

## Stress-induced solidification in colloidal suspensions

---

Michael Cates\*

SUPA, School of Physics, JCMB Kings Buildings, Edinburgh EH9 3JZ, United Kingdom

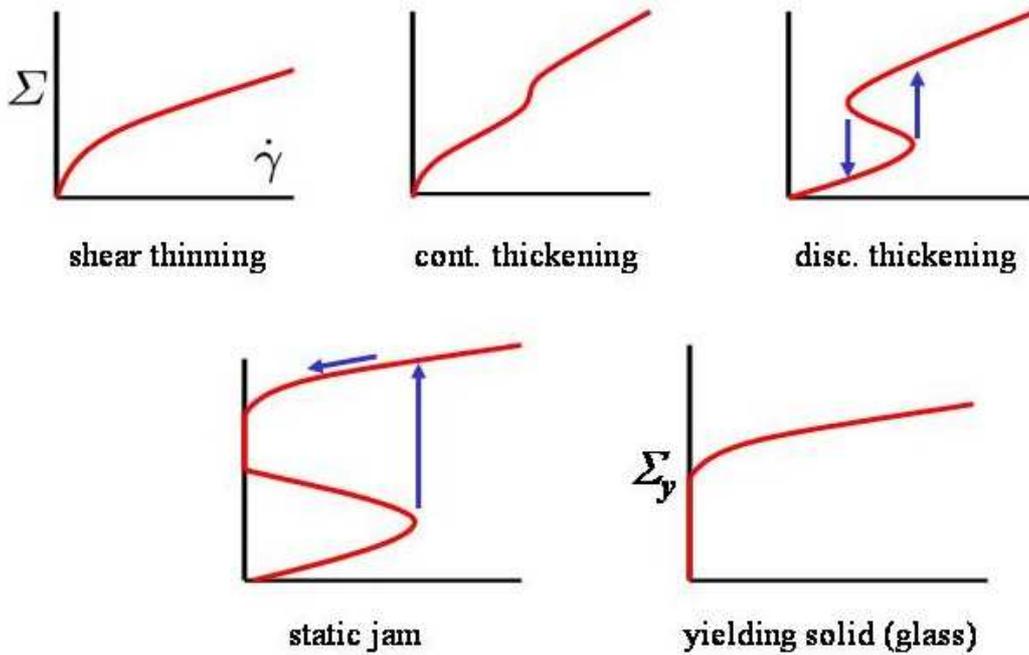
*E-mail:* m.cates@ed.ac.uk

I review recent work on the idea that jamming of colloidal suspensions under shear can be viewed as a stress-induced glass transition. A schematic model, incorporating ideas from mode coupling theory but entirely neglecting hydrodynamic interactions, admits in certain parameter ranges an extreme shear-thickening material that is flowable at low stresses but which seizes up above a certain threshold of order the Brownian stress scale. The jammed material can be brittle in the sense that it will fracture, not shear-melt, at still higher stresses. This scenario can be used to explain some bizarre experimental findings concerning the process of ‘granulation’, whereby a small volume of colloidal suspension can bistably exist in one of two states, a solid granule and a flowable droplet.

*International conference on Statistical Mechanics of Plasticity and Related Instabilities  
August 29-September 2, 2005  
Indian Institute of Science, Bangalore, India*

---

\*Speaker.



**Figure 1:** Various schematic flow curves of steady state shear stress  $\Sigma$  vs strain rate  $\dot{\gamma}$  for dense colloidal suspensions. Arrows denote possible hysteretic trajectories on ramping  $\dot{\gamma}$  up and then down.

## 1. Introduction

In this brief review I discuss recent speculative models of jamming in colloidal suspensions based on the idea of a stress-induced glass transition. These models are heuristic adaptations of the mode coupling theory (MCT) [1] that has been widely used to address the colloidal glass transition. This theory predicts correctly many features of that transition which occurs at a certain volume fraction  $\phi = \phi_g$  of colloid. As this is approached from below, the structural relaxation time diverges in a specific fashion, and for  $\phi \geq \phi_g$  the colloidal fluid phase is replaced by an amorphous solid phase of finite yield stress [2].

## 2. Flow curves for dense suspensions

Ref. [2] in fact provides a rather detailed theoretical account of yielding and shear-thinning in colloidal glasses using an extension of the MCT methodology. Although these phenomena are well-established experimentally [3], they form in fact only two members of a wider class of behaviors. Each type of behavior is characterized by a steady-state ‘flow curve’, that is a plot  $\Sigma(\dot{\gamma})$  of shear stress against strain rate in simple shearing. Figure 1 shows some of the wider range of behaviors seen in colloids, including not only shear-thinning and the yielding solid predicted by [2], but also continuous and discontinuous shear thickening.

Continuous shear thickening involves upward curvature on the flow curve; in the discontinuous case, the curve seemingly develops an S-shape with a region of negative slope. This region is

mechanically unstable [4], and likely to be bypassed by a hysteresis cycle involving shear-banding. That is, if one slowly increases the applied stress, as measured by the torque on a rheometer, an apparently vertical section of the flow curve is encountered, within which regions of high and low stress coexist in layers, with layer normals along the vorticity (neutral) direction. The measured torque then comes from a volume-weighted average of the stresses in the two bands. The upward and downward section of the discontinuous curve need not coincide (hysteresis); moreover, unsteady, possibly chaotic, flow, is often found to accompany discontinuous shear thickening (e.g., [5]). Simple models showing such chaotic behavior have recently been proposed and explored [6, 7], as have analogous behaviors in systems showing discontinuous shear-thinning [8]. (The latter can include colloids with strong attractive interactions, but that is not our subject here.)

An extreme version of discontinuous shear thickening is the curve denoted ‘static jam’ in Fig. 1. Here the S-shape curve has extended all the way back to the vertical axis. What this means is that a system that is fluid at low stresses is maintained in a state of zero shear rate, within a certain window of finite stress values. This kind of behavior has been reported in Ref. [9], albeit in a colloidal system with rather poorly-characterized interactions. However, indirect evidence for much the same picture in well-characterized, hard-sphere colloids is given in Ref. [10]; we discuss this further below.

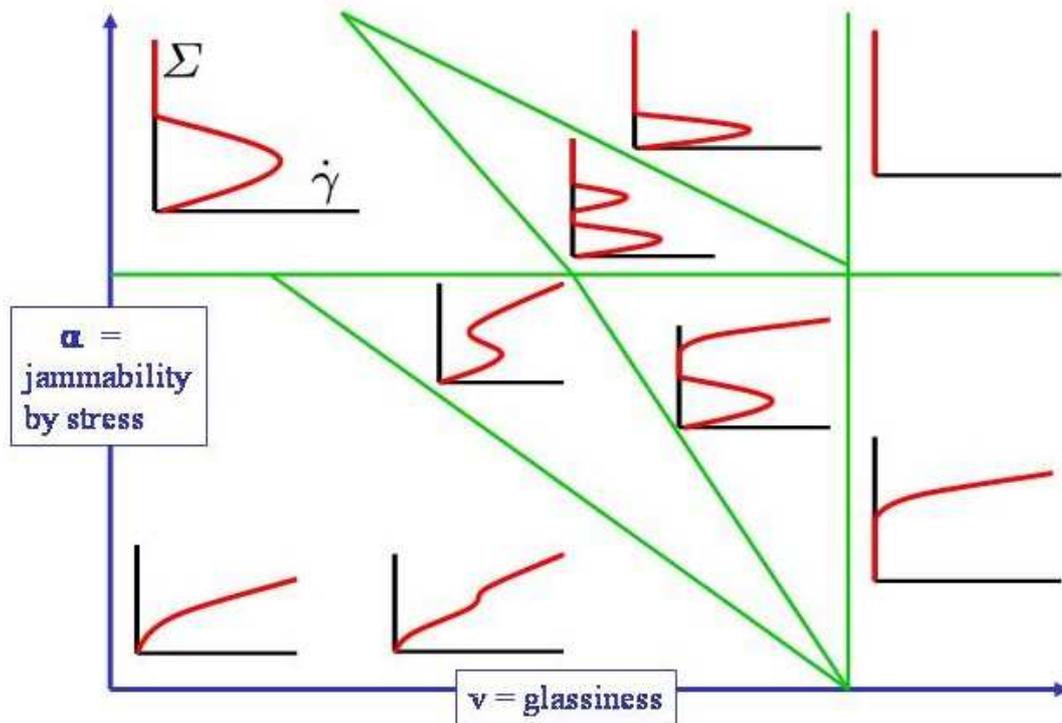
The observation of static jamming has important consequences for colloid rheology. This is because shear-thickening is often attributed to enhanced dissipation arising from lubrication forces in the narrow gaps between colloids [3]. However, all such forces vanish when the rate of strain  $\dot{\gamma}$  is zero. Accordingly, if one accepts static jamming as a special (extreme) case of shear-thickening, one must seek an alternative mechanistic explanation. Since shear thickening is often found close to the colloidal glass transition, it is natural to look to the physics of glass formation as a candidate mechanism.

The reader should however be warned that a ‘static jamming’ flow curve strictly requires only that the strain rate tends to zero in steady state within the given window of stress. It is conceivable that creep, in which  $\dot{\gamma}(t) > 0$ , but  $t^{-1} \int_0^t \dot{\gamma}(t') dt' \rightarrow 0$  as  $t \rightarrow \infty$ , combined with ever-decreasing gaps between the colloids, could conspire to maintain a static stress in the formal limit  $\dot{\gamma} \rightarrow 0$ .

### 3. A simple shear-thickening model

A heuristic extension of the MCT calculations to address shear-thickening and static jamming within a glass-transition context is presented in [11, 12]. The resulting model (of which there are several technical variants, which we do not discuss here) has two phenomenological parameters; a ‘glassiness’ parameter  $\nu$  and a ‘jammability’ parameter  $\alpha$ . Setting the latter to zero gives a good schematic representation of the complicated MCT-based shear-thinning and yielding-solid calculations of [2]. The main physics of those calculations is that continuous straining destroys the caging effect that causes the glass transition, restoring fluidity selfconsistently at high stresses  $\Sigma$ . The parameter  $\nu$  then controls how close one is to the static glass transition.

The additional parameter  $\alpha$  in the model of Refs. [11, 12] gives a new coupling, effectively setting  $\nu \rightarrow \nu + \alpha|\Sigma|$ , whereby the presence of a shear stress promotes arrest (we assume  $\alpha > 0$ ). This is plausible, since shear stress requires distortion of cages. Imagining a sphere trapped initially



**Figure 2:** Schematic flow curves of steady state shear stress  $\Sigma$  vs strain rate  $\dot{\gamma}$  within the model of [11, 12]. The ‘phase boundaries’ delineating different regimes are also schematic (e.g. they are shown straight though the real ones are somewhat curved).

within a spherical cage, one notes that affinely shearing the cage (creating an elliptical shape) reduces the free volume available to the sphere, and in fact reduces this to zero in finite strain.

Hence there is an antagonistic tendency, captured in a simple way by the model, in which the restoration of fluid behavior at large, cage-breaking strains is opposed by the tendency of anisotropic cage distortions (that is, stress) to promote arrest. Figure 2 depicts a nonequilibrium ‘phase diagram’ of the regimes in the  $(v, \alpha)$  parameter space, and the flow curves in each regime.

#### 4. Brittle jamming and brittle glasses

As well as the curves shown in Fig. 1, the model of [11, 12] shows several new regimes that were not expected. In particular, at high jammability ( $\alpha \geq 1$ ) there are flow curves in Fig. 2 where the jammed state persists up to indefinite stress. For a system that is a glass at zero stress ( $v > 4$ ), the resulting flow curve is degenerate: it becomes simply a vertical line segment between the origin and infinity. This describes a material that is solid at low stresses (a colloidal glass), and moreover that becomes ever more arrested as stress is applied. Accordingly there is no yield stress beyond which ordinary fluidity is restored. Of course, a sufficient stress will cause something to happen: but the natural candidate is now brittle failure, not the shear-melting or homogeneous yielding predicted for colloidal glasses (with  $\alpha = 0$ , effectively) in Ref. [2].

Similarly at  $\nu < 4$  but  $\alpha > 1$  one finds (alongside another more complex regime not discussed here) a material which is fluid at low stresses, but is statically jammed for all stresses above a certain minimum. This is an extreme case of static jamming, in which higher stresses just jam the system more and more, so that the jammed state is again brittle ('brittle jamming') and will fail by fracture, not by homogeneous yielding.

## 5. Discussion

Due to the extremely schematic nature of the model, it is not possible to say exactly how  $\nu, \alpha$  should depend on the volume fraction  $\phi$  of colloids nor on the interaction potential between the particles. However, it seems safe to assume that, for most interactions, increasing  $\phi$  will give a trajectory across Figure 2 from bottom left towards either the top right sector (brittle glass) or the bottom right sector (yielding glass). In either case it is possible that the brittle jam will be encountered in a range of  $\phi$  below the static glass transition  $\phi_g$ .

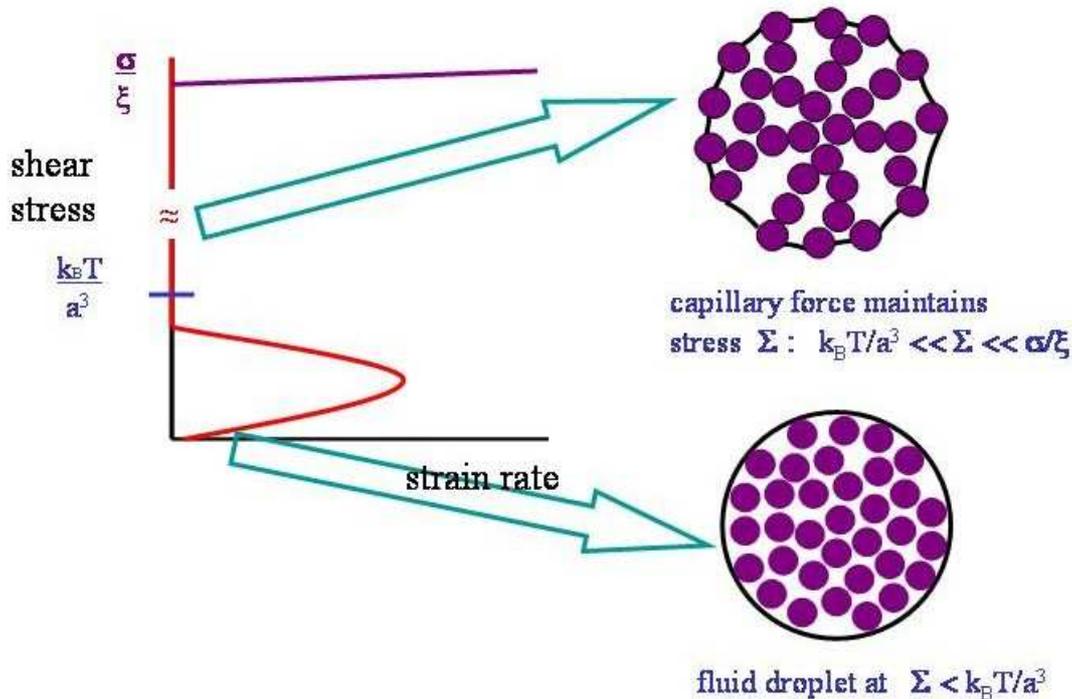
The possibility of brittle jamming, suggested by this admittedly a very simple model, is intriguing from a physical viewpoint. In particular, it may help explain a phenomenon called granulation [10], that is widely used in industry but little understood by physicists. In this process, a shear-thickening dense suspension is sheared relentlessly and ends up fragmenting into small granules, each containing hundreds or thousands of colloidal particles and a certain amount of the solvent, surrounded by air. This can be done under controlled evaporation conditions, so that there is no difference in  $\phi$  between the initial flowable bulk state and a final granule. The resulting bistability of material properties is made evident by data (reviewed in [10]) showing that (i) a granule reverts to a fluid droplet on vibration; (ii) a fluid droplet created this way, placed next to an unmelted granule, will fuse with it, causing it to melt; (iii) a fluid droplet can be transformed back into a granule, at least temporarily, by poking it with a spatula.

These peculiar phenomena can be explained by a scenario (depicted in Fig. 3) that combines brittle jamming in the droplet interior with strong capillary forces at the periphery. The latter arise as soon as colloidal particles force their way partially through the fluid-air interface as a result of their dilatant tendency under shearing; moreover, such capillary forces are, once the interior is jammed, capable of sustaining a shear stress throughout the interior of the granule [10].

Although the observation of granulation thus lends strong support to the brittle jamming scenario, it remains to be seen whether this is truly an aspect of the glass transition in colloids, or something more mechanical in origin. The author suspects that, once the granular state is achieved, there is a strong mechanical contact network between particles so that glass-transition physics, which has at its core their Brownian motion, ceases to be relevant. Nonetheless, such physics might be essential in explaining how such a material can fluidize completely at low stresses; and this is a core element in the mechanical bistability that allows transformation between a granule and a fluid droplet with precisely the same contents.

## 6. Acknowledgements

I thank M. Fuchs, M. Haw, C. Holmes, P. Sollich for their collaboration on this topic and W. Poon, M. Greenall, T. Voigtmann for discussions. Work funded in part by EPSRC/GRS10377.



**Figure 3:** Schematic explanation of granulation and granular bistability. The flow curve for a brittle jamming material is supplemented with a fracture curve; the stress required is of order  $\sigma/\xi$  where  $\sigma$  is the interfacial tension between solvent and air, and  $\xi$  is a structural length-scale (no smaller than the colloid radius  $a$ ). The onset of jamming is set by the Brownian stress scale  $k_B T/a^3$ . Between this onset stress and the fracture stress, one has a granule in which an arrested solid is selfconsistently maintained by capillary forces. At much lower stresses, a flowable droplet can arise. The initial stages of granulation require the fracture stress to be exceeded, causing the homogeneous suspension to fracture into small granules by ingress of air. For a more complete description of this simplified picture, see [10].

## References

- [1] W. Goetze and L. Sjoegren, *Rep. Prog. Phys.*, **55**, 241 (1992); W. M. van Meegen, S. M. Underwood and P. N. Pusey, *Phys. Rev. Lett.*, **67**, 1586 (1991); K. N. Pham, et al., *Science*, **296**, 104 (2002).
- [2] M. Fuchs and M. E. Cates, *Phys. Rev. Lett.*, **89**, 248304 (2002); *Faraday Discuss.*, **123**, 267 (2003); *J. Phys. Cond. Mat.*, **17**, S1681 (2005).
- [3] J. F. Brady, *Curr. Opin. Colloid Interface Sci.*, **1** 472 (1996).
- [4] P. D. Olmsted, *Curr. Opin. Colloid Interface Sci.*, **4** 95 (1999).
- [5] H. M. Laun, *J. Non-Newtonian Fluid Mech.*, **54**, 87 (1994).
- [6] D. A. Head, A. Ajdari and M. E. Cates, *Europhys. Lett.*, **57**, 120 (2002); M. E. Cates, D. A. Head and A. Ajdari, *Phys. Rev. E*, **66**, 025202 (2002).
- [7] A. Aradian and M. E. Cates, *Europhys. Lett.*, **70**, 397 (2005).
- [8] S. M. Fielding and P. D. Olmsted, *Phys. Rev. Lett.*, **92**, 084502 (2004).

- [9] E. Bertrand, J. Bibette and V. Schmitt, *Phys. Rev. E*, **66**, 60401(R) (2002).
- [10] M. E. Cates, M. D. Haw and C. B. Holmes, *J. Phys. Cond. Matt.*, **17**, S2517 (2005).
- [11] C. B. Holmes, M. Fuchs and M. E. Cates, *Europhys. Lett.*, **63**, 240 (2003).
- [12] C. B. Holmes, M. Fuchs, M. E. Cates and P. Sollich, *J. Rheology*, **49**, 237 (2005).