Theory of Thermodynamic Stresses in Colloidal Dispersions at the Glass Transition

D. Hajnal*, O. Henrich*, J. J. Crassous†, M. Siebenbürger†, M. Drechsler†, M. Ballauff† and M. Fuchs*

*Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany
†Physikalische Chemie I, University of Bayreuth, 95440 Bayreuth, Germany

Abstract. We discuss the nonlinear rheology of dense colloidal dispersions at the glass transition. A first principles approach starting with interacting Brownian particles in given arbitrary homogeneous (incompressible) flow neglecting hydrodynamic interactions is sketched. It e.g. explains steady state flow curves for finite shear rates measured in dense suspensions of thermosensitive core-shell particles consisting of a polystyrene core and a crosslinked poly(N-isopropylacrylamide)(PNIPAM) shell. The exponents of simple and generalized Herschel Bulkley laws are computed for hard spheres.

INTRODUCTION

Soft materials, such as particle dispersions, exhibit a wide range of rheological properties. While dilute colloids flow with a viscosity only slightly higher than that of the solvent, concentrated dispersions behave as soft amorphous solids. Under large deformations, they may yield and flow with a strongly shear-rate dependent viscosity, while their structure can remain amorphous and homogeneous [1].

In order to address the nonlinear rheology of such viscoelastic colloidal dispersions, recently, a first-principles constitutive equation under arbitrary time-dependent homogeneous flow was developed [2]. It includes transitions to arrested glassy states as function of the thermodynamic control parameters, thus allowing the interaction between slow structural relaxation and time-dependent external flow to be investigated. The approach generalizes the integrations through transients (ITT) approach developed for steadily sheared dispersions [3] to the general situation. It concentrates on the thermodynamic stresses arising from potential and Brownian interactions between the particles, because they overwhelm hydrodynamic contributions close to vitrification and at low deformation rates, and because they are dominated by slow structural rearrangements, which can be approximated using mode coupling techniques [4].

A colloidal model system of hard spheres was developed [5], and experiments at high densities were performed [6] to test the connection between glassy dynamics and nonlinear rheology, which is at the heart of the theoretical approach. To this end, linear frequency dependent shear moduli and nonlinear shear rate dependent flow curves were measured and analysed in parallel [6]. Here, we summarize some of the observations on the steady state flow curves and provide some new insights into the flow curves close to the glass transition.

THEORY

The microscopic theoretical approach [2] starts with a system of N spherical Brownian particles interacting via internal forces and dispersed in a solvent with a specified velocity profile $\mathbf{v}(\mathbf{r},t) = \kappa(\mathbf{t}) \cdot \mathbf{r}$. The time-dependent velocity gradient tensor $\kappa(\mathbf{t})$ is assumed spatially constant, thus excluding the non-homogeneous flows which occur in shear-banded and shear-localized states. While hydrodynamic interactions and fluctuations in the velocity profile are thus neglected from the outset, this Statistical Mechanics model can be investigated by Brownian dynamics simulations [7], and constitutes a first microscopic approach to real glassy colloidal suspensions. The properties of this microscopic model have been worked out for low densities (partially even including hydrodynamic interactions [8]), and it provides the starting point for various (approximate) theories for intermediate concentrations.

Considering, for the sake of discussion, the example of steady shearing [3], the aim of the microscopic approach is to compute the stationary many-body distribution function, which is possible albeit only approximately. It describes
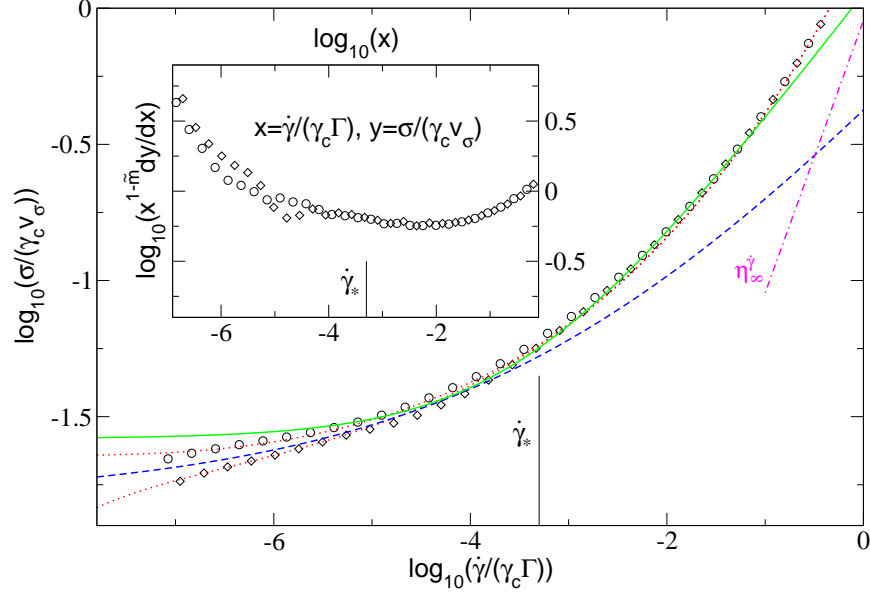
FIGURE 1. (Color online) Flow curves of a suspension of colloidal hard spheres for two densities close to the glass transition, $\phi_{\text{eff}} = 0.580$ (fluid state, diamonds) and $\phi_{\text{eff}} = 0.608$ (glassy state, circles) rescaled to collapse at high shear; from Ref. [6]. Parameters are $\Gamma = 60D_0/R_H^2$, $\gamma_c = 0.1$ and $v_\sigma = 50k_BT/R_H^3$ for $\phi_{\text{eff}} = 0.580$, and $\Gamma = 84D_0/R_H^2$, $\gamma_c = 0.105$ and $v_\sigma = 77k_BT/R_H^3$ for $\phi_{\text{eff}} = 0.608$, respectively, where R_H is the hydrodynamic radius and D_0 the single particle diffusion coefficient at infinite dilution; k_BT is the thermal energy. Fits using the $F_{12}^{(\dot\gamma)}$-model are given as dotted red lines [6]. The blue dashed cuves gives the generalized Herschel-Bulkley law Eq. (1) with $m = 0.143$, which holds asymptotically for $\dot\gamma \ll \dot\gamma_*$ at the glass transition; $\sigma_c^+ = 0.10k_BT/R_H^3$ is the dynamic yield stress at the transition. The green solid curve is the Herschel-Bulkley law (2) which holds for intermediate shear rates $\dot\gamma_* \ll \dot\gamma \ll \Gamma$ at the transition; the exponent $\tilde m = 0.473$ follows for hard spheres using the Percus-Yevick approximation for the equilibrium structure factor [9, 4]. The magenta dot-dashed straight line labeled $\eta_\infty^{\dot\gamma}$ denotes the (extrapolated) linear high-shear asymptote. The inset tests the exponent $\tilde m$, as $d\sigma/d\dot\gamma \times \dot\gamma^{1-\tilde m} \propto \text{const.}$ should hold for the Herschel-Bulkley law.

the complete probability distribution of the particle positions, and using it any stationary average can be computed. Its computation is achieved using formally exact projection operator manipulations and generalized Green-Kubo relations, followed by mode coupling approximations, which share similarities with mean field approximations [3]. The approximations implement the assumption that slow structural rearrangements dominate the thermodynamic stresses in dense dispersions, and that they can be approximated using (transient) density correlation functions. The later are taken from equations of motions closed with (again) mode coupling approximations. Competition of structural slowing down (called 'cage effect') with flow induced decorrelation ('flow advection' entering via Cauchy-Green tensors [2]) and cut-off of memory, determines the distorted microstructure and the stresses. Universal aspects of the predicted rheology can be captured in 'schematic models', like the $F_{12}^{(\dot\gamma)}$-model, which retain the nontrivial dynamical scaling laws of the microscopic approach, but simplify its spatial structure.

EXPERIMENTAL SYSTEM

The particles consist of a solid core of poly(styrene) onto which a network of crosslinked poly(N-isopropylacrylamide) (PNIPAM) is affixed. Immersed in water the shell swells at low temperatures. Raising the temperature above 32^oC leads to a collapse within the shell. Screening the remaining electrostatic interactions by adding salt, the system crystallises such that its phase diagram can be mapped onto the one of hard spheres[5]. The dependence of the packing fraction ϕ_{eff} (viz. the relative volume taken by the spheres) on the temperature is given by the hydrodynamic radius R_H determined from dynamic light scattering in the dilute regime. The flow curves were measured with a stress-controlled rotational rheometer MCR 301 (Anton Paar), equipped with a Searle system [6], upon decreasing the shear rate $\dot\gamma$ and checking carefully for stationarity.

COMPARISON OF THEORY AND EXPERIMENT

The microscopic ITT equations contain a non-equilibrium transition between a fluid and a shear-molten glassy state. Close to the transition, (rather) universal predictions can be made about the non-linear dispersion rheology and the steady state properties. A qualitative change in the flow curves is predicted, where the stationary stress exhibits a Newtonian viscosity $\sigma(\dot{\gamma} \to 0) \to \eta_0 \dot{\gamma}$ in fluid states, while it exhibits a dynamic yield stress $\sigma(\dot{\gamma} \to 0) \to \sigma^+$ in glassy ones. Non-trivial power-laws in the flow curves exist close to the glass transition itself; for hard spheres, it is estimated to lie at $\phi_{\text{eff}} = 0.580$ [6]. Right at the glass transition, a generalized Herschel-Bulkley law

$$\sigma(\dot{\gamma} \to 0) \to \sigma_c^+ \left(1 + |\dot{\gamma}/\dot{\gamma}_*|^m + c_2 |\dot{\gamma}/\dot{\gamma}_*|^{2m} + c_3 |\dot{\gamma}/\dot{\gamma}_*|^{3m} \right) \tag{1}$$

holds and describes the flow curves over an appreciable part of the range $\dot{\gamma} \leq \dot{\gamma}_*$; the exponent is $m = 0.151$ for the exponent parameter $\lambda = 0.735$ computed within mode coupling theory for hard spheres using the Percus-Yevick approximation.

Beyond the asymptotic regime, a (simple) Herschel-Bulkley law appears in the flow curves of the $F_{12}^{(\dot{\gamma})}$-model [9]

$$\sigma(\dot{\gamma} \gtrsim \dot{\gamma}_*) = \tilde{\sigma}_0 + \tilde{\sigma}_1 |\dot{\gamma}|^{\tilde{m}} . \tag{2}$$

Its exponent can again be calculated from λ, which for hard spheres gives $\tilde{m} = 0.473$. This law provides a semi-quantitative fit of the flow curves for around two decades in $\dot{\gamma}$ close to the glass transition as shown in Fig. 1.

The dynamic yield stress σ^+ can be read off by extrapolating the flow curve in the glass to vanishing shear rate. While this agreement supports the prediction of a dynamic yield stress in the ITT approach and demonstrates the usefulness of this concept, small deviations in the flow curve at low $\dot{\gamma}$ are present. They indicate the existence of an additional slow dissipative process which may correspond to a melting of the glass at even longer times or smaller shear rates beyond the experimental window.

CONCLUSIONS AND OUTLOOK

Recently, the connection was emphasized between the physics of the glass transition and the rheology of dense colloidal dispersions, including in strong homogeneous flow [2, 3]. The equilibrium structure factor and one time scale (obtained from matching to short time motion and affected by hydrodynamic interactions) are required as inputs to the derived constitutive equation. Using model colloidal particles made of thermosensitive core-shell particles the predictions could be investigated in the vicinity of the transition between two stationary states under steady shear, a shear-thinning fluid and a shear-molten glass [5, 6].

ACKNOWLEDGMENTS

REFERENCES

1. G. Petekidis, A. Moussaïd and P. Pusey, Phys. Rev. E **66**, 051402 (2002).
2. J.M. Brader, Th. Voigtmann, M.E. Cates, and M. Fuchs, *Phys. Rev. Lett.* **98**, 058301 (2007); in preparation (2008).
3. M. Fuchs and M. E. Cates, *Phys. Rev. Lett.* **89**, 248304 (2002); *Faraday Disc.* **123**, 267 (2003); *J. Phys.: Condens. Matter* **17**, S1681 (2005); *in preparation* (2008).
4. W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
5. J. J. Crassous, M. Siebenbürger, M. Ballauff, M. Drechsler, O. Henrich and M. Fuchs, *J. Chem. Phys.* **125**, 204906 (2006).
6. J. J. Crassous, M. Siebenbürger, M. Ballauff, M. Drechsler, D. Hajnal, O. Henrich and M. Fuchs, *J. Chem. Phys.* submitted (2008).
7. P. Strating, Phys. Rev. E **59**, 2175 (1999); D. R. Foss and J. F. Brady, J. Fluid Mech **407**, 167 (2000).
8. J. Bergenholtz, J. F. Brady, and M. Vicic, J. Fluid Mech **456**, 239 (2002).
9. D. Hajnal and M. Fuchs, *Eur. Phys. J.* **E** to be submitted (2008).