Schematic Mode Coupling Theories for Shear Thinning, Shear Thickening, and Jamming

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Mode coupling theory (MCT) appears to explain several, though not all, aspects of the glass transition in colloids (particularly when short-range attractions are present). Developments of MCT, from rational foundations in statistical mechanics, account qualitatively for nonlinear flow behaviour such as the yield stress of a hard-sphere colloidal glass. Such theories so far only predict shear thinning behaviour, whereas in real colloids both shear thinning and shear thickening can be found. The latter observation can, however, be rationalised by postulating an MCT vertex that is not only a decreasing function of strain rate (as found from first principles) but also an increasing function of stress. Within a highly simplified, schematic MCT model this can lead not only to discontinuous shear thickening but also to complete arrest of a fluid phase under the influence of an external stress ('full jamming').

1. INTRODUCTION

1.1. Arrest in Colloidal Fluids

Colloidal fluids can be studied relatively easily by light scattering [1, 2]. This allows one to measure the dynamic structure factor $S(q, t_1 - t_2) = \langle \rho(\mathbf{q}, t_1)\rho(-\mathbf{q}, t_2)\rangle/N$ and also the static one, $S(q) = S(q, 0)$. Here $\rho(\mathbf{r}, t) = \sum_i \delta(\mathbf{r}_i(t) - \mathbf{r}) - N/V$; this is the real space particle density (with the mean value subtracted), and $\rho(\mathbf{q}, t)$ is its Fourier transform. For particles of radius a with short-range repulsions, $S(q)$ exhibits a peak at a value q^* with $q^* a = \mathcal{O}(1)$. The dynamic structure factor $S(q, t)$, at any q, decays monotonically from $S(q)$ as t increases. In an ergodic colloidal fluid, $S(q, t)$ decays to zero eventually: all particles can move, and the density fluctuations have a finite correlation time. In an arrested state, which is nonergodic, this is not true. Instead the limit $S(q, \infty)/S(q) = f(q)$ defines the *nonergodicity parameter*. The presence of nonzero $f(q)$ signifies frozen-in density fluctuations. Although $f(q)$ is strongly wavevector dependent, it is common to quote only $f(q^*)$ [3]. The above formulas assume time-translation invariance; nonergodic systems can violate this (showing e.g. aging phenomena) in which case $S(q, t_1 - t_2)$ as defined above must be written $S(q, t_1, t_2)$ with two time arguments.

In many colloidal materials the effective interparticle interaction $u(r)$ comprises a hard sphere repulsion, operative at separation $2a$, perhaps combined with an attraction at larger distance. (For simplicity one can imagine a square well potential of depth ϵ and range ξa, with $\xi < 1$ typically.) Colloidal fluids of this type are found to undergo nonergodicity transitions into two different broad classes of arrested nonequilibrium states. One is the colloidal glass, in which arrest is caused by the imprisonment of each particle in a cage of neighbours. This occurs even for $\epsilon = 0$ (i.e. hard spheres) at volume fractions above about $\phi \equiv 4\pi a^3 N/3V \simeq 0.58$. The nonergodicity parameter for the colloidal glass obeys $f(q^*) \simeq 0.8$. The second arrested state is called the colloidal gel. Unlike the repulsive glass, the arrest here is driven by attractive interactions, resulting in a bonded, network-type structure. Such gels can be unambiguously found, for short range attractions, whenever $\beta\epsilon \gtrsim 5 - 10$. (Here $\beta \equiv 1/k_B T$.) Hence it is not necessary that the local bonds are individually irreversible (this happens, effectively, at $\beta\epsilon \gtrsim 15 - 20$); and when they are not, the arrest is a collective, not just a local, phenomenon. It is found experimentally that for colloidal gels, $f(q^*) \gtrsim 0.9$, which is distinctly different from the colloidal glass. The arrest line for gel formation slices across the equilibrium phase diagram (e.g., plotted on the $(\phi, \beta\epsilon)$ plane), and, depending on ξ, parts of it lie within two phase regions. This, alongside any metastable gas-liquid phase boundary that is present, can lead to a lot of interesting kinetics [4, 5], in which various combinations of phase separation and gelation lead to complex microstructures and time evolutions.

1.2. Mode Coupling Theory (MCT)

We do not review MCT in detail here. One widely used form of the theory [6] is based on projection methods. However, in a stripped down version (see e.g. [7, 8]) the resulting equations can be viewed as a fairly standard one-loop selfconsistent approximation to a dynamical theory for the particle density field.

We take $\beta = 1$, bare particle diffusivities $D_0 = 1$, and start from the overdamped Langevin equations $\dot{\mathbf{r}}_i = \mathbf{F}_i + \mathbf{f}_i$ for independent particles of unit diffusivity subjected to external forces $\mathbf{F}_i$ and random forces $\mathbf{f}_i$. One proceeds by a standard route to a Smoluchowski equation $\dot{\Psi} = \Omega\Psi$ for the N-particle distribution function Ψ, with evolution operator $\Omega = \sum_i \nabla_i.(\nabla_i - \mathbf{F}_i)$. Now take the forces $\mathbf{F}_i$ to originate (via $\mathbf{F}_i = -\nabla_i H$) from an interaction Hamiltonian

$$H = -\frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')c(|\mathbf{r} - \mathbf{r}'|) \tag{1}$$

where $Nc(q) = V[1 - S(q)^{-1}]$. This is a harmonic expansion in density fluctuations; $c(q)$ is the direct correlation function, and this form ensures that $S(q)$ is recovered in equilibrium. We neglect solvent mediated dynamic forces (hydrodynamic couplings). Also, in principle these couplings mean that the noise in the Langevin equation should be correlated between particles, in contrast to the independent white noise assumed here. In addition we neglect anharmonic terms in H; to regain the correct higher order density correlators (beyond the two point correlator $S(q)$) in equilibrium, these terms would have to be put back.

From the Smoluchowski equation (or the corresponding nonlinear Langevin equation for the density $\rho(\mathbf{r})$[7, 9]), one can derive a hierarchy of equations of motion for correlators such as $S(q,t)$, more conveniently expressed via $\Phi(q,t) \equiv S(q,t)/S(q)$. Factoring arbitrarily the four-point correlators that arise in this hierarchy into products of two Φ's,

one obtains a closed equation of motion for the two point correlator

$$\dot{\Phi}(q,t) + \Gamma(q)\left[\Phi(q,t) + \int_0^t m(q,t-t')\dot{\Phi}(q,t')dt'\right] = 0 \tag{2}$$

where $\Gamma(q) = q^2/S(q)$ is an initial decay rate, and the memory function obeys

$$m(\mathbf{q},t) = \sum_{\mathbf{k}} V_{\mathbf{q},\mathbf{k}}\Phi(\mathbf{k},t)\Phi(\mathbf{k}-\mathbf{q},t) \tag{3}$$

with the vertex

$$V_{\mathbf{q},\mathbf{k}} = \frac{N}{2V^2 q^4}S(q)S(k)S(|\mathbf{k}-\mathbf{q}|)[\mathbf{q}.\mathbf{k}c(k) + \mathbf{q}.(\mathbf{k}-\mathbf{q})c(|\mathbf{k}-\mathbf{q}|)]^2 \tag{4}$$

Equations 2-4, which are slightly simpler than the ones used in molecular glasses because of the justified neglect of inertial terms in an overdamped environment, completely define the MCT as usually applied in colloidal systems [6].

The MCT equations exhibit a bifurcation that corresponds to a sudden arrest transition, upon smooth variation of either the density ϕ or any interaction parameters that control $c(q)$ (equivalently, $S(q)$). Here the nonergodicity parameters $f(q)$, suddenly jump (for all q at once) from zero to nonzero values. Near this (on the ergodic side, which is always the direction MCT approaches from), $\Phi(q,t)$ develops interesting behaviour. Viewed as a function of time, it decays onto a plateau of height $f(q)$, stays there for a long time, and then finally decays again at very late times. The two decays are called β and α respectively. Upon crossing the bifurcation, their relaxation times diverge smoothly with the parameters; upon crossing the locus of this divergence, $f(q) \equiv S(q,\infty)$ jumps discontinuously from zero to a finite value.

2. MCT & DYNAMIC HETEROGENEITY

It is interesting to compare the MCT approach with the concept of dynamical heterogeneity and/or 'assisted dynamics' (e.g. [10]). MCT ignores locally activated processes but treats collective density fluctuations in a relatively sophisticated way; for most theories of dynamic heterogeneity, exactly the reverse applies. Therefore, neither theory can claim to offer a complete picture. Much evidence on colloids suggests that there are indeed localized regions of enhanced mobility (e.g. [11, 12]); but this very idea requires some sort of immobilized background state within which such excitations arise. MCT addresses the onset of this collectively arrested state. Ignoring the excitations may be only a modest error if the density of excitations near the MCT transition is small enough, but could undermine the whole approach if it is large. Conversely, any theory of localized defect dynamics within a frozen matrix (modelled, e.g., on a lattice [10]) should work only if, on coming from the glass side, the proliferation of defects is not pre-empted by a collective unfreezing of the matrix through an MCT-like mechanism.

The adequacy of either theory may depend on what type of glass is under study. For colloids, MCT seems surprisingly adequate [13]. A striking recent success concerns systems with both attractive interactions and hard-core repulsions. First, MCT unambiguously predicts [14, 15, 16] that adding a weak, short range attraction to the hard sphere system should melt the glass (which has $f(q^*) \sim 0.8$). Second, MCT predicts that adding more

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of the same attraction should mediate a second arrest, this time into a 'gel' state of high nonergodicity parameter ($f(q^*) \sim 0.95$). Third, MCT predicts that as parameters are varied, a higher order bifurcation point should enter the picture, resulting in a characteristic logarithmic decay for $\Phi(q, t)$. Although not every detail of this scenario is yet confirmed, there is clear experimental evidence for both the re-entrance, and the logarithmic decay [17, 18]. The latter is also seen clearly in recent simulations [19, 20]. These successes of MCT pose a notable challenge to dynamical heterogeneity theories of the glass transition in colloids. Until such a theory can explain the three features just outlined, it is fair to conclude that MCT remains the least inadequate theory of the colloidal glass transition [9].

3. SHEAR THINNING

3.1. A Microscopic Approach

In Ref.[21], a theory is propounded, along MCT lines, of colloidal suspensions under flow. The work was intended mainly to address the case of repulsion-driven glasses, and to study the effect of imposed shear flow either on a glass, or on a fluid phase very near the glass transition. In either case, simplifications might be expected because the bare diffusion time $\tau_0 = a^2/D_0$ is small compared to the 'renormalized' one $\tau = a^2/D$, which in fact diverges (enslaved to the α relaxation time) as the glass transition is approached. If the imposed steady shear rate is $\dot{\gamma}$, then for $\dot{\gamma}\tau_0 \ll 1 \leq \dot{\gamma}\tau$, one can hope that the details of the local dynamics are inessential and that universal features related to glass formation should dominate. Note, however, that by continuing to use a quadratic H (Eq.1), we will assume that, even under shear, the system remains 'close to equilibrium' in the sense that the density fluctuations that build up remain small enough for a harmonic approximation to be useful. This may well be inadequate for hard spheres, but a systematic means of improvement upon it is not yet available.

The basic route followed in Ref.[21] is quite similar to that laid out above for standard MCT, modulo the fact that an imposed shear flow is now present. A key simplification is to neglect velocity fluctuations so that the imposed shear flow is locally identical to the macroscopic one; this cannot be completely correct, but allows progress to be made. For related earlier work see Refs.[22, 23].

We again take $\beta = 1$, $D_0 = 1$, and start from the Langevin equations $\dot{\mathbf{r}}_i = \mathbf{u} + \mathbf{F}_i + \mathbf{f}_i$ for independent particles of unit diffusivity subjected to external forces $\mathbf{F}_i$ and, now, an imposed flow velocity $\mathbf{u}(\mathbf{r}_i)$. We take this to be a simple shear flow with $\mathbf{u}(\mathbf{r}) = \dot{\gamma}y\hat{\mathbf{x}}$. The Smoluchowski equation $\dot{\Psi} = \Omega\Psi$ is unchanged but the evolution operator is now $\Omega = \sum_i \nabla_i.(\nabla_i - \mathbf{F}_i - \mathbf{u}(\mathbf{r}_i))$. So far, the adaption to deal with shearing is fairly trivial. The next stages are not. We assume an initial equilibrium state with $\Psi(t = 0) \propto \exp[-H]$, and switch on shearing at $t = 0+$. We define an *advected correlator*

$$\Phi(\mathbf{q}, t) = \langle \rho(\mathbf{q}, 0)\rho(-\mathbf{q}(t), t)\rangle / S(q)N \tag{5}$$

where $\mathbf{q}(t) = (q_x, q_y + q_x\dot{\gamma}t, q_z)$. This definition subtracts out the trivial part of the advection, which merely transports density fluctuations from place to place. The nontrivial part comes from the effect of this transport on their time evolution; the main effect (see e.g. [23]) is to kill off fluctuations by moving their wavenumbers away from q^* where

restoring forces are weakest (hence the peak there in $S(q)$). Hence the fluctuations feel a stronger restoring force coming from H, and decay away more strongly. This feeds back, through the nonlinear term, onto the other fluctuations, including ones transverse to the flow and its gradient (i.e., with $\mathbf{q}$ along z) for which the trivial advection is absent.

There follow a series of MCT-like manipulations which differ from those of the standard approach because they explicitly deal with the switching on of the flow at $t = 0+$. We integrate through the transient response to obtain the steady state correlators, under shear, as $t \to \infty$. (There is no integration through transients in standard MCT; one works directly with steady-state quantities.) Despite all this, the structure of the resulting equations is remarkably similar to Eqs. 2,3:

$$\dot{\Phi}(\mathbf{q}, t) + \Gamma(\mathbf{q}, t) \left[\Phi(\mathbf{q}, t) + \int_0^t m(\mathbf{q}, t, t') \dot{\Phi}(\mathbf{q}, t') dt' \right] = 0 \tag{6}$$

This equation describes transient density fluctuations; that is, time zero in Eq.5 corresponds to the switch-on time of a shear flow, so that Φ is a particular instance of a two-time correlator rather than a one-time one. For a related approach based on the one-time correlator of fluctuations around steady state (but assuming a fluctuation-dissipation theorem which need not apply here), see [24]. Eq.6 involves a time dependent, anisotropic "initial decay rate":

$$\Gamma(\mathbf{q}, t) S(q) = q^2 + q_x q_y \dot{\gamma} t + (q_x q_y \dot{\gamma} t + q_x^2 \dot{\gamma}^2 t^2) S(q) - q_x q_y \dot{\gamma} S'(q)/q \tag{7}$$

The memory kernel is no longer a function of the time interval $t - t'$ but depends on both arguments separately

$$m(\mathbf{q}, t, t') = \sum_{\mathbf{k}} V(\mathbf{q}, \mathbf{k}, t, t') \Phi(\mathbf{k}, t) \Phi(\mathbf{k} - \mathbf{q}, t) \tag{8}$$

through a time-dependent vertex V whose detailed derivation will appear in [25]:

$$
\begin{aligned}
V(\mathbf{q}, \mathbf{k}, t, t') = {}& [N S_k S_p / (2V^2 S_q \Gamma(\mathbf{q}, t) \Gamma(\mathbf{q}, t'))] \\
& [\, \mathbf{q}(t).\mathbf{k}(t{-}t') c(k(t{-}t')) + \mathbf{q}(t).\mathbf{p}(t{-}t') c(p(t{-}t')) + \\
& \quad S(q(t{-}t')) \mathbf{q}(t).\, (\mathbf{q}(t{-}t') c(q(t{-}t')){-}\mathbf{q} c(q)) \,] \\
& [\, \mathbf{q}.\mathbf{k} c(k) + \mathbf{q}.\mathbf{p} c(p) + \\
& q_x q_y \dot{\gamma} t \, S(q) \left(c(k) + c(p) - \tfrac{N}{2V}(c(q)c(k) + c(q)c(p) + c(k)c(p)) \right)]
\end{aligned} \tag{9}
$$

Here the abbreviation $\mathbf{p} = \mathbf{q} - \mathbf{k}$ is used, and advected wavevectors (see below Eq. 5) carry a time dependence.

Using a nonequilibrium Kubo-type relationship [21] one can also obtain an expression for the steady state viscosity $\eta = \sigma(\dot{\gamma})/\dot{\gamma}$ where $\sigma(\dot{\gamma})$ is the shear stress as a function of shear rate. The viscosity is expressed as an integral of the form

$$\eta = \int_0^\infty dt \sum_{\mathbf{k}} V_\eta(\mathbf{k}, t) \Phi^2(\mathbf{k}, t) \tag{10}$$

where the function V_η may be found in Ref. [21].

The above calculations give several interesting results. First, any nonzero shear rate, however small, restores ergodicity for all wavevectors (including ones which are transverse

to the flow and do not undergo direct advection). This is important, since it is the absence of ergodicity that normally prevents MCT-like theories being used inside the glass phase, at $T < T_g$ or $\phi > \phi_g$. Here we may use the theory in that region, so long as the shear rate is finite.

In the liquid phase $(\phi < \phi_g)$ the resulting flow curve $\sigma(\dot\gamma)$ shows shear thinning at $\dot\gamma\tau \gtrsim 1$, which is when the shearing becomes significant on the timescale of the slow relaxations. This is basically as expected. Less obviously, throughout the glass, one finds that the limit $\sigma(\dot\gamma \to 0+) \equiv \sigma_Y$ is nonzero. This quantity is called the yield stress and represents the minimum stress that needs to be applied before the system will respond with a steady-state flow. (For lower stresses, various forms of creep are possible, but the flow rate vanishes in steady state.)

The prediction of a yield stress in colloidal glasses is significant, because glasses, operationally speaking, are normally defined by the divergence of the viscosity. However, it is quite possible for the viscosity to diverge without there being a yield stress, for example in 'power law fluids' where $\sigma(\dot\gamma) \sim \dot\gamma^p$ with $0 < p < 1$ [27]. This does not happen in the present calculation, where the yield stress jumps discontinuously from zero to a nonzero value, σ_Y^c, at ϕ_g. The existence of a yield stress seems to be in line with most experimental data on the flow of colloidal glasses, although one must warn that experimentalists definitions of what a yield stress is, do vary across the literature [28]. Ours is defined as the limiting stress achieved in a sequence of experiments at ever decreasing $\dot\gamma$, ensuring that *a steady state is reached* for each shear rate before moving onto the next one. The latter requirement may not be practically achievable since the equilibration time could diverge smoothly at small $\dot\gamma$: certainly one would expect to have to wait at least for times t such that $\dot\gamma t \gtrsim 1$. But unless the flow curve has unexpected structure (absent in this approach) at small shear rates, the required extrapolation can presumably be made.

3.2. Schematic MCT models

It has long been known that the key mathematical structure behind Eqs. 2-4 can be captured by low-dimensional schematic models in which the full **q** dependence is suppressed [29, 6]. In other words, one chooses a single mode, with a representative wavevector around the peak of the static structure factor, and writes mode coupling equations for this mode treated by itself. At a phenomenological level, one can capture the physics similarly even with shearing present (despite the more complicated vectorial structure that in reality this implies). Specifically one can define [21] the $F_{12}^{\dot\gamma}$ model — the sheared extension of a well known static model, F_{12} — via

$$\dot\Phi(t) + \Gamma\left[\Phi(t) + \int_0^t m(t-t')\dot\Phi(t')dt'\right] = 0 \tag{11}$$

with memory function (schematically incorporating shear)

$$m(t) = [v_1\Phi(t) + v_2\Phi^2(t)]/(1 + \dot\gamma^2 t^2) \tag{12}$$

The vertex parameters $v_{1,2}$ are smooth functions of the volume fraction ϕ (and any interactions). To calculate flow curves, etc., one also needs a schematic form of Eq.10; here we take the first moment of the correlator to fix the time scale for stress relaxation (which is, in suitable units, simply the viscosity):
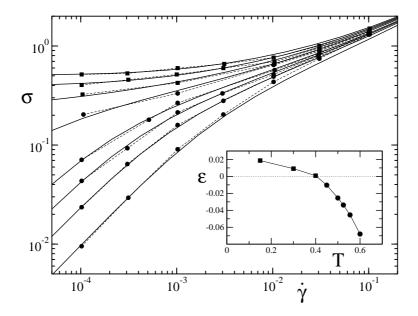
$$\eta = \int_0^\infty \Phi(t)dt \tag{13}$$

Figure 1. Symbols are shear stress data of a super–cooled Lennard–Jones binary mixture in reduced units taken from Ref. [31]; from top to bottom, the temperatures are 0.15, 0.3, 0.4, 0.45, 0.5, 0.525, 0.555 & 0.6 while the transition lies at $T \approx 0.435$. The solid lines give fits by eye using the $F_{12}^{\dot{\gamma}}$–model with parameter ε measuring the separation from the transition shown in the inset. Units are converted by $\sigma = 1.5\sigma^{\text{theo.}}$ and $\dot{\gamma} = 1.3\dot{\gamma}^{\text{theo.}}$. More details and a preliminary fit can be found in [30].

(Note that a different choice, e.g. with $\Phi(t)^2$ in this equation to closer resemble Eq.10, would yield quite similar results.) This simplest of schematic models gives very similar results to a much more sophisticated (but still schematic) approximation of the full equations [21], with $\sigma - \sigma_Y \sim \dot{\gamma}^{0.16}$ and $\sigma_Y - \sigma_Y^c \sim (\phi - \phi_g)^{1/2}$. Such predictions can be compared with experiment [30] and, as shown in Figure 1, suggest that the more advanced schematic models are at least semi-quantitative.

4. SHEAR THICKENING AND JAMMING

The calculations described above predict, generically, shear thinning behaviour: advection kills fluctuations, reducing the α relaxation time, which causes the system to flow more easily at higher stresses. However, in some colloidal systems, the reverse occurs. This is shear thickening, and gives a flow curve $\sigma(\dot{\gamma})$ with upward curvature. In extreme cases, an essentially vertical portion of the curve is reported [32, 33]. One interpretation of the latter scenario (called 'discontinuous shear thickening') is that the underlying flow curve is actually S-shaped. Since any part of the curve with negative slope is mechanically unstable (a small increase in the local shear rate would cause an acceleration with positive feedback), this allows a hysteresis cycle in which, at least according to the simplest models, discontinuous vertical jumps on the curve bypass the unstable section (see Figure 2).
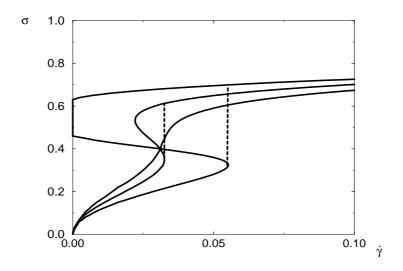
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Figure 2. Three possible flow curves for a shear thickening material. The monotonic curve corresponds to continuous shear thickening. The remaining two curves are S-shaped; one expects, on increasing the shear rate, the stress to jump from the lower to upper branch at (or before) the vertical dashed line shown in each case. One curve shows the full jamming scenario: the existence of an interval of stress, here between 0.45 and 0.63, within which the flow rate is zero, even in a system ergodic at rest. (Stress and strain rate units are arbitrary.)

If this viewpoint is adopted, there seems to be nothing to prevent the upper, re-entrant part of the curve from extending right back to the vertical axis (see Figure 2) in which case there is zero steady-state flow within a certain interval of stress. The system has both an upper and a lower yield stress delimiting this region. (If it is nonergodic at rest, it could also have a regular yield stress on the lower part of the curve near the origin – we ignore this here.) This case has been called 'full jamming' [34]. Although mostly a theoretical speculation, at least one experimental report of this kind of behaviour has appeared in the literature recently [35].

The above discussion suggests that shear thickening and full jamming might be viewed as a stress-induced glass transition of some sort [36]. If so, it is natural to ask whether this idea can be accommodated within an MCT-like approach. Since the analysis of Ref. [21] gives only shear thinning, this is far from obvious. In particular, a stress-induced glass transition would require the vertex V to 'see' the stress; this might require one to go beyond harmonic order in the density, that is, it might require improvement to Eq.1. Indeed, since it is thought that jamming arises by the growth of chainlike arrangements of strong local compressive contacts [36], it is very reasonable to assume that correlators beyond second order in density should enter.

In [37] we develop a schematic model along the lines of Eqs.11–13 to address shear

thickening (with, for simplicity, $v_2 = 0$). This is the $F_1^{\dot{\gamma},\sigma}$ model

$$\dot{\Phi}(t) + \Gamma \left[\Phi(t) + \int_0^t m(t - t')\dot{\Phi}(t')dt' \right] = 0 \tag{14}$$

with memory function

$$m(t) = [v_0 + \alpha\sigma] \exp[-\dot{\gamma}t]\Phi(t) \tag{15}$$

and viscosity $\eta = \sigma/\dot{\gamma}$ obeying

$$\eta = \int_0^\infty \Phi(t)dt \,. \tag{16}$$

The memory function now schematically incorporates both the loss of memory by shearing and a stress-induced shift of the glass transition. (Without stress or shear, the latter occurs at $v_0 = 4$.) The choice of an exponential strain rate dependence is purely for algebraic convenience, whereas the form in Eq. 12 is closer to the one found in the full **q**-dependent vertex under shear (see section 3.1 above and [21]). The choice of a linear dependence of the vertex on stress (rather than the quadratic one that would arise in a Taylor expansion about the quiescent state) can be viewed as a linearization about a finite stress chosen to lie close to the full jamming region: this, rather than the behaviour at very small stresses, is the interesting region of the model. In any case, the qualitative scenarios that emerge from Eqs.14–16 are relatively robust to the precise details of the model [37].

This model results in a 'full jamming' scenario as part of a wider range of rheological behaviour. Fig. 3 shows three kinds of thickening behaviour, dependent on model parameters; v_0 is varied close to the quiescent glass transition, and for the chosen α there is a progression from a monotonic, continuously shear-thickening curve, via a nonmonotonic S-shaped curve, to a curve that extends right back to the vertical axis. For the largest values of the parameter v_o, in Fig. 3, there is therefore a range of stress for which the shear rate returns to zero: there is then no ergodic solution, and the jammed state is stable. This represents full jamming. Note that if, as seems likely, α depends on the details of interparticle interactions, then the evolution between these scenarios does too. This makes sense since one would certainly expect hard particles to be more 'jammable' than soft ones.

Fig.3 is qualitatively similar to Fig.2 – whose data actually comes from [34]. In that work a somewhat similar theory is developed, based not on MCT but on the trap model of glasses. The emergence of the same qualitative scenario from two quite different approaches to glass rheology is reassuring, although in each case the ansatz of a stress-dependent glass transition was, effectively, put in by hand.

The lower and upper endpoints σ_{c1} and σ_{c2} of the stable jammed state represent distinct jamming transitions. Their critical stresses obey

$$f_c \left[(v_o + \alpha\sigma_c) f_c - 2 \right] = \sigma_c, \tag{17}$$

where f_c is given by the largest solution of $\frac{f_c}{1-f_c} = (v_o + \alpha\sigma_c)f_c^2$. Such transitions exist provided that both v_o and α are sufficiently large. Bertrand *et al* [35] found that, for concentrations below a certain value, their samples showed ordinary thickening, whilst above this value the shear-induced solid was seen. The behaviour illustrated in Fig. 3 is
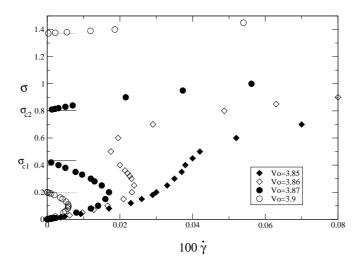
Figure 3. Flow curves for $\alpha = 0.95$. For the two largest values of v_o, it appears that for a window in σ, the relaxation time has diverged. Analytic calculations of the limits of this window are indicated as horizontal lines near the stress axis. These values of the stress are dubbed σ_{c1} and σ_{c2}, as shown here for one of the parameter sets.

reminiscent of this. Note that the re-fluidisation under increasing stress depends on α: if this is too large (for a given v_o) this re-fluidisation is not present. The resulting 'phase diagram' of the model, dividing parameter space into ergodic and nonergodic regions, is shown in Fig. 4. At large enough stresses, jammed states arise for $\alpha > 1$. However, for particle densities close to but below the quiescent glass transition, for $\alpha < 1$ the system jams in an intermediate window of stress.

5. GLASSY VERSUS HYDRODYNAMIC THICKENING

Shear thickening is widely reported (e.g. [32, 33, 38, 39]) and usually attributed to a buildup of hydrodynamic forces between clusters of particles [40, 41]. Our work suggests that, at least in some systems, this may not be the only mechanism at work. In particular, Fig. 3 admits shear thickening at Peclet numbers $\dot{\gamma}\tau_0 \sim 10^{-4}$, rather than values of order unity predicted by most theories of hydrodynamic clustering. Such theories do not so far appear to offer any natural explanation of the S shaped flow curve that appears to underly *discontinuous* shear thickening (see e.g. [42], and references therein). On the other hand, simulations of dense colloids do predict, for hard spheres in the absence of Brownian motion, a catastrophic jamming transition. In this transition, a network of close contacts propagates to infinity at *finite strain*, creating a solid [43]. The relation between this and our own model in which Brownian motion of course plays an essential role, is yet to become clear.

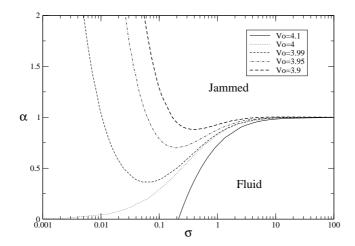It should also be pointed out that, to whatever extent full jamming is actually observed

Figure 4. 'Phase diagrams' for the model for various v_o. The lines denote transitions in the (α, σ)-plane. All states below the curve for a given value of v_o are fluid states, whilst those above (and on) the line are nonergodic, jammed states.

[35], hydrodynamic theories cannot explain it. This is because hydrodynamic forces are dynamical in origin and therefore cannot be responsible for maintaining a purely static state of arrest. It is however conceivable that a limit exists in which interparticle velocities and separations both vanish at late times in such a fashion that the resulting forces approach constant values. However, we do not find this particularly plausible.

Note in any case that existing hydrodynamic theories (rather than simulations [43]) of colloid rheology, by taking no account of the glass transition, predict that the zero shear viscosity diverges only at random close packing (volume fraction $\phi = 0.63$) [44]. This appears inconsistent with experimental observations where the viscosity divergence occurs instead at the colloidal glass transition ($\phi = \phi_g = 0.58$) [45]. Accordingly it is necessary to develop a new theory, as outlined in Section 3, to describe flow curves at $\phi > \phi_g$. The hypothesis of the work on colloidal jamming reported here is that the proximity of this transition also affects flow properties in a window of densities *below* ϕ_g, to the extent that one should treat hydrodynamic forces as a perturbation to the dynamics of collective arrest, rather than vice versa.

6. CONCLUSION

Mode Coupling Theory (MCT) has had important recent successes, such as predicting, in advance of experiment, the re-entrant glass/gel nonergodicity curves that arise in colloidal systems with short range attractions [14, 15, 16, 17].

Theoretical developments directly inspired by MCT now offer a promising framework for calculating the nonlinear flow behaviour of colloidal glasses and glassy liquids [21].

In fact, this offers the only current prospect for *quantitative* prediction of yield behaviour and nonlinear rheology in this or any other class of nonergodic soft materials. (Other work on the rheology of glasses [27, 46] does not, as yet, offer quantitative prediction of experimental quantities.) While promising, many things are missing so far from the approach initiated in [21]: velocity fluctuations, hydrodynamic forces, anharmonicity in H etc., are all ignored. The fact that only shear thinning is predicted in this case is excusable.

The schematic work of Ref.[37] on shear thickening is preliminary, but interesting in that it suggests how new physics (beyond two-point correlations) may need to be added to MCT before the full range of observed colloidal flow behaviour is properly described. Hydrodynamic interactions, and perhaps velocity fluctuations, are certainly also important in some aspects of shear thickening, as discussed in Section 5, though we might hope that these do not dominate very close to the glass transition where the longest relaxation time is structural rather than hydrodynamic. Of course, even for systems at rest, it is known that some important physics is missing from MCT, in particular, the kinds of activated dynamics discussed in Section 2. These allow the system to move exponentially slowly despite being in a region of phase space where, according to MCT, it cannot move at all (see e.g. [8]). Qualitatively, stress-induced jamming seems a quite different phenomenon from this, although one cannot rule out a link of some sort (e.g. if stress switches off the activated processes [34]). Accordingly we can suspect that there are more things missing from MCT than just activated processes. In particular a more general treatment of anharmonic terms (or equivalently, a treatment of three-point and higher order correlations) may be required before one has a fully workable theory of sheared colloidal glasses.

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