Delayed collapse of concentrated dispersions flocculated in a secondary minimum.

R. Buscall\textsuperscript{1,3}, J.W. Goodwin\textsuperscript{2}, S.J. Partridge\textsuperscript{2}.

\textsuperscript{1}MSACT Research & Consulting, Exeter EX2 8GP, UK.
\textsuperscript{2}School of Chemistry, University of Bristol, BS8 1TS, UK.
\textsuperscript{3}ICI Corporate Colloid Science Group, Runcorn WA7 4QE, UK.

Email: r.buscall@physics.org

It is possible to arrange for the controlled secondary minimum flocculation of colloidal particles by deliberately choosing stabiliser moieties that are too short to attenuate the VdW force entirely. This trick has been used in aqueous media by us [1,7] and by Bergstrom in non-aqueous [2], to obtain well-depths of magnitude 5 kT upwards.

It has been argued from the scaling of delay times that whereas the delayed collapse of such systems is undoubtedly an activated process, it depends upon the diffusion of particles in environments that are significantly less concentrated that the average [1]. The interface between particulate and medium is one such environment and hence that could be taken as a hint that interfacial diffusion might be important. Furthermore, the delay and collapse time scaling reported by Teece et al. [3] can be interpreted this way [4]. The most compelling case for the importance surface diffusion is however made by the recent work of Zia et al. [5] who used large-scale LAMPPS simulations to study coarsening in detail.

Because monodisperse non-ionic surfactants are very difficult to make and hard to source, only one chain-length was used in the current work (C\textsubscript{12}E\textsubscript{6}), together with three particle sizes, as shown in the table nearby; the well-depth and particle size being proportional: the fourth column to be explained below.

| PS latex | Particle radius a (nm) | Well depth \( \frac{U}{kT} \) | Delay time ratio |
|----------|------------------------|----------------|-----------------|
| SJP8     | 490                    | - 6.4          | 1               |
| SJP10    | 710                    | -10.8          | 0.88            |
| SJP11    | 960                    | -13.7          | 0.63            |

Delay times were measured as a function of volume-fraction, both under normal gravity and in a swing-out centrifuge at 1.5 and 7g. The storage modulus \( G' \) measured at ca. 200 Hz and a strain ~ 1ppm by means of wave-propagation will be reported too. The latter is plotted in fig. 1. The moduli vary like \( \varphi^{3.9} \), the exponent being similar to that seen for strong (coagulated) PSL gels, although the magnitude is ca. 500 times smaller, as is shown in appendix on p.3. \( G' \) appears to be independent of particle size, the scatter notwithstanding, which is surprising at first sight, since scaling on \( kT U / a^3 \sim a^{-2} \) might have been expected. The latter fails to recognise though that the network strains might be rope rather than thread like, whereas Zia et al. [5] suggest an additional proportionality to the characteristic strand thickness \( L/a \).

Interpreted in these terms the data in fig. 1 imply \( L/a \sim a^{-2} \), which could also be \( L/a \sim a^{-1}/U \) in this case (cf. the table above).
The delay times are plotted in fig. 2. They scale like $\phi^{2.8}/g$, where $g$ is the dimensionless acceleration (normal gravity = 1). They are found to be nearly, but not quite, independent of particle size too. The average ratio of times obtained from fits to each size separately is shown in the fourth column of the table above.

Fig. 1 $G'$ versus volume-fraction for the three latices.

The inverse linear dependence on $g$ might again be thought surprising, given that collapse is an activated process, since then tilting of the energy landscape by the body force might have been expected to give an exponential increase in rate and indeed this feature puzzled us for some time.

Induction time scaled by mean acceleration versus volume fraction for SJP8, 10 & 11

Interfacial diffusion and the presence of a fluid interfacial region [5] could however account for this perhaps, with gravity driven surface flow superposed on the interfacial diffusion and enabled near the interface. By such means particles might be transported to the bottom of the gel, by gravity imposing a bias or drift on the surface diffusion. One problem with this scenario is that it would not appear to explain the Rayleigh-Taylor instability seen in very weak gels [6]. The parameter space over which delayed collapse occurs is huge [1] however and hence it cannot be assumed necessarily that the mode and mechanism of collapse are the same across the
parameter space, a general scaling of delay and collapse times not withstanding [1]. Furthermore, there has to be a return upward flow in the pores, hence transport of particles upwards by erosion cannot be precluded in marginally rigid gels, as can not local variations, given that the particle and fluid flows need only be opposite and balanced net.

It is ca. 30 years since the phenomenon of delayed collapse was first recognised as a physical effect [7], as opposed to, say, being a result of colloidal or chemical instability, yet it still remains poorly understood. It was mentioned earlier that the parameter space (of well-depth, particle size, particle concentration, etc.) for collapse is huge. It is thus almost inevitable that it has only been explored sparsely, with volume-fraction as a neglected variable; this being true for the zero-shear viscosity too [8]. Be that as it may, the effects of particle size and volume-fraction would benefit from further systematic exploration. The effect of centrifugal acceleration looks to be worth exploring further too.

**Acknowledgement:** M A Faers is thanked for helpful discussions.

**References:**

[1] Buscall, R., T. H. Choudhury, M. A. Faers, J. W. Goodwin, P. A. Luckham & S. J. Partridge, Soft Matter (2009), 5, 1345 - 1349
[2] Bergström, L., J. Chem. Soc., Faraday Trans. 1, 88, 3201 (1992).
[3] Teece, L. J., M. A. Faers, and P. Bartlett, Soft Matter 7,1341 (2011).
[4] Supplementary material in arxiv version.
[5] Zia R.N., B.J. Landrum & W.B. Russel, J. Rheol., 58 1121-1157 (2014).
[6] Poon, W.C.K. L. Starrs, S.P. Meeker, A. Moussaid, R.M.L. Evans, P.N. Pusey & M.M. Robins, Faraday Discuss., 1999, 112, 143; L. Starrs, W.C.K. Poon, D.J. Hibbert & M.M. Robins, J. Phys.: Condens. Matter, 14, 2485 (2002).
[7] S. J. Partridge, Ph.D. dissertation, School of Chemistry, University of Bristol (1985).
[8] Buscall, R., J I McGowan & A J Morton-Jones, J. Rheol., 37 621 (1993).

**Appendix** – comparison of the moduli of SM flocculated and coagulated polystyrene latex. Also shown is the compressive strength of the coagulated gel and, for comparison, similar data for SM flocculated alumina from [2].

Supplementary material follows.
Modelling sedimentation

Mass-momentum conservation

\[ 0 = \partial_t \phi + \frac{1}{\mu} \partial_x \left[ \kappa \left( f_g - \partial_x p_s \right) \right]; \quad (1) \]

Gravity term

Gel strength term

\[ \equiv \partial_t \phi + \frac{\Delta \rho g}{\mu} \partial_x \left[ \phi \kappa \right] - \partial_x \left[ D \partial_x \phi \right]; \quad (2) \]

The diffusion eqn 2 follows when the stress is not time-dependent except via \( \phi(t) \).

If it is, e.g. fluctuations cause \( \kappa \) to relax, or because \( \kappa \) and \( \kappa \) change as a result of coarsening, then eqn 2 only applies if the stress is factorable thus, \( p_s(\phi,t) = p_s(\phi,0)f(t) \)

Just for the sake of argument let suppose it is and likewise for \( \kappa(\phi,t) \)...

\* There is a wall interaction term also, but I have invoked slip here for the sake of clarity

Because there are 2 time-dependent functions even this simplistic result does not imply homogeneous time-compression scaling in general. Does it at all?

**Creep** \( (d_t f_k < 1; f_k = 1) \) would not.

**Coarsening** \( (d_t f_k < 1, d_t f_k < 1) \) would not except perhaps

where the third term, does not much affect on the rate of descent of the upper interface, i.e. where it is permeability-controlled in effect.
**Teece et al.**[3] see a simple collapse law at lower volume-fractions with time scaled on the Kramers’ time and then compressed.

This can be expressed as a simple temporal transformation

\[ t \Rightarrow \left( \frac{t}{\tau_{esc}} \right)^{3/2} \]

... the implication then, given \( \kappa \sim R^2 \) is that the time-scale transformation might simply be,

\[ t \Rightarrow \text{const.} \int ds R^2(s) \]

Where \( R(t) \) is the growth law for typical cluster size. If so, the experimental results in turn imply the following growth law at low to intermediate volume-fractions

\[ R \propto \left( \frac{t}{\tau_{esc}} \right)^{1/4} \]

cf (e.g.) Oswald ripening exponent of 1/3. Surface diffusion of 1/4.

**Teece et al. time scaling implies surface diffusion perhaps.**

**Individual delay time fits:**

Induction time scaled by mean acceleration versus volume fraction for SJP8

\[ t_d g = k \nu^{2.8} \text{ with } k = 8.10^5 \]
Extended Abstract of a contribution offered to “Arrested Gels”, Cambridge, 23-25 March 2015.
http://www.constableandsmith.com/arrestedgels/

Induction time scaled by mean acceleration versus volume fraction for SJP11

\[ t_d \phi^2 = k v^{2.8} \]
\[ k = 5 \times 10^5 \]

Induction time scaled by mean acceleration versus volume fraction for SJP10

\[ t_d \phi^2 = k v^{2.8} \]
\[ k = 7 \times 10^5 \]