli, effectively swapping between excluding agglomerates (lower moduli data set) and coupling via inclusion of agglomerates (the upper moduli data set). That it is coarse particle solids depletion and not complete solids depletion, *i.e.* fines remain at the boundary, is attested to by the mirrored parallel trend of increasing moduli in both data sets. Despite this effect, the difference in compatibility between the two samples in the same liquid remains distinct, *i.e.* SA GCC is more compatible to hexadecane than the UT GCC.

However, as solids is increased the dual data set effect disappears, Figure 7. This finding supports the hypothe-

Figure 6: Viscoelastic stress moduli reduction and recovery under oscillation as strain is ramped up and then down – finally measurements continue under conditions of constant low-level strain: (a) untreated UT GCC at 30 w/w% solids in hexadecane, (b) fatty acid treated SA GCC at 30 w/w% solids in hexadecane.

sis proposed under conditions of dynamic shear, in that higher solids content provides more complete coupling between the boundary and the inner bulk dispersion. In this case, data smoothing by noise reduction, adopting Tikhonov regularisation, could be applied since the data set was single and unique [26].

The viscosity of the medium does once again play a role in providing more consistent coupling between the boundary and the bulk material. Figure 8 shows the same strain ramp regime applied to suspensions in linseed oil. Undoubtedly, the data are so noisy that smoothing would be unrealistic, but it is clear to see that the system in the more viscous linseed oil, though not fully stable against boundary decoupling effects, even at the lower solids content, does provide better coupling and maintenance of solids content at the boundary. In addition, the greater

Figure 7: Viscoelastic stress moduli reduction and recovery under oscillation as strain is ramped up and then down – finally measurements continue under conditions of constant low-level strain: (a) untreated UT GCC at 80 w/w% solids in hexadecane, (b) fatty acid treated SA GCC at 80 w/w% solids in hexadecane.

compatibility of the untreated sample to linseed oil is reflected in the lower minimum moduli values achieved at maximum strain.

As an example of the difference in dispersion state between the case where the particles are unwetted, and thus agglomerated and poorly dispersed, versus being at least partially wetted, two images are shown in Figure 9. The optical microscope images were taken using a Leica DM 750, employing digital camera software data collection, to study agglomeration of pigments in hexadecane and linseed oil, using magnifications of 20 $\times$ and 40 $\times$ in transmission mode, in which the suspension samples were smeared onto a glass microscope slide.

That agglomerates remain even in the surface treated case under static conditions confirms the viscoelastic findings reported from the rheological analysis and goes some way to support at least the starting state proposed in the hypothetical schematic previously shown in Figure 4. Combining the hypotheses of structure and shear coupling-decoupling between the boundary and bulk suspension, in the case where the particles can in principle be dispersed in the organic solvent medium due to close surface energy matching, the following further schematic is pro-

Figure 8: Viscoelastic stress moduli reduction and recovery under oscillation as strain is ramped up and then down – finally measurements continue under conditions of constant low-level strain: (a) untreated UT GCC at 20 w/w% solids in linseed oil, (b) fatty acid treated SA GCC at 20 w/w% solids in linseed.

posed as a representation of the three major states of the structure-strain relationship, Figure 10. The starting static state is one of relatively strong aggregation, which upon application of oscillatory strain then breaks down under stress to yield a combination of the majority part consisting of dispersed particles and a minority part consisting of some retained (or induced) agglomerates. If the agglomerates are not excluded from the boundary, the coupling is complete into the bulk and the data follow the upper stress moduli curve. However, if the particles, mainly agglomerates, are excluded from the boundary only the reduced solids layer contacting the boundary yields, recording a much lower decoupled stress state.

Figure 9: Optical microscope images contrasting the state of dispersion for (a) untreated and (b) surface treated (lyophilised) GCC samples dispersed in the purely dispersive liquid, hexadecane: the improved dispersion, albeit imperfect, is clearly visible.

Figure 10: Schematic proposed to represent the three major states of structure in relation to the static condition followed by strain coupling with, or decoupling from, retained (or induced) agglomerates. The stochastic transition between the two states provides an indicator of the state of dispersion versus structuration of the particles in suspension.

3.4 Surface adsorption via Lewis acid base interaction on untreated GCC

To elucidate further the assumption that there is an adsorption of via Lewis acid-base interaction in the case of untreated GCC suspended in linseed oil, a sample of untreated GCC was paste mixed with linseed oil and baked in an oven at 60°C for 48 h. The particles, which effectively became dry-varnished, were then ground in a stone pestle

and mortar to break up agglomerates glued by the hardened oil. This sample was then suspended in liquid linseed oil and the strain sweep experiment repeated. The result is shown in Figure 11.

Visible in Figure 11 is a distinct repeatable secondary structure recovery, which is clearly seen as a second hysteresis curve folding as strain is reduced, at which the effective stochastic decoupling completely stops [27]. This is definitive evidence of a two-level structure recovery, which

Figure 11: The transitory decoupling at the start of stress relaxation for linseed oil surface treated (varnished) calcium carbonate. The formation of a secondary agglomeration is revealed as a thinning of the boundary-coupled state followed by the disappearance of the decoupled state.

to our knowledge has so far not been discussed in this or similar context of organic solvent before (agglomerates building weakly after the formation of more strongly agglomerated material). It is the reverse of that which was published by Dimic-Misic *et al.* [27] for flocculated carbonate in water under extension, where in that case the weak secondary flocs, made by secondary flocculation of the primary flocs, breakdown first under extension followed by the primary stronger flocs. Here the system records the first strong aggregation followed by the formation of a thinning state made based on those aggregates, which then go further to form secondary structures. The latter fully structured system then provides the necessary coupling to hold it in a stable structured state, *i.e.* disappearance of the decoupled state.

3.5 Small angle light scattering (SALS) – probing the validity of the coupling-decoupling structure hypothesis

Optical low angle light scattering (SALS) intensity images provide insight into the structural state, either under motion, as is the classical case for dynamic viscosity study, or in the transition from the static state to the sheared state, as the classic case for viscoelastic structure displaying a pseudo yield point, or, as is the case here, a viscoelastic material which additionally is thought to exhibit boundary wall solids depletion. Resulting from the boundary solids

depletion, dual or multiphase flow behaviour under applied strain occurs. In evaluating the SALS intensity images two main interpretation criteria are considered here:

1. Is the particulate being uniformly sheared?

- If yes, then the speckle pattern at rest transitions into a homogeneous halo of intensity, which for a close to monodisperse (single sized particulate system) will display a limited diameter high intensity Airy disk and multiple concentric diffuse rings of diffracted intensity, whereas for a highly polydisperse sample, as is sampled in this case, a very broad diffuse Airy disk which will likely cover the entire sample diameter.
- If no, then the scattered intensity pattern will remain a static speckle pattern as if no shear was being applied – in this study case such a situation represents the solids depleted decoupled boundary effect.

2. Is an existing structure being aligned or newly formed and then aligned under shear?

- If yes, then the light scatter intensity will represent the combined polarisation of the illuminating beam convoluted with the global structural alignment in the sample, itself polarising, displaying as a result an oriented intensity.
- If no, then 1a).

Following the above criteria, we now focus on the images in Figure 12, in which three intensity patterns have been captured, firstly, just after the application of low shear during the initial ramp up in dynamic shear rate, secondly, at the highest shear rate of 500 s^{-1} and, finally, as the internal structure is regenerating during the ramp down in shear rate shortly before cessation of shear.

Untreated UT GCC in hexadecane, Figure 12, starts with a speckle pattern of transmitted light that remains fairly static, and then slowly rearranges as shear increases reaching a semi-homogeneous state of agglomerate motion at maximum shear, followed by a prolonged reforming static structure as effective two-phase flow occurs against the boundary wall as shear is slowly reduced. Eventually, the system recovers to the first static structure after shear is slowly removed. Thus, intermediate transition states are readily observed prior to and after the isotropic coupled shear regime.

In clear contrast to the untreated incompatible dispersion, Figure 12, the more compatible dispersion between surface treated SA GCC and hexadecane is visible in Fig-

Figure 12: Untreated UT GCC in hexadecane, 3 w/w% solids, under shear between parallel counter-rotating plates, gap 0.3 mm: *left to right* low shear under ramp-up, high shear, and low shear under ramp-down. Enlarged images from the rectangular inserts reveal the structural change from remaining static, despite shear, to homogeneous shearing and return to a structured state, despite continuing low shear, respectively.

Figure 13: Treated SA GCC in hexadecane 3 w/w% solids under shear between parallel counter-rotating plates, gap 0.3 mm: *left to right* low shear under ramp-up, stochastic transition via partial total rotation as shear increases (indicated by the arrow), high shear, re-occurrence of stochastic total structure rotation transition (indicated by the arrow), and low shear under ramp-down. Enlarged images from the rectangular inserts reveal the structural change from remaining static despite shear, to homogeneous shearing and return to a structured state despite continuing low shear, respectively.

Figure 14: Untreated UT GCC in linseed oil, 3 w/w% solids, under shear between parallel counter-rotating plates, gap 0.3 mm: *left to right* low shear under ramp-up, high shear, and low shear under ramp-down, respectively.

ure 13, where, once again, a 3 w/w% solids suspension is used. The sequence begins with the high speckle pattern of the static structure continuing though shear is being applied, indicating initial boundary two-phase decoupled flow, followed by a sudden structure change point with full boundary coupling but internal banding retaining the static bulk state in rotation. At this stage, transitions occur into a rapidly changing state of inhomogeneity and, thus, sudden wall depletion re-occurs (dark shadows appear as an indication of simultaneous air inclusion), breaking down rapidly into a more homogeneous flow as coupling is re-established when approaching maximum shear. The lack of large aggregates in this better dispersed, but highly diluted, system in fact makes the shear coupling less stable introducing instantaneous shear banding occurring randomly within the structure, seen as the short-lived static fine grain transmission structure patterns appearing and disappearing before the very diffuse fully homogeneous scattering begins under isotropic shear. On reducing shear once again, a transitory slip banding precedes the return to the static state two-phase flow under low shear. Finally, once again the system relaxes. These findings follow precisely the concepts proposed when studying the dynamic shear and oscillating strain previously.

Untreated UT GCC in linseed oil, Figure 14, shows a very interesting progression which includes an irreversible increase in dispersion as a function of applied shear and potential adsorption of species due to Lewis acid-base interaction, enhancing the end-point wettability and, hence, dispersibility. Initially, a static structure state is maintained for a prolonged period, and then a series of transition states occur (not shown), each short-lived but displaying instantaneous transition between the structures. Then a fully homogeneous diffuse light state is observed at high shear. The homogeneous state lasts longer than for hexadecane samples, probably due to the higher viscosity in combination with the improved dispersion. This prolonged homogeneity confirms the relationship between

Figure 15: Striking image data from SALS measurement under shear for the linear molecule *N*-(4-methoxybenzylidene)-4-butaniline (MBBA) – shown here as an example of aligned structure creation under shear. The shear rate is increased steadily in the images from *left to right*.

high viscous coupling and more homogeneous stress transmission, as suggested earlier in the analysis.

Clearly, the suspensions show no polarisation effect, and so the structures are isotropic. As an example of what might be expected should alignment structures have been induced, such as quasi nematic liquid crystal structures, we include for completeness Figure 15, in which a polarisation oriented light transmission intensity is seen for the linear molecular structure of *N*-(4-methoxybenzylidene)-4-butaniline (MBBA).

MBBA forms two stages of nematic liquid crystal under shear, and one sees this using SALS as a combination of directional polarised light transmission first forming an elongated ellipse and then a definite band as shear increases. This then reverses as shear is reduced again. That the calcium carbonate particles do not display such effects confirms their isotropic shape and particle-particle interaction nature.

4 Conclusions

The dispersibility between carbonate fillers (surface treated and untreated) suspended in purely dispersive

non-polar (hexadecane) and fractionally polar (linseed oil) liquid solvents, respectively, has been studied. Arising from extensive rheological analysis, hypotheses of how the particles are structured in suspension and how they progressively become dispersed, or partially dispersed, under strain at different solids content were proposed.

Translating these hypotheses between dynamic shear, including small angle light scattering experiments under shear (SALS), and when applying strain, we can draw conclusions and parallels between the presence and nature of structural elements and the overall dispersibility of the particles in the suspension, as follows:

The static state at rest before shear stress is experienced and during recovery is viscoelastic, with the elastic component reflecting the network of interacting forces both acting to structure the particles together and/or to trap liquid within the long-range matrix of weakly attracting particles. As strain is re-applied, stress builds within this matrix of particulate elements. However, if a selected group of structures become size-excluded at a planar boundary, liquid-solid phase separation occurs (solids depletion) and a loss of coupling between the wall and the bulk large particle-containing suspension occurs. This can lead to a stochastic transient effect induced particularly at and after high strain, leading to discrete separation into two measured stress data sets, *i.e.* that with full coupling at the boundary, sampling the complete range of suspension structures, or that with only partial coupling at the wall, sampling only the liquid rich layer, which may or may not contain fine particles to the exclusion of coarse particles and/or aggregates. By following the structure recovery as strain is once again step-wise reduced, the presence of the stochastic transient phenomenon, and its parallel change in magnitude, is used to describe the progressive formation of primary agglomerates out of individual particles or from the remaining aggregates. Cessation of the phase separation indicates the rebuild of the more complete static structure. Under certain conditions it is observed that the cessation of strain may be accompanied by a secondary relaxation of state, indicating the build of a secondary but weaker structure. Rheo-optical observations (SALS) are used to support the validity of the proposed structure model.

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