General Discussion

Prof. Weitz opened the discussion of Dr Bartlett's paper: Does the friction coefficient of the particle depend on frequency? If it did, the factor of 2.25 that you find could be frequency-dependent.

Dr Bartlett responded: Both the individual ξ_{11} and joint friction coefficients ξ_{12} are functions of frequency, reflecting the viscoelasticity of the polymer solution in which the particles are diffusing (see the inset in Fig. 6 of our paper). However, the ratio ξ_{12}/ξ_{11} of the two coefficients, over the range of frequencies which we are able to probe reliably in our experiments ($10^1 \leqslant \omega \leqslant 10^4$), seems to be frequency-independent. It is an interesting question if this observation still holds at frequencies lower than those we can access using our optical trapping technique. In such a long-time limit, the polymer molecules will be able to freely diffuse around the particle and so could well modify the slip boundary condition seen here. It would be fascinating to combine our short-time measurements with slower video-microscopy methods[1] to establish whether the ratio ξ_{12}/ξ_{11} changes over a wide range of frequencies, as simple arguments would suggest.

1   J. C. Crocker, M. T. Valentine, E. R. Weeks, T. Gisler, P. D. Kaplan, A. G. Yodh and D. A. Weitz, *Phys. Rev. Lett.*, 2000, **85**, 888.

Prof. Pusey commented: I like your suggestion that the discrepancy between experiment and theory might result from an effective slip condition of the polymer solution at the particle surface. The experimental literature on the diffusion of isolated particles in polymer solutions is quite confused. It seems likely to me that, by analogy with a concentrated particle suspension, one can view the particle at any instant as being "caged" by the polymer molecules. Then there will be two regimes of particle diffusion. At times small compared to the relaxation of the polymer (the time a polymer molecule takes to diffuse its own radius) the particle will move inside the polymer cage, interacting with it only through hydrodynamic interactions, *i.e.* it will "slip" against the polymer. At long times, however, over which both the polymer and the particle move significantly, the particle will diffuse through the solution, seeing its macroscopic rheological properties. It is possible that the single particle data of Fig. 4 in the paper lie in the transition region between faster, in-cage slipping, diffusion at short times and slower macroscopic diffusion at longer times.

Some years ago an Edinburgh student, Paul Golz, studied particle diffusion in polymer solutions and found evidence for this transient caging of the particles by the polymer (unpublished).

Dr Bartlett replied: Many thanks for your comments. The physical picture you have described of a two-stage dynamics in a colloid-polymer system is a very interesting one and one which suggests a number of interesting experimental tests. For instance, it would be worthwhile repeating our single particle measurements (shown in Fig 4 of the paper) at a range of different trap strengths (or laser intensities). In the data shown in Fig. 4 of the paper we have found that at the mean-squared displacement of the particles grows as a power law of time, $\langle \Delta x^2 \rangle \sim t^n$ with $n \sim 0.8$, rather than linearly in time. If this physical picture is correct, one might expect the exponent n to be a function of the trap force constant since in the limit of a vanishingly small harmonic trap, the mean-square displacement must become linear in time $\langle \Delta x^2 \rangle \sim t$. Finally we are currently in the process of analysing our trajectory data to quantify the extent by which the single particle diffusion deviates from a Gaussian. The non-Gaussian parameter

$$\alpha(t) = \frac{\langle \Delta x^4(t) \rangle}{3 \langle \Delta x^2(t) \rangle^2} - 1 \tag{0.1}$$

should be a sensitive function of the fluctuations in the local environment around each colloidal particle and should enable us to test the physical picture you suggest.

Dr Cipelletti said: Your measurements probe much higher frequencies (shorter times) than in previous experiments. Do you have to worry about the time it takes for shear waves or elastic modes to propagate from one particle to the second one?

Dr Bartlett responded: The speed of the propagating transverse sound waves in a elastic medium of density ρ and shear modulus G is of order $c \sim \sqrt{(G/\rho)}$. Taking as representative values, $G \sim 10$ Pa and $\rho \sim 10^3$ kg m^{-3}, then the time to propagate between two particles separated by 10 µm is *ca.* 10^{-4} s. This is comparable with our shortest timestep so while sound propagation effects may make a small contribution they are unlikely to have a major influence on our measurements.

Dr Fuchs asked: You raised the interesting question about the boundary condition of a particle in a viscoelastic medium. There could be two origins for the deviations, one connected to the curvature of the particle, the other to the viscoelasticity of the surrounding medium. You could check for the first effect by changing the particle size.
Do you have further information on this?

Dr Bartlett replied: This is a very interesting suggestion. Unfortunately I do not have any idea of the relative importance of the curvature of the particle. The physical picture outlined by Prof. Pusey above would suggest that the important parameter determining the boundary conditions should be the ratio of the mean-square displacement of the particle $\langle \Delta x^2(t) \rangle^{1/2}$ to the width of the polymer depletion zone ζ. Slip would be expected if $\langle \Delta x^2(t) \rangle^{1/2} \sim \zeta$ and stick otherwise. However at the moment I have no further experimental data to check this conjecture.

Prof. Dawson said: You have noted a few uncertainties in the interpretation of your experiments, including the nature of effective boundary conditions.
Is there any reason why simulations of the experiment have not been carried out to resolve the issues: they seem feasible?

Dr Bartlett responded: To the best of my knowledge I don't know of any simulations which have addressed this issue but I think such simulations should be feasible and would certainly be interesting.

Dr R. A. Penfold asked: Given that intense illumination is required to achieve adequate signal-to-noise levels for accurate estimation of multi-point correlation functions by this technique, I can imagine that some degree of localised heating occurs at the beam focus in the region of a trapped particle. If this effect is significant, would some independent measure of local temperature become necessary to correctly account for perturbations of the Brownian diffusion? Has there been any theoretical analysis of thermal inhomogeneities induced by optical tweezers?

Dr Bartlett answered: As suggested by Dr R. A. Penfold, there is undoubtedly some localized heating due to solvent and particle absorption in the intense fields at the focus of the laser beam. However absorption coefficients at the 1064 nm laser wavelengths used here are small. The degree of localised heating in the focus has been measured experimentally in a number of previous studies[1] and analysed theoretically.[2] We estimate the laser power in the focal plane in our experiments as *ca.* 10 mW and the corresponding temperature rise as $\leqslant 1$ K. Consequently in comparison to a typical thermal temperature of 293 K localised heating is expected to have a negligible effect on the Brownian motion of a trapped particle.

1   Y. Liu, D. K. Cheng, G. J. Sonek, M. W. Berns, C. F. Chapman and B. J. Tromberg, *Biophys. J.*, 1995, **68**(5), 2137.
2   P. M. Celliers and J. Conia, *Appl. Opt.*, 2000, **39**(19), 3396.

Prof. Weitz asked: Have you considered two particle microrheology measurements for particles in concentrated suspensions of hard spheres? Early measurements using diffusing wave spectroscopy were able to use one particle microrheology to measure the viscoelasticity of hard sphere suspensions.[1] However, it is not clear to me how the spatially heterogeneous motion, such as that seen by Weeks,[2] will affect the microrheology.

1   T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.*, 1995, **74**, 1250
2   E. R. Weeks, J. C. Crocker, A. C. Levitt, A. Schofield and D. A. Weitz, *Science*, 2000, **287**, 627.

Dr Bartlett replied: Along with a Bristol student, Steve Mitchell, I have measured the thermal fluctuations of two PMMA particles immersed in a host suspension of index-matched silica spheres at a range of particle volume fractions between $0.05 \leqslant \phi \leqslant 0.30$ (unpublished). However we have not so far analyzed this data using the microrheology formalism presented here but I agree that it would be very instructive to try. Unfortunately because of difficulties with handling and controlling the silica/PMMA system we were unable to study very concentrated suspensions so I doubt whether we will be able to see the spatial heterogeneous dynamics expected near the glass transition.

Dr Vollmer commented: A possibility to check whether the laser locally is heating up the polymer solution might be *via* measurements close to phase separation. A local phase separation should be reflected in the single-particle friction coefficient, respectively, the ratio of the one- and two-particle friction coefficients. For example solutions of polystyrene in a mixture of diethylether ($C_4H_{10}O$) and orthotrimethylformamide ($CH(OCH_3)_3$) phase separates under heating. The phase separation temperature strongly depends on the ratio of diethylether and orthotrimethylformamide.

Dr Bartlett responded: Thank you for the suggestion however I worry that the phase separation may lead to very complex hydrodynamic coupling which could prove rather difficult to analyse quantitatively.

Dr Frith commented: 1. The biological community have been routinely using optical traps to confine living cells for some years which implies there is very little effect of heating.
2. We can use trapped particles in a similar set-up to the authors' to measure the viscosity of water with good accuracy, which indicates little or no heating.

Prof. Lyklema opened the discussion of Dr Koenderink's paper: The hydrodynamic drag between a pair of approaching colloid particles has been analysed by Spielman[1] and others. This refers to non-rotating spheres. As the charges on colloid particles are often not homogenously distributed it is likely that rotation of the particles may also take place and the question arises whether the incurred rotational drag is larger or smaller than the translational one. Spielman himself, in a personal communication, stated that the rotational drag would be much lower than the translational one but did not elaborate that. Is nowadays anything known about this issue? It is relevant for the interpretation of the kinetics of coagulation.

1   L. A. Spielman, *J. Colloid Interface Sci.*, 1970, **33**, 562.

Dr Koenderink replied: Non-homogeneously charged colloidal spheres exert mutual torques on each other. These torques and the orientation dependence of the underlying pair potential give rise to an additional hydrodynamic mobility contribution to the 2-sphere Smoluchowski equation which describes translational-rotational coupling (*cf.*, *e.g.*, refs. 11 and 48 in the paper). In accord with Spielman's statement, we expect the drag arising from these additional mobility contributions (related to rotational-translational shearing motion), and the resulting influence on the coagulation rate, to be of secondary importance as compared to the translational drag, although we can not quantify this expectation presently in terms of the pair probability distribution. The translational drag originates from the squeezing motion of two spheres approaching each other along their line of centres, with the relative hydrodynamic mobility going to zero near contact distance proportional to $r - (a_1 + a_2)$ due to strong lubrication stresses in the thin fluid gap (*cf.* ref. 1). We are not

aware of theoretical work done on the coagulation kinetics of colloidal spheres with non-homogeneous surface charge distributions.

1   S. Kim and S. J. Karrila, *Microhydrodynamics: Principles and Selected Applications*, Butterworth-Heinemann, Oxford, 1991.

Dr R. B. Jones commented to Prof. Lyklema: The frictional forces between two rotating spheres or between a rotating sphere and a fixed wall are known to arbitrary accuracy for any separation of the two spheres or of the sphere from the wall.[1,2] As the spheres approach each other (or as one sphere approaches a wall) the frictional torques do not vanish. For simplicity, consider one sphere held fixed and the other sphere rotating at given angular velocity. If the axis of rotation is normal to the line of centres (or parallel to the wall) then the relative rotational friction coefficient diverges weakly to infinity as the logarithm of the surface–surface separation. If the axis of rotation is along the line of centres (or normal to the wall), then the relative rotational friction coefficient tends to a finite but non-zero value which is given in terms of the zeta function.

1   D. J. Jeffrey and Y. Onishi, *J. Fluid Mech.*, 1984, **139**, 261.
2   B. Cichocki and R. B. Jones, *Physica A*, 1998, **258**, 273.

Prof. Felderhof commented: Following eqn. (7) of your paper you mention hydrodynamic pair interactions. The references you give concerning their calculation are not quite accurate and incomplete. Mazur and van Saarloos (ref. 27 of the paper) did not calculate the mobility functions to order r^{-12}, but rather up to order r^{-7}. They considered spheres with stick boundary conditions. In fact the mobility functions to order r^{-7} were calculated some years earlier by a simpler method and for more general spherical particles by myself[1] and by Reuland *et al.*[2] The calculation up to order r^{-12} was performed by Schmitz and myself.[3] The calculation was extended to order r^{-20} by Jones and Schmitz[4] with the aid of computer algebra. Somewhat later it was found by Cichocki *et al.*[5] that it is more convenient to calculate the coefficients in the expansion numerically for given sizes and boundary conditions. An efficient algorithm was constructed which allows rapid calculation of hundreds of coefficients of the expansion. The calculation can be performed for spheres of different radii with arbitrary boundary conditions, for permeable spheres, as well as for droplets kept spherical by high surface tension. The algorithm can be programmed easily and calculations can be performed on a personal computer. Thus hydrodynamic pair interactions between spherical particles are fully known.

1   B. U. Felderhof, *Physica A*, 1977, **89**, 373.
2   P. Reuland, B. U. Felderhof and R. B. Jones, *Physica A*, 1978, **93**, 465.
3   R. Schmitz and B. U. Felderhof, *Physica A*, 1982, **116**, 163.
4   R. B. Jones and R. Schmitz, *Physica A*, 1998, **149**, 373.
5   B. Cichocki, B. U. Felderhof and R. Schmitz, *PCH PhysicoChem. Hydrodyn.*, 1988, **10**, 383.

Dr Koenderink replied: As stated in our paper, we have calculated the translational/rotational tracer diffusion coefficients using a truncated expansion of the pair mobility functions up to order r^{-12}, with analytic expressions for different particle radii taken from Jeffrey and Onishi (ref. 28 of the paper). Moreover, we have accounted for the long-distance asymptotic hydrodynamic three-body hydrodynamic contribution (*cf.* ref. 1 for additional details on these calculations). Calculations of the two-body mobilities up to order r^{-12} have been performed in a paper by Schmitz and Felderhof[2] two years earlier than in ref. 28. Errors in some of the expressions published in ref. 2 have been corrected somewhat later in the work of Jones and Schmitz.[3] For identical spheres only, ref. 3 includes also explicit results for the mobility functions up to order r^{-20}. Our use of a truncated inverse distance expansion up to order r^{-12} is certainly justified for charge-stabilized suspensions, where configurations of closely spaced spheres are very unlikely.

For a complete quantitative description of tracer diffusion in hard-sphere mixtures, it is certainly necessary to fully account for hydrodynamic pair interactions. For this purpose, the algorithm developed in ref. 4 may be used, as suggested by Prof. Felderhof. It is clear that our results for short-time tracer diffusion are valid only approximately. However, we expect that our general conclusions regarding the tracer/host size ratio dependence and volume fraction dependencies of the diffusion coefficients remain valid once two-body HI have been fully accounted for. This

expectation is supported by the observation that our approximate calculation of the translational first order virial coefficient in eqn. (23) of the paper agrees, within a few per cent for all size ratios considered, with corresponding numerical results for hard-sphere mixtures by Batchelor (refs. 51 and 54 of the paper) where near-field two-body HI has been accounted for. As we have discussed in our paper, three-body and higher order hydrodynamic contributions become increasingly important for larger tracer-host size ratios and larger host volume fractions. Eventually, these higher order contributions dominate the two-body contributions left out in our truncated expansion.

1   H. Zhang and G. Nägele, *J. Chem. Phys.*, 2002, **117**, 5908.
2   R. Schmitz and B. U. Felderhof, *Physica A*, 1982, **116**, 163.
3   R. B. Jones and R. Schmitz, *Physica A*, 1998, **149**, 373.
4   B. Cichocki, B. U. Felderhof and R. Schmitz, *PCH PhysicoChem. Hydrodyn.*, 1988, **10**, 383.

Prof. Lyklema asked: Prof. Felderhof, does it make a difference whether the driving force for the rotation is directional or random?

Prof. Felderhof replied: The hydrodynamic pair interaction functions are elements of a twelve-dimensional mobility matrix relating the translational and rotational velocities of the two suspended spherical particles linearly to the forces and torques acting on them. The origin of the forces and torques is immaterial, but they act as vectors, and both their magnitude and direction matter. The pair interaction functions depend on the distance between centers, and on the boundary condition for the flow at each spherical surface. The mobility matrix can be generalized to include the effect of an incident flow acting on the particles.

Dr Saunders said: If there was rotation of a charged particle (*i.e.* anionic polystyrene latex) in water without friction then one would expect a net spin for the particle. This could be investigated. We performed a preliminary experiment at Monash University (Australia) in which the magnetic susceptibility of a 10% w/w polystyrene latex was measured. The result was that the dispersion was diamagnetic (not paramagnetic). This may suggest a slow rotation and the presence of significant friction.

Prof. Felderhof commented: Frequency-dependence of the rotational diffusion coefficient can arise in various ways. In the high-frequency range corrections to the Stokes formula due to inertia of the fluid may be taken into account.[1] Frequency-dependence in the Stokes-regime may be caused by viscoelasticity of the ambient fluid. One can then simply replace the viscosity in Stokes' formula by the frequency-dependent viscosity. At higher concentrations interactions between solute particles can cause frequency-dependence *via* relaxation of the pair distribution function. These effects are much more difficult to calculate. Some years ago such a calculation was performed for a suspension of spheres with isotropic orientational interaction by R. B. Jones and myself.[2] The pair Smoluchowski equation for rotational diffusion of two spheres with anisotropic orientational interaction has been solved only recently.[3] Hydrodynamic interactions and translational diffusion have not yet been taken into account in these calculations.

1   H. Lamb, *Hydrodynamics*, Dover, New York, 1945, p. 642.
2   B. U. Felderhof and R. B. Jones, *Phys. Rev. E*, 1993, **48**, 1142.
3   B. U. Felderhof, *J. Chem. Phys.*, 2002, **117**, 3583.

Dr R. B. Jones said: I want first to comment that rotational diffusion can be a powerful tool to explore the nature of caging in dense suspensions. To illustrate this I have calculated the rotational mobility of a sphere of radius a, located at the centre of a fixed spherical container of radius R, ($R > a$), filled with Newtonian fluid of shear viscosity η. The rotational mobility of the small sphere then has the form.

$$\mu^{\mathrm{rr}} = \frac{1 - (a/R)^3}{8\pi\eta a^3}$$

This expression shows that even if the particle is quite tightly constrained ($R \approx a$), there is still an appreciable rotational mobility and hence rotational diffusion. By measurement of the rotational diffusion coefficient one can get an estimate of the average size of the cage.

My question then is to what extent is it now possible experimentally to observe rotational diffusion in dense suspensions?

Dr Koenderink replied: It is indeed possible experimentally to observe rotational diffusion in dense suspensions. In fact, experiments on dense suspensions have already been performed in our group.[1] In that paper we used time-resolved phosphorescence anisotropy to study the rotational diffusion of tracer spheres in a random packing of host spheres, varying the ratio between the radius of the tracer and the host spheres. The anisotropy decay curves (a measure for the rotational diffusion) could always be fitted by a single exponential decay plus a plateau stemming from the fraction of immobilized particles. Our results thus suggest that the tracer sphere is rotationally mobile up to close contact. Furthermore, in accordance with Dr R. B. Jones' suggestion, we were able to link this fraction of immobilized particles to the average pore size of a random-closed-packing. The decrease of the rotational mobility showed a dependence similar to the dependence suggested by Dr R. B. Jones, although we are considering here the rotation of a sphere in a cage with a few contact points rather than the rotation of a sphere in a spherical cage. Using luminescence techniques, like time-resolved phosphorescence anisotropy and fluorescence photobleaching recovery, together with particle synthesis techniques which allow to vary tracer dimensions and surface properties, we are able to study pore size distributions and local interactions between tracers and complex media.

1   M. P. Lettinga, C. M. van Kats and A. P. Philipse, *Langmuir*, 2000, **16**(15), 6166–6172.

Dr Fuchs asked: Concerning the rotational diffusion in dense suspensions, R. Schilling and co-workers from Mainz have made an interesting prediction about what could happen if one considers elongated molecules and changed the elongation. At small elongations, the molecule can be trapped in a cage but still perform head-to-toe flips so that angular momentum relaxation curves of odd order decay to zero. At larger elongations, however these flips become arrested as well.

Could these be studied with your techniques in dense colloidal suspensions?

Dr Koenderink replied: It would certainly be possible to study flipping of elongated particles with either of the two techniques mentioned in our paper, *i.e.* time-resolved phosphorescence anisotropy (TPA) and depolarized dynamic light scattering (DDLS). The main limitation is the availability of suitable particles. TPA requires tracer particles labeled with a phosphorescent dye with a lifetime of a few milliseconds. TPA may not be too suitable for monitoring very slow orientational relaxation. Instead, fluorescence photobleaching recovery, a novel technique in our lab, might be employed. DDLS requires optically anisotropic particles. In principle, rod-like particles already have form anisotropy leading to depolarized scattering, but especially for small elongations this will most likely not give a sufficiently high signal. Suitable optically anisotropic particles are for instance polytetrafluoroethylene rods.

If a suitable system is found one still has to deal with the interpretation of the results, which is not free of ambiguities. The ambiguity lies in the fact that it is difficult, if not impossible, to distinguish between an ensemble of rods that is rotating within a cone of a certain angle and an ensemble of rods of which a fraction is freely rotating and a fraction is completely immobilized. Both situations will lead to a decay of the measured orientational correlation function towards a non-zero plateau. In the answer to the comment of Dr R. B. Jones we refer to experiments done in our group similar to the experiment suggested in this comment. In these experiments we considered the rotation of spheres in a confining medium. In the case of spheres there is no ambiguity as to the interpretation of a non-zero plateau of the rotational decay, since it is solely due to immobilization of the tracer on the experimental time-scale. With caged rods, this is not the case.

Dr Hopkinson opened the discussion of Dr Melrose's paper: Would the faster relaxation of an emulsion droplet mean that such force chains are not observed in a sheared emulsion system?

Dr Melrose answered: Assuming the drops are deformable on the scale of the applied stress, then the squeeze lubrication forces have a much weaker divergence, and I would not expect thickening and the emergence of a contact network. However, emulsion systems are a broad church. I suspect everything is possible depending on the nature of the surface coat and viscosity of the droplet phase.

Prof. Wagner commented: In response to the restricted Stokesian dynamics simulations of idealized, polymer coated colloids presented by John Melrose, we have measured the steady shear viscosity of charge stabilized colloidal silica (Nissan, 450 nm, aqueous) over a range of volume fractions and shear rates and compared this to the same suspension coated with poly(vinyl alcohol) (AirProducts AIRVOL-540, 88% hydrolyzed, $\sim$140 000 MW) at 750 ppm in aqueous solution. The result is a low density, porous steric layer of approximately 50 nm in thickness coating the particles. Presented in Fig. 1 are results that demonstrate that a porous polymer layer can suppress the onset of shear thickening at high volume fractions. The volume fractions are based on the colloidal silica only. This directly supports the simulations results if one assumes that the very low concentration of adsorbed polymer (less than $\sim$1% in the layer) does not significantly modify the lubrication hydrodynamics, but rather, hinders particles from approaching. Note also that the polymer layer also improves flowability in the glassy state. If one further compares with the measurements of Mewis and coworkers on colloids with very dense brushes, there one sees the opposite effect, where the dense brush acts to increase the overall hydrodynamic size of the particles, which leads to shear thickening at lower stresses.

Dr Melrose replied: I think this is in accord with the simulations. I should make it clear that the effects of a coat on thickening. On the one hand the coat conservative forces will, for some range of applied stress, inhibit thickening (*e.g.* Brownian hard spheres show thickening starting at the end of shear thinning, adding polymer coats suppresses this and leads to a second Newtonian plateau). However when the applied stress is sufficient to compress the coat, thickening may occur depending on the strength of the coat lubrication forces. If these are weak then the simulation would predict a 'weak' thickening response. In the context of the arguments presented in the text, everything hangs on how the relaxation time of the coat varies with compression of the coat. I find the experimental data presented most exciting. I wonder however if the 'bare spheres' can be considered as true hard spheres? The simulations and theoretical arguments suggest that hard sphere lubrication systems that show thickening, can only have a viscosity diverging as the log of the inverse gap between particle surfaces. Therefore, a model with just hard sphere lubrication could not physically explain
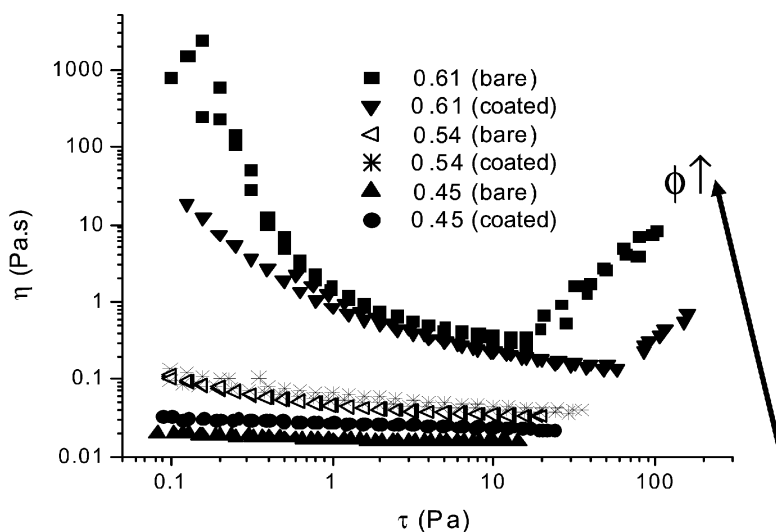

Fig. 1

the order of magnitude change in viscosity observed in the data: even in this system a close range deviations from hard sphere lubrication must be acting.

Prof. Cates said: I realize that in the simulations you describe, Brownian motion is neglected and shear thickening is controlled by lubrication and coat forces. But can you rule out a shear thickening regime in some systems at much lower Peclet numbers where the stresses are mainly Brownian in origin?

Dr Melrose answered: Brownian hard spheres do show a thickening response (see simulations by ourselves, ref. 2 of the paper, but also by Brady and co-workers). The thickenings starts right at the end of shear thinning, but it is a mild thickening with a divergence as the log of the inverse stress (as predicted by eqn. (13) of the paper, see ref. 12 and more detailed publications to be submitted shortly). However in these simulations the enhanced stress is also from the dissipative forces. The question is: can a thickening response with increasing shear rate be found where the thickening contribution to the stress comes from the thermodynamic forces rather than the dissipative forces? The scaling argument in the text at the end of Section 2, in eqns. (5) and (6), suggests that this is in principle not possible (the argument covers Brownian forces which in the reduced form of eqn. (6) scale as $1/Pe$). However O'Brien and Mackay[1] have reported at high volumes fractions (> 0.6) that they observe thickening with a diverging elastic contribution: this result needs further study. Note that the above dominance of the dissipative forces in the divergent stress does not mean that the thermodynamic forces do not have role in the thickening effect: see the pair argument reviewed in Section 3 of the text.

1   O'Brien and Mackay *Langmuir*, 2000, **16**, 7931–7938.

Prof. Cates asked: Can you clarify the relationship, if any, that you see between "classical" shear thickening at high *Pe* (with viscous/lubrication forces dominant) and "jamming", in which the system stops flowing altogether. In the latter case, the forces must be essentially thermodynamic.

Prof. Wagner replied: Reversible shear thickening as seen in colloidal dispersions is a consequence of the singularity of the short range lubrication forces acting between the colloidal particles. In principle, this occurs without any direct surface-to-surface contact between particles, as would be observed in a static granular system. Reversible shear thickening results in "jamming", but has a well-understood micromechanical basis that has been verified experimentally and theoretically, as well as simulated by Stokesian dynamics methods, such as those presented by John Melrose. It requires an applied deformation or stress field (*e.g.* an applied shear stress) and results in microstructural rearrangement leading to stress jamming. Experiments have shown the phenomena to be controlled by stress.

Prof. Wagner asked: Inspired by the restricted SD simulations of Dr Melrose and the SD simulations of John Brady, we have undertaken an experimental elucidation of the mechanisms of shear thickening by studying model hard-sphere and charged-sphere colloidal dispersions. The measurements have been complemented by modeling based upon analysis of the Smoluchowski equation for two particles, with a mean-field correction for the hydrodynamic effects at higher concentrations. Based upon the mechanism of lubrication hydrodynamics leading to hydrocluster formation at high shear rates, a force balance results that connects the lubrication forces in the hydrocluster to the stabilizing interparticle forces at the point of shear thickening. Based upon the additional time-scale arguments presented by Dr Melrose, the force balance model has been evolved into a *predictive* model for the onset of shear thickening in concentrated suspensions. Good comparison with detailed experimental measurements has been presented in a series of recent papers, the latter of which includes detailed SANS measurements of the hydrocluster microstructure as well.[1–3]

1   B. J. Maranzano and N. J. Wagner, *J. Chem. Phys.*, 2001, **114**(23), 10514–10527.
2   B. J. Maranzano and N. J. Wagner, *J. Rheol.*, 2001, **45**(5), 1205–1222.
3   B. J. Maranzano and N. J. Wagner, *J. Chem. Phys.*, 2002, in press.

Dr Melrose responded: I should note that the pair argument presented was developed by Prof. Robin Ball in collaboration with myself. The solution of the pair Smoluchowski equation is a more formal setting for the pair argument. However this requires ad-hoc closures of the higher order distribution functions and I note that the lubrication law in the theory of Wagner *et al.* is modified by use of high frequency hydrodynamic viscosity. I do not think that the high frequency viscosity is active in the gap between the particle rather this is a assumption about the relative squeezing rates of the particles varying with volume fraction. I think this amounts to a choice of the pre-factor in the simple pair argument presented in the text. However the success in this modification in predicting the data is clear and to be noted.

Prof. Pusey said: You have modelled the stabilising polymer coatings on colloidal particles by springs which impart a force perpendicular to the particles' surfaces. I have sometimes wondered whether, in reality, there is an additional effect whereby the coatings become enmeshed, like cogwheels, so that relative motions parallel to the particle surfaces become hindered and therefore correlated. For example, at least in dilute suspensions, a shear flow causes the particles to rotate. Then the bottom surface of one particle will move in the opposite direction to the top surface of a particle which (instantaneously) lies below it. If the two surfaces become enmeshed this relative motion will be hindered. Indeed one might guess that the particles would then tend to rotate as a doublet, significantly changing the suspension's rheological properties. I wonder, first, whether Dr Melrose would like to comment on this possible effect, and, second, whether he has modelled it or could do so.

Dr Melrose replied: The model for the coat interaction we use is crude. It models the coat as Brinkman-like porous layer and assumes that the coat remains in its linear response regime under compression. The interaction model restricts itself to the squeeze lubrication terms. For hard spheres shear lubrication terms diverge only as the log of the inverse gap a far weaker than the inverse gap divergence of the squeeze terms. At the time the work was done we did not have an equivalent coat model for shear lubrication, but we have since developed one.[1] The results will be submitted for publication shortly, at level of this model the effects of the shear terms are to lower the onset of thickening and to enhance the thickening curve. However the picture you give is of stronger coat response in a non-linear regime. Quite generally strong modification of shear interactions would radically alter the flow curve. I tried some simulations where the shear lubrication terms were arbitrarily allowed to diverge like the squeeze terms. This produces a dramatic thickening response with the viscosity diverging by over two orders of magnitude in a narrow range of shear rates. A future research line here is to measure the dynamic force laws of coats in shear and squeeze and to develop coat interaction models for use in these simulations (see also comments in reply to Prof. Dawson's question.) Some measurements have been made by Israelachvili and co-workers, but much more could be done.

1   R. Farr, J. Melrose and A. Catheral, unpublished work.

Prof. Dawson asked: So from what you said it would be interesting to study shear-thickening across a transition where the polymer coating has a transition in characteristic relaxation time. Particles with a coating that undergoes a brush–mushroom transition are available. Do they exhibit a transition in shear thickening behaviour at the brush–mushroom transition?

Dr Melrose answered: Something like that is already present in the model simulated. Fig. 2 shows a plot of the contact relaxation time against gap between the hard particle surfaces, from left to right the coats are under increasing compression. The relaxation time of the coat (see eqn. (7) of the paper) has a maxima: at low compression the lubrication coefficient of the coat rise steeply whilst at high compression the steric repulsion of the coat grows strongly. However the (crude) coat model used assumes that at each compression the coat remains is in its linear response regime. You allude to an effect in which the coat response is non-linear and indeed I would expect such changes would couple to flow curve at high shear rates, but I know of no such observations. Quite generally the response of brushes or adsorbed polymers to the particle relative motion could involve a rich set of phenomena to investigate. However theoretical developments of interaction models will need be

informed by dynamic force measurements. In the case you mention, I wonder if strong effects on shear lubrication would occur (see question by Prof. Pusey). The interesting prediction of the simulation is that this local small-scale behaviour would show itself up in the thickening flow-curve, see the discussion at the end of Section 5 of the paper.

Mrs Grayeff asked: Does Dr Melrose consider that in a water–glass aluminium oxide system where the excluded volume may be varied, in order to maintain the constant energy potential a metastable system may exist in this case (and others)?

For example in the case of vermiculite gels, surely the excluded volume changes when the ionic concentration of the system varies is significant? Qualitative extrapolation values of excluded volumes obtained from the experimental data of Williams *et al.* are in approximate agreement. For example the layer distances which are indicated in Table 1 for varying concentrations of butyl ammonium vermiculite.

Further, the gelation time[3] and the swelling ratios of inorganic polymeric (vermiculite) gel matrices change according to the electrolyte: aqueous ratio and energy potentials calculated.[4] For example the swelling ratio of glutamic acid vermiculite 1.32 in an aqueous solution and 10.9 in a (0.142) water–glass aqueous system.

Thus, when the above gel matrices are observed, do you consider that the systems are metastable ones and that this is a general premise for specific gel entities?

1 I. Lin (deceased), M. V. Smalley and S. G. Grayeff, *Overview of Vermiculite Modifications*, The Technion, Israel Institute of Technology, Haifa, 1994.
2 G. D. Williams, K. R. Moody, M. V. Smalley and S. M. King, *Clays Clay Miner.*, 1994, **42**(5), 614–627.
3 N. Lesley, S. Dent, N. Glasser and G. Harvey, *J. Chem. Soc., Chem. Commun.*, 1984, 1250–1252.
4 S. G. Grayeff, *Vermiculite Modifications*, MPhil Thesis, Birkbeck College, The University of London, 1992, p. 124.

Dr Melrose replied: As far as I can understand the question, gels are usually thermodynamically metastable states. Swelling of some gels *e.g.* clays is complicated as in principle 'entanglements' of plates must limit the swelling, yet we do not have an understanding of this issue.

Prof. Nicolai opened the discussion of Dr Elliott's paper: 1. The relation between the power law exponents of the autocorrelation function and the shear modulus is model dependent.

2. Eqns. (12) and (13) of the paper are derived assuming that the shear modulus has an entropic origin and can be described in terms of conformational relaxation of highly flexible clusters. An alternative approach characterizes the clusters by a spring constant of the backbone of singly connected particles. The two approaches are compared in ref. 26 of the paper for gelling colloidal disks and it was concluded that the latter approach was more appropriate for colloidal gels like the system described in the paper.

3. The inverse scattering vector is smaller than the elementary particles. It appears therefore necessary to consider not just the translational diffusion, but also rotational diffusion and internal modes of the clusters to explain the slow decay.

Prof. Wagner and **Dr Elliott** responded: It is true that there are several theoretical expressions that relate the power law exponents in the autocorrelation function and the moduli. This is why we chose to initially use the semi-empirical expression for the autocorrelation function containing the

Table 1 Layer distances in vermiculite gels for different concentrations of butyl ammonium vermiculite.

Concentration/ M	Distance/ Å (obtained from swelling results) (ref. 1)	Expt. distance/ Å (plate thickness = 19.4 Å) (ref. 2)
0.0014	600	620 (0.001 M)
0.005	637.5	430 (0.003 M)
	410 (excluded volume considered)	
0.011	235	260

exponent n employed by Norisuye *et al.* We now need to understand the implications of its success in terms of the microscopic interactions. Perhaps this will lead us to an appropriate relation between n and the fractal dimension.

In the text immediately following eqns. (12) and (13), we caution against blindly using these expressions and note that any fractal dimensions calculated from them are not expected to be strictly correct. As you mention, eqn. (2) from ref. 26 could have been used as well. However, it also involves assumptions about microscopic details that we cannot quantify (*e.g.* hydrodynamic interactions, the fractal dimension of the cluster backbone, polydispersity, *etc.*).

We mention in Section 3.2 of the paper that rotational diffusion of the anisotropic clusters may contribute to the autocorrelation function and that, when it is significant, produces a faster decay. Therefore, it should not impact the power law region. In addition, Norisuye *et al.* have found no dependence of the power law exponent on scattering angle in a system where the same complication would be expected to occur. Given the limitations of our FOQELS apparatus, we cannot adjust the wave vector to perform such an experiment, but Norisuye's results lead us to believe the effect should not change our results.

Dr Vollmer commented: A power law dependence of the elastic and storage modulus can also be obtained for colloids dispersed in anisotropic media.

Fig. 2 shows the frequency dependence of the elastic and storage modulus for a mixture of sterically stabilized hard spheres (radius of 610 nm) dispersed in the low molecular thermotropic liquid crystal (5′-cyanobiphenyl). In the isotropic phase the particles perform Brownian motion. Under cooling the liquid crystal passes the phase transition isotropic to nematic, thereby expelling the particles locally. For a large range of cooling rates and compositions the particles form a three dimensional network of high elastic modulus. This network can show self-similarity that might cause the power law dependence. However the meaning of entropic and enthalpic contributions is not clear yet, nor is it obvious how to relate this behaviour with those observed for polymers close to the gel point.

Prof. Horne asked: I refer to your statement that the gel time measured by rheology is much shorter than that detected by your FOQELS technique. My understanding would suggest that FOQELS because it does not apply a disruptive probe would detect the presence of the gel, as a self-sustaining (against gravity), container-spanning network, before the rheometer whose mechanical impulse might disrupt the forming gel. How are you defining gel point and do you think that they are measuring the same point in the evolution of the gel? As a supplementary, if your gel is evolving, should the fractal dimension not also be continuously changing, moving over perhaps from RCLA to a particle–cluster aggregation scheme which has a higher d_f.
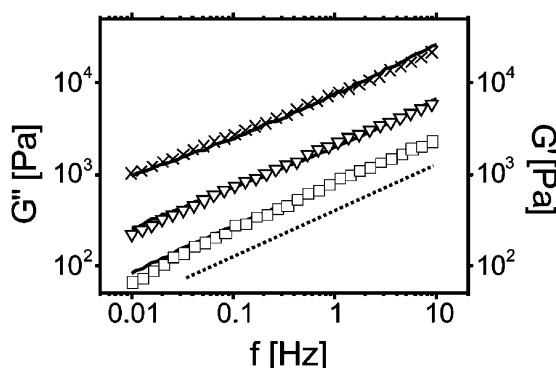

Fig. 2 Dependence of the storage modulus G'' and the elastic modulus G' on frequency f, for a mixture of 5 wt.% polymethylmethacrylate spheres dissolved in the low molecular liquid crystal 5-cyanobiphenyl. The symbols denote the frequency dependence of the elastic modulus and the solid lines denote the corresponding values for the storage modulus. The dashed line corresponds to a $G' \propto f^{1/2}$ dependence. (Crosses: $T = 302.7$ K; triangles $T = 304.7$ K; squares: $T = 305.7$ K.)

My concern is that since the structure is evolving with time, the 'gel times' from the two techniques relate to two different points in that history and cannot describe identical structures. Indeed, for system D2, these structures are characterized by a difference of at least two orders of magnitude in elastic modulus (Fig. 7 of the paper). Also, in Fig. 5 of the paper, whilst the exponent n extracted from the FOQELS data starts below that determined from rheology, implying the expected larger fractal dimension at the later gel time, the trend is for the FOQELS exponent to increase with reaction time, indicating that the fractal dimension measured by this technique is decreasing as the reaction proceeds and more material is incorporated into the gel network. How do you explain this?

Dr Elliott replied: We explain the determination of the gel point from the rheology in Section 3.1 and the light scattering in Section 3.2. The two gel times are different and thus we are not extracting power law exponents at the exact same point during the aggregation. However, comparing the values suggests that the structures are similar. Furthermore, we are cautious in choosing the applied strains during the rheological measurements and do not believe we are significantly influencing the aggregation process. We discuss in detail (Section 4) why the FOQELS detects gelation later. In short, we believe it is because the rheology is biased towards the large fractal aggregates and the light scattering to the small sub-fractal clusters.

We also expect that the fractal dimension should change at some point when the small sub-fractal aggregates begin to fill in the network, but we do not clearly detect this change. Rather, we observe a window of time over which the power law exponent exists and is nearly constant. This window in time is limited by the experimentally accessible frequency range in the rheology and numerous experimental limitations associated with the light scattering discussed in Section 3.2. We do not interpret this to mean that the fractal dimension does not increase, just that we cannot detect it.

You misread Fig. 7 of the paper, which shows the time evolution of the measured moduli and the effective diameter extracted from the autocorrelation function. We do not try to extract the moduli from the light scattering data. Also, we do not attempt to interpret the slight increase in n over time because there is some degree of ambiguity in fitting the data. This is particularly true at the longer times when the autocorrelation function begins to plateau above the baseline and can skew the power law region making $n - 1$ appear smaller.

Dr Kroy commented: I want to comment on two issues raised. First, the relation of systems undergoing flocculation (as presented by Dr Elliott) to those undergoing weak gelation (as presented by Dr Scheffold and earlier during this *Faraday Discussion* also by Prof. Weitz, by Dr Vliegenthart, by Prof. Zukoski and others). And second, the high fractal dimensions reported for the latter case, as just mentioned by Dr Scheffold.

In a classical flocculation experiment the attractive energy E is very high (ideally infinite) compared to the thermal energy kT. At common colloid volume fractions this corresponds to a strongly super-critical quench, whereas in the typical weak gelation experiments quenches are usually close to critical (or in case of an interfering binodal sometimes even sub-critical). In the former case, the aggregation is essentially irreversible (typically DLCA or RLCA depending on the presence of a repulsive potential barrier), and gelation corresponds to a geometric transition, namely the (rigidity) percolation of non-equilibrium (DLCA/RLCA) clusters. The system passes through criticality but is not at criticality at the end of the aggregation process (see the sketch). The critical gel is a fractal percolation cluster that is only present for a short moment, whereas the final long-lived gel has absorbed all the remaining free particles and clusters. On the other hand, weak gelation corresponds to a critical quench (for simplicity let us disregard interference of a binodal) and is the end result of a reversible aggregation process, where cluster breakup plays an important role. Since the attractive energy is only just high enough to gel the sample, the critical gel is not fractal at finite volume fractions and not long-lived (sintering). We think that the clusters which make up a weak critical gel are not fractal but exhibit a structural crossover: locally they are far from equilibrium and resemble clusters obtained in irreversible aggregation, while they become increasingly compact on larger length scales. In particular the gel itself is thought to be compact on length scales beyond the correlation length that corresponds to the size of the constituent clusters (see Fig. 3). This may explain the apparent high fractal dimension (compared to irreversible
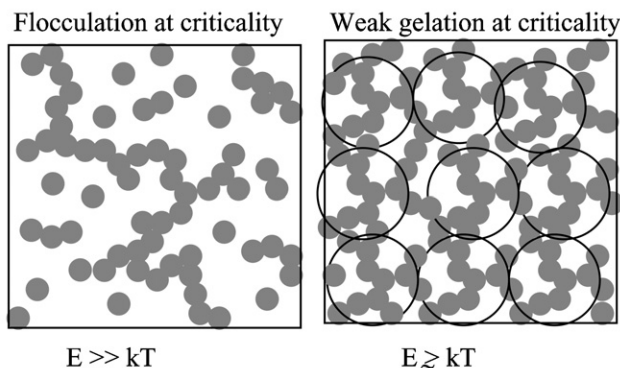
Fig. 3   Strong and weak gelation at the onset of solid like behavior (here called "criticality" since it corresponds to critical behavior of the transport properties).

DLCA), and has to be distinguished from a higher fractal dimension obtained through different kinetics (*e.g.* RLCA). In reponse to a private remark by Prof. Weitz to my oral comment, I also want to point out that the two scenarios contrasted above become in practice increasingly indistinguishable with decreasing particle volume fraction, which entails an increasing cluster size (or correlation length in the gel) as well as an increasing critical attraction. Theoretically, however, the outlined distinction of critical and off-critical quenches is still applicable, except at the renormalization fixed point of irreversible cluster aggregation itself.

Prof. Vincent asked: I am just wondering whether you are actually seeing RCLA behaviour in your systems, or initial weak, basically DCLA, followed by aggregate "strengthening" due to the relatively low T_g particles you are using (the T_g of the particle surface may be lower than the bulk T_g of the particles)? What worries me is the higher ionic strength you are using (Table 1 of the paper): 0.15 with 0.2 M NaCl. The Debye decay length is < 1 nm under these conditions. Also the higher CCC value reported in that table is very high for a typical hard latex particle (more like 100–200 mM). Could it be that your particles have a soft, gel-like, layer of polymer at their surface (containing a high fraction of the acrylic acid used in the preparation). One might expect this if the particles were prepared in a "one-shot", batch process. Interfacial pair potentials (electrostatic and steric and van der Waals) are not well-defined in these types of systems.

Prof. Wagner and **Dr Elliott** replied: The particle surface can be quite complicated making these valid concerns. However, these clean model particles have been extensively studied under dilute conditions; and the results suggest that the particle surface is well behaved.[1] Specifically, DLVO (Derjaguin–Landau–Verwey–Overbeek) theory describes the interaction potential to separations approaching 0.3 nm which contrasts many particle systems that show deviations at about 2 nm. This strongly suggests that the particles have a smooth surface and uniform charge distribution.

1   L. H. Hanus, R. U. Hartzler and N. J. Wagner, *Langmuir*, 2001, **17**, 3136.

Prof. Weitz commented: The structures that form for the gels made by Elliott may be independent of the exact mechanism of the aggregation, whether it is screening or some other destabilization mechanism. Regardless of the mechanism, you can still have a fractal structure and a power-law behavior for the rheology. However, it should be possible to make some more estimates about the nature of the structure. If the power-law response of the rheology is due to the fractal structure of the network, the rheology must be probing length scales that lie within the fractal structure, and not length scales that are so large that the network has become homogeneous, which it must at sufficiently large length scales. Since both the modulus and the frequency are known, it is possible to estimate the length scale probed by the rheology. Can you compare this length scale

the characteristic size of the largest fractal objects in your network? It should at least give some reasonable estimate for what this length scale is.

A crude estimate of the length scale is given by: $\xi \sim \omega \sqrt{G'/\rho}$, where ξ is the characteristic length and ρ is the density. Using typical values from your paper, $\omega \sim 1$ rad s^{-1}, $G' \sim 10^{-2}$ Pa, and $\rho \sim 10^3$ kg m^{-3}, I get a length of $\xi \sim 3$ mm. This is an enormous correlation length for particles that are about 100 nm in radius. If I further assume that the fractal dimension is $d_f \sim 1.8$ the effective volume fraction of the particles that are in the solid gel right at the gel point would be only $\phi_{eff} \sim [\phi_0(\xi/a)^{d_f-3}] \sim 3 \times 10^{-5}$, which is a very small fraction of particles. This is the number that would have to be compared to other gel structures in comparing the modulus. The essential assumption I am making here is that the gel network must be fractal over the length scales probed by the rheology if the power-law behavior of the modulus is due to the fractal structure. Perhaps there are other possible origins for the power-law behavior.

Dr Elliott and **Prof. Wagner** answered: A length scale of 3 mm estimated with $\sqrt{G'/\rho\omega^2}$, which is the penetration depth of a shear wave in an elastic medium, is consistent with an aggregate that spans the sample volume. The sample is bound by the couette geometry, which has a gap thickness of 1 mm. The gel point, as defined in the crosslinking polymer literature, is marked by the formation of the first infinite or sample spanning fractal cluster. Consequently, the fraction of particles actually incorporated in the network at the gel point should be small relative to the overall volume fraction. Finally, the constant power law exponent that exists at the higher frequencies before and after the gel point is evidence for self-similar or fractal aggregates.

Prof. Cates commented: To see a rheological power law in a given frequency range arising from fractal microstructure, you need the frequency to lie in a range that corresponds to the inverse relaxation time of pieces of cluster that lie in the fractal range. Rheology is a $q = 0$ method and does not probe directly the structure on any particular wavelength, though a length scale does enter indirectly *via* the above frequency criterion.

Dr Bartlett said: I would just like to point out that our measurements using confocal microscopy[1] show that for a colloid–polymer system at high concentration it is impossible to reliably identify a fractal structure.

1   V. Anderson, A. C. Campbell and P. Bartlett, in preparation.

Prof. Weitz commented: The depletion gels that you look at with confocal microscopy are exactly the same as the ones I discussed in my lecture. They have a very different rheological response than those studied by Dr Elliott, and do not show any power-law regime that is characteristic of a fractal structure in their rheology.

Prof. Felderhof commented: Recently I have studied the linear viscoelastic response of a suspension of Brownian hard spheres without hydrodynamic interactions in an approximation in which the influence of neighboring particles on a selected pair is taken into account *via* the potential of mean force.[1] It was shown that the cage imposed by neighbors has a profound effect on the frequency-dependence of the viscoelastic response. For a square-well-barrier model for the equilibrium radial distribution function the dynamical viscosity was calculated analytically from the pair Smoluchowski equation in the above approximation. Both the mean relaxation time and the coefficient of the long-time tail of the stress relaxation function depend explicitly and in complicated fashion on the depth and width of the well, and on the height and width of the barrier. It may be well worthwhile to study the predictions of the model more closely.

1   B. U. Felderhof, *J. Chem. Phys.*, 2001, **114**, 6426.

Prof. Weitz commented: It would certainly be of great interest to compare our results to your theoretical prediction. However, I would caution that our results depend explicitly on the formation of a network of particles, which involve a large number of particles, and that the dominant elastic response is due to the solid network, which presumably has little or no effects of hydrodynamic interactions.

Prof. Weitz then opened the discussion of Dr Scheffold's paper: In the calculation of the form of the correlation function for DWS from gels, have you correctly included the contributions of the non-ergodic component? The way you have done it is to include the non-ergodic contribution after you calculate the full correlation function. The way one normally calculates the correlation function for DWS is to begin with the single scattering dynamic structure factor, and average that first over scattering wave vectors and then over scattering events within a single path and then over all paths. If you were to follow this approach, you might then have to correctly account for the static, non-ergodic component of the scattering at the level of the individual scattering events, which you have not done. I am not sure if the effective averaging that you do implicitly when averaging over scattering wave vectors and paths yields the same results as correctly averaging the single scattering correlation function to incorporate the non-ergodic component.

Dr Scheffold replied: It is true that in our work, and those of others, *e.g.* refs. 1 and 2, it has been assumed that the implicit averaging (over scattering wave vectors and paths) leads to the result given in the paper, provided the initially non-ergodic DWS signal is properly averaged.[2–4]

The role of non-ergodicity in DWS has also been discussed in detail by Nisato and coworkers.[4] They show that the Pusey/van Megen method[5] can be applied to DWS. Subsequently they claim that the DWS correlation function can be related to the DLS correlation function the same way we do.

Though physically intuitive I agree that a final answer to this question will likely require a more profound theoretical analysis, beyond the scope of this short reply. Furthermore a combination of single (3D-DLS) and multiple scattering (DWS) could provide experimental information about non-ergodicity and light scattering. Following these lines we intend to address this question again in a future publication.

1   M. Heckmeier and G. Maret, *Opt. Commun.*, 1998, **148**, 1–5.
2   A. Knaebel, M. Bellour, J.-P. Munch, V. Viasnoff, F. Lequeux and J. L. Harden, *Europhys. Lett.*, 2000, **52**, 73–79.
3   F. Scheffold, S. E. Skipetrov, S. Romer and P. Schurtenberger, *Phys. Rev. E*, 2001, 613, 61 404.
4   G. Nisato, P. Hebraud, J. P. Munch and S. J. Candau, *Phys. Rev. E*, 2000, **61**(3), 2879.
5   P. N. Pusey and W. van Megen, *Physica A*, 1989, **157**, 705.

Prof. Vincent asked: Your method of controlling the ionic strength of the medium is very interesting. I am just wondering, however, if the enzyme you use (urease) adsorbs onto the polystyrene latex particles, and hence effects the interparticle pair-potential? If the depth of the attractive well is not as large (because of some steric interaction component), then you may have particle rearrangement within the aggregates. Alex Routh and I have recently been studying, with small-angle light scattering, the fractal dimensions of poly NIPAM microgel particles (in 1 M NaCl), over the temperature range from around the critical flocculation temperature, where we see weak reversible aggregation, to higher temperatures, where the poly NIPAM particles have collapsed sufficiently to ensure strong irreversible aggregation (*i.e.* true DCLA conditions). The fractal dimensions decrease over this range from ∼2.2 to 1.75.

Dr Scheffold replied: We have no knowledge about the adsorption properties of urease on polystyrene latex. However, as far as I know, no (strong) systematic dependence of the final gel elastic properties on the urease content have been yet observed, neither for polystyrene[1,2] nor for alumina suspensions.[3]

This is despite the fact that the urease concentration does influence the dynamics of the gelation process,. Nevertheless the influence of the enzyme on the particle interactions is an interesting open question that should be addressed in the future.

1   H. Bissig, S. Romer, V. Trappe, F. Scheffold and P. Schurtenberger, in preparation.
2   S. Romer, F. Scheffold and P. Schurtenberger, *Phys. Rev. Lett.*, 2000, **85**, 4980.
3   H. Wyss, S. Romer, F. Scheffold, P. Schurtenberger and L. J. Gauckler, *J. Colloid Interface Sci.*, 2001, 241, 89–97; H. Wyss, private communication.

Prof. Weitz commented: The gels formed by Dr Elliott are qualitatively different from those formed by the Fribourg group. The Elliott gels have an extended range of power-law behavior in

their rheology, and thus apparently have an extended range of fractal structure. This is presumably because they are right at the gelation point when the data with the extended power-law behavior are obtained. By contrast, the gels discussed by the Fribourg group are fractal at short length scales, and are homogeneous at larger length scales. Therefore, their rheology does not exhibit an extended fractal range. It would be interesting to see the frequency-dependent viscoelasticity of Elliott gels well after the gel point, at which time they would, presumably, have a shorter correlation length, and therefore no longer exhibit a power-law response in their frequency-dependent rheology.

Prof. Wagner and **Dr Elliott** responded: It is true that power law behavior is no longer observed well beyond the gel point. To clearly illustrate, we present Fig. 4, containing data for sample D1 at times much longer than the gel time. The moduli become nearly independent of frequency and continue to increase in magnitude over time.

Prof. Weitz replied: It should be possible to compare the elastic modulus of Elliott gels at the critical limit with the master curve for gel moduli produced by the Fribourg group to determine the volume fraction of a DLCA gel that gives the same modulus. This might provide a way to determine the volume fraction of the particles in Elliott gels that are actually part of the network.

Dr Scheffold replied: This question refers to our finding[1] that for colloidal gels (polystyrene latex), over a large range of concentrations, the experimental values of the gel modulus times the particle size collapse onto a master curve. The master curve itself is reasonably well described by a power law dependence (exponent *ca.* 3.5), at least for low and intermediate concentrations up to $\Phi \sim 0.1$. To obtain this master curve colloidal gels have been studied, well after the point of gelation, in a regime where the gel elasticity changes only little over several days or more.[1]

To use this master curve the way suggested by Prof. Weitz is appealing. It should indeed be possible to obtain information about the gel microstructure simply from elasticity measurements. An example for such behaviour is given by the heterogeneous aluminum oxide gels we have studied recently.[2] The elastic modulus of these materials varies significantly between a homogenous gel and a microscopically heterogeneous gel, obtained by changing the destabilization conditions. The latter appears much stronger since in the solid parts of the mesoporous material the density is significantly higher.
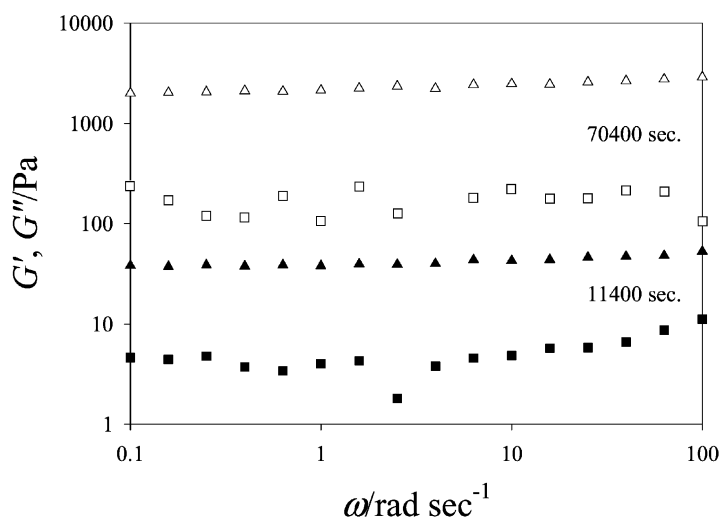

Fig. 4 Dependence of the storage modulus G'' and the elastic modulus G' on frequency ω for sample D1.

Hence for the final elastic modulus of colloidal gels our master curve could indeed serve as a reference provided the absolute values are rescaled according to the particle-particle interactions based on the specific particle chemistry.[1]

At the moment however it seems premature to use the master curve for the interpretation of time dependent results, *e.g.* those discussed by Dr Elliott *et al.* Obviously the detailed mechanisms leading to the strengthening of the gel in this regime are not yet quantitatively understood. While Dr Elliott claims to still see many free particles close to the gel point this is not the case for our systems, as shown in ref. 3. Nevertheless our gels continue to strengthen typically for about 24 h.[1–3]

1   H. Bissig, S. Romer, V. Trappe, F. Scheffold and P. Schurtenberger, in preparation.
2   H. Wyss, S. Romer, F. Scheffold, P. Schurtenberger and L. J. Gauckler, *J. Colloid Interface Sci.*, 2001, **241**, 89–97.
3   S. Romer, F. Scheffold and P. Schurtenberger, *Phys. Rev. Lett.*, 2000, **85**, 4980.

Prof. Dawson opened a general discussion: I would like to remark that our language and pictures have changed throughout the conference. Earlier we discussed dense colloidal systems in terms of glasses, then Dr Bartsch showed that similar ideas may be used to describe dense particle gels. Later, at moderate volume fractions, we have begun to use the language of fractal clusters.

From a deeper point of view, from what we know about the emerging framework of the ergodic-non-ergodic transition (loosely called the "glass transition") it is likely that there is no real difference in the manner these high density and moderate density gels arise. In general the whole ergodic–non-ergodic transition is probably describable in a coherent manner, and colloidal science could make a great contribution in driving the developments of that emerging description.

Prof. van Blaaderen commented: Prof. Dawson, you are optimistic that a general encompassing theoretical description will emerge in which glass transitions and gelation can be treated and explained on a similar footing. It seems unlikely to me that such a theory can also describe processes that become non-ergodic early on, long before the structure that eventually will give the sample a yield stress has emerged. An extreme example is the case in which two colloidal particles if they collide immediately and irreversibly stick. It seems to me that a theory based on statistical mechanics cannot describe the process of gel formation in such a system. What is your view on this?

Prof. Dawson replied: Yes, I think that an encompassing theory incorporating the various density regimes will emerge, and that its form and outline are already present. In fact, many of the features of such a theory will be hammered out in our community.

At high density we have spoken about the existing types of theory and simulation that can (summarized in a recent Current Opinion article) be carried out with quite a lot of satisfactory agreement. At moderate densities we confront the possibility that there is also a tendency to phase separate and the formation of the 'glass' (*i.e.* gel) must be understood in those terms. That is, in general the kinetics of phase-separation is mixed in with the arrest. This situation is no different in principle from what I have presented here in a much simpler case where we have a 'hard-particle' phase separation involving a crystal and fluid. There we show how the dynamically available volume is the order parameter also for the non-equilibrium situation where arrest is mixed up with phase separation. In fact we have generalised such models to accommodate attractions, and will be able to discuss some of that detail soon. There are similar activities that seem very promising in Naples and Rome.

In fact there is no in principle reason to doubt the possibility to deal with this (intermediate) regime even within microscopic MCT-like formalisms. Now, we (and others) have recently published the MCT-like framework within which the arrest would be determined self-consistently with the evolving structure factor. This framework has not yet been applied, but the path seems open in principle. Of course, we could also solve these equations in an ad hoc manner, basically sticking in a trial structure factor that reflects the clustering of particles prior to them arresting. This involves use of a structure factor a larger scale assembly. Prof. Poon has alluded to some sort of idea like this also. However, I would note that the use of only one of the sets of equations, and inserting in a guessed structure factor leads to errors in terms of the second memory kernel that would now be implicitly ignored, and there is no self-consistency in finding the arrest. I think it would be nice to solve these two coupled equations for non-equilibrium MCT by making a simpler model of how the

structure factor evolves in time, and then insert that into the exact equations. This should lead to an 'automatic' arrest when the aggregates are of the correct size. My feeling is that this type of detailed microscopic theory offered by these non-equilibrium equations will work out, but with a bit of effort. Possibly it is wise to deal with the problem at a simpler level for now, and use the types of simple lattice models that I have explained, at least until we are sure that everything is working and checked, or we are in danger of 'curve-fitting'.

I would remark that all of these phenomena are in some sense only a specialized type of aging scenario. They require a two-time formalism, and need to have the structure factor evolving at the same time.

One part of your question goes deeper, however. That is the very dilute system. I think there is no real problem with the irreversibility, since we know well how to deal with kinetic models in the arrest scenarion and can keep the stickyness as a parameter. And within the lattice model approaches there are no particular problems and we can accommodate smoothly DLA, to dense glassification. The real problem for me is that long term development of microscopic theory here. Density variables are still used in all these microscopic approaches (such as MCT, and what I have described above). The closure that have been designed so far do not really deal fairly with fractal type behaviors, and this is a serious limitation in dealing with the low density and high density regime in a unified manner. In fact the theoretic challenge is not unlike that for the dilute to semidilute problem in polymer science. We pass from natural usage of particle coordinates to densities. This requires work.

Even so, I would not conceptually separate the dilute sticking problem from the 'aging-arrest' scenario, though the system is so 'wait-time' dependent that such an approach becomes less useful. Rather, along the lines mentioned above, it is necessary to rephrase the whole structure of what we mean by 'arrest' in a manner where the two times (analogous to 'wait' and 'elapsed' time) are developed at a more fundamental level. This would finally give us an elegant synthesis of aggregation and clustering along with the other arrested phases.

Prof. Vincent commented: As a general remark, I would be interested to know how close people consider we are to achieving the 'Holy Grail' of true hard-sphere colloids, especially in terms of rheology, gel/glass-like behaviour, *etc.* Many of the systems reported here still have some deficits in this regard, in that they appear to have an (albeit thin) soft shear around the hard core. Even the ubiquitous polystyrene latex particles in aqueous media, are thought to be somewhat "hairy"! Our own studies (*e.g.* in our paper) and that of the Utrecht group and others, have used silica particles with grafted alkyl (*e.g.* C18) chains, in hydrocarbon media. However, we are very much aware that many properties of these mode systems depend on the grafted layer density (*e.g.* their critical flocculation temperature).