

## Introduction

The nuclear industry worldwide has stored large amounts of waste material in ponds, silos and tanks that need processing. In the UK there are significant quantities of radioactive sludge that have arisen from the corrosion of early Magnox fuel cans. These sludges are polydisperse colloidal systems based on magnesium hydroxide in an aqueous alkaline medium. More generally, however, at other sites throughout the world radioactive sludge can have alternative composition [1] [2]. The development of methods and machinery for the recovery and immobilisation of these radioactive waste slurries is long overdue and currently poses a particularly awkward problem. Blockages of radioactive material in engineering equipment are particularly undesirable and plant must be designed to run for its lifetime with little or no intervention. Furthermore, the monitoring of pumping processes may be difficult because of shielding [1]. Hence, in the nuclear industry in particular, computer simulation on many scales is being used to inform the design of recovery technologies. An understanding of sludge rheology is central to the optimisation of machinery for the recovery of these materials. The aim of this study was investigate the suitability of mesoscopic models, in particular dissipative particle dynamics, for the simulation of these materials.

We developed a flexible Dissipative Particle Dynamics (DPD) code and used it to model colloid rheology using a core-modified model [3]. The latter uses DPD particles with an excluded volume to represent colloidal particles and standard DPD particles [4] to model the suspension fluid.

One reason for using this type of model was to enable comparison with established Brownian Dynamics (BD) and Stokesian Dynamics (SD) models. These models essentially treat the fluid phase as a continuum while the particulate nature of DPD model renders the fluid phase “coarse-grained”. As a result, “colloidal” particles in the early core-modified model were found to agglomerate as the result of depletion forces – a problem not seen in BD or SD simulations. A study was made of this force and an appropriate extra term was introduced to counteract it. While this achieved the desired effect in dispersing the “colloidal” particles at equilibrium, it remains unknown how the depletion force evolves in a shearing non-equilibrium system. Equilibrium studies using the core-modified model generated viscosities that match the expected Krieger-Dougherty curve[5] by the Green-Kubo route as shown in Figure 1.

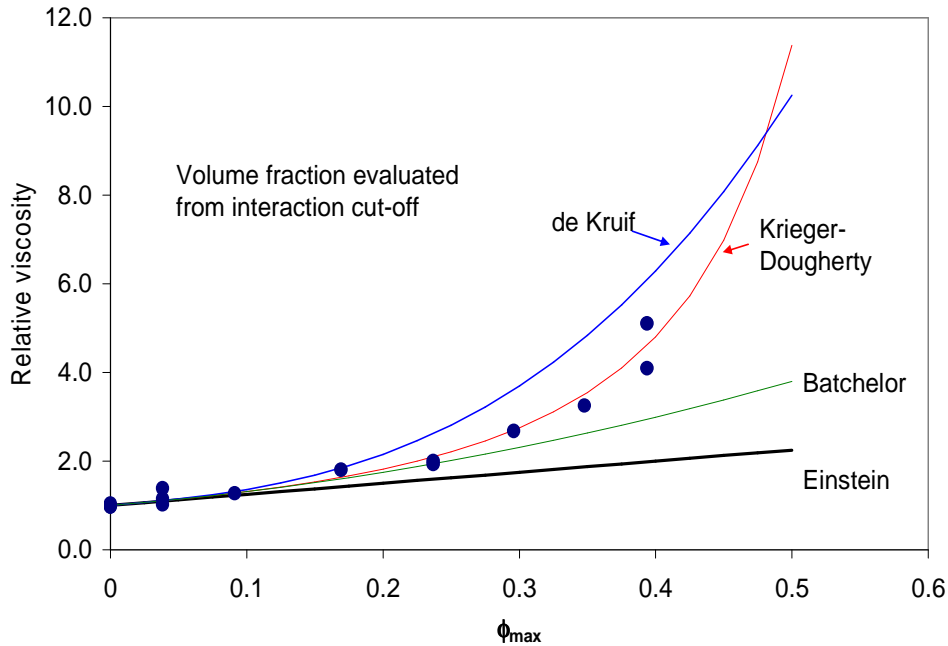


Figure 1 Green Kubo results for the relative viscosity  $\bullet$ . The theoretical Einstein limit and predictions of Batchelor, KriegerDougherty and de Kruif are also shown [5].

DPD relies on a balance between the stochastic force and a dissipative term to maintain a constant temperature. However, under the non-equilibrium conditions of an imposed shear rate we found that the measured temperature of the system increased markedly. The shear rate is expressed as the dimensionless Péclet number given by the ratio of shear to Brownian forces or diffusivity[5]

$$Pe = \frac{6\pi R^3 \eta_s \dot{\gamma}}{k_B T} . \quad [1]$$

For  $Pe > 1$  the externally applied field exceeds the thermal fluctuations and a temperature rise is not unexpected. Indeed, the effect has been studied extensively for Molecular Dynamics (MD) simulations but appears to have been largely ignored in the literature for non-equilibrium DPD. We applied number of sophisticated auxiliary thermostats in an effort to maintain the temperature. Under an imposed shear rate a Galilean invariant definition of the local velocity must be used to calculate a kinetic energy. The thermostats differ in the way the local streaming velocity is defined. We found significant differences in the colloidal structure at high strain-rate depending on which thermostat was used (Figure 2) – in particular a simple polynomial fit to the streaming velocity biased the system to adopt a string phase. String phases have frequently been seen in Brownian Dynamics simulations, but have often been treated as spurious in MD despite sometimes existing in nature. A thermostat based on relative particle velocities did not induce a string phase and for these results the model reproduced the four classical

regions of colloid rheology: a first Newtonian plateau at low strain rate, a shear-thinning region, a second Newtonian plateau and finally a shear-thickening region at high strain rate. The most unexpected result of this exercise was that the un-thermostatted model almost exactly mirrored this curve despite recording a temperature increase of factor  $\sim 2.5$  over the range. At these high volume fractions and shear rates the rheology of colloidal systems is dominated by the hydrodynamic interaction and the thermodynamic (Brownian) component is much reduced [6] – this could account for our observations if the DPD is able to model the hydrodynamic component properly. However, it probably doesn't, since at these volume fractions there are relatively few “water” particles. It seems more likely that interactions between colloidal particles dominate in this regime and these are less affected by temperature through thermal motion because of their relatively high mass. Thus it could be that the system mimics rather than properly models real colloids.

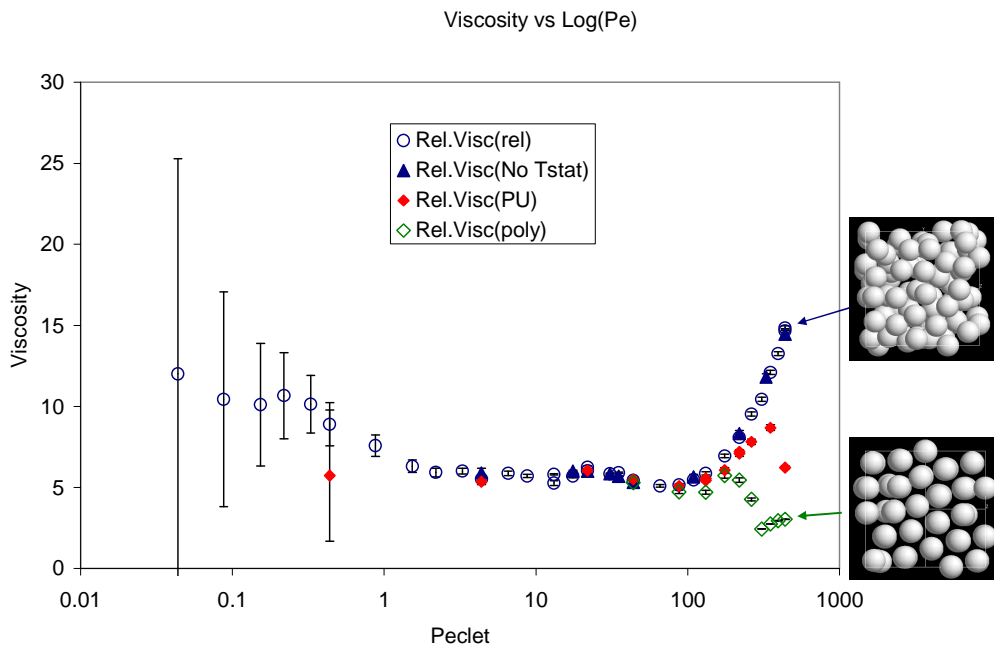


Figure 2. Shear-rate dependence of relative viscosity at  $\phi = 0.3374$  for:  $\circ$ , relative velocity thermostat;  $\blacktriangle$ , no auxiliary thermostat;  $\blacklozenge$ , profile unbiased thermostat;  $\diamond$  polynomial thermostat. Images show the particle structure in the direction of shear; the lower figure a hexagonal packed string phase, the upper figure is more amorphous in character.

At higher volume fractions, there is a significant increase in viscosity at low strain-rate, but only a moderate increase at high strain-rate. Figure 3 compares the results at volume fraction 0.3374 and 0.4031. This appears at odds with Stokesian dynamics results[7] which show a comparable increase at high strain-rate as the volume fraction is increased.

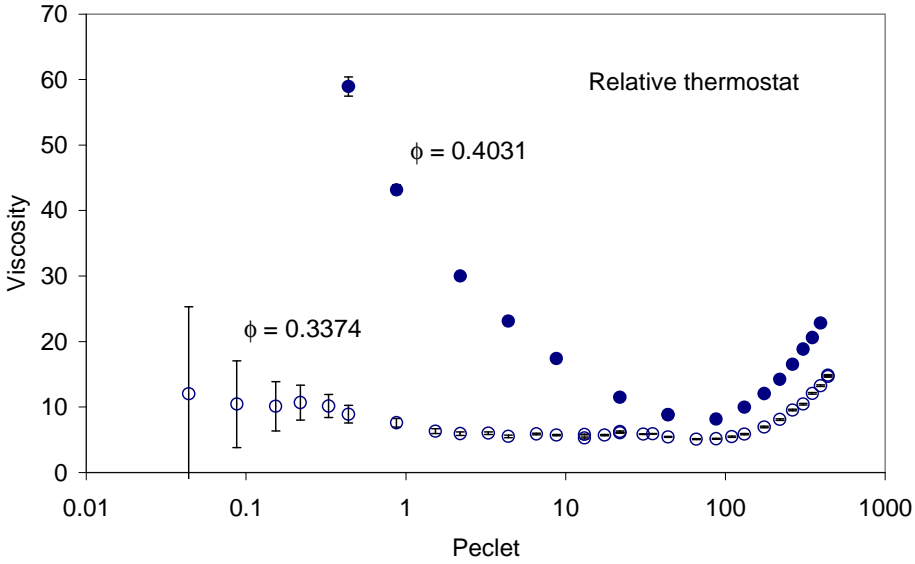


Figure 3. Shear-rate dependence of relative viscosity using the relative thermostat for:  $\circ$ ,  $\phi = 0.3374$ ;  $\bullet$ ,  $\phi = 0.4031$ .

Viewed as a stress-strain plot the higher volume fraction results reveal a plastic or pseudoplastic region at low  $Pe$ , Figure 4. It is not possible by this means to ascertain whether the results indicate a yield stress (as found in Magnox sludge); to do this a constant stress algorithm is required.

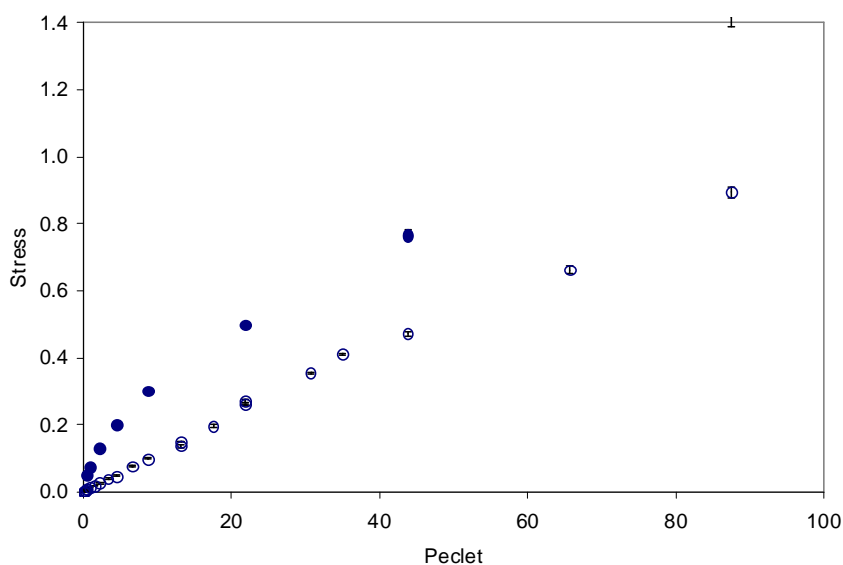


Figure 4. Shear-rate dependence of stress for the core-modified model for a core size  $3.0r_c$  using the relative thermostat for:  $\circ$ ,  $\phi = 0.3374$ ;  $\bullet$ ,  $\phi = 0.4031$ .

It is in the nature of mesoscopic models, and DPD in particular, that they are approximations designed to simulate fluids too complex to approach by rigorous methods such as molecular dynamics. With this in mind perhaps the drawbacks of the method can be tolerated or accommodated. However, these approximations and their consequences need to be investigated more extensively before the method can be adopted for important real-world problems such as the removal of radioactive sludge.

## References

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