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## Shear induced order of hard sphere suspensions

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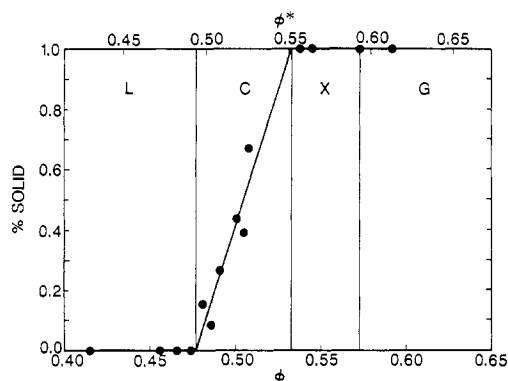
**Abstract.** Hard spheres serve as one of the basic models in classical equilibrium statistical mechanics, as well as, in fluid mechanics. Sterically stabilized polymethylmethacrylate (PMMA) spheres suspended in certain organic solvents have interparticle interactions which approximate the hard sphere interaction. Thus the equilibrium properties of PMMA particle suspensions should correlate with theoretical and computer simulation results of pure hard sphere systems. However, non-equilibrium properties must be compared with theories which include the hydrodynamic effects of the suspending medium. Experimental results are presented which suggest hard sphere behaviour: a solid–liquid phase transition, equilibrium crystal structure, liquid and crystal sedimentation velocities. Non-equilibrium microstructure in steady and oscillatory shear flows is then examined using light scattering from samples where the solvent index of refraction matches that of the particles. Oscillatory shear flows of the proper strain amplitude can shake crystal-like order into an equilibrium liquid-like sample. These results may be understood in terms of a simple hard sphere model.

### 1. Introduction

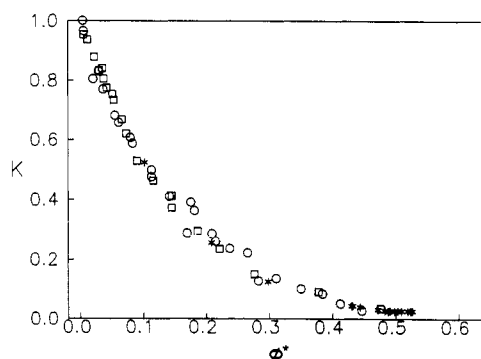
Hard spheres serve as a basic model of condensed matter in equilibrium statistical mechanics and in nonequilibrium statistical mechanics and suspension dynamics. There are analytic approximations for the liquid phase structure [1] and molecular dynamics simulations indicate a first order phase transition with melting and freezing particle volume fractions of 0.494 and 0.545, respectively [2]. Crystallization may be bypassed to produce glass phases, the closest packed glass having a volume fraction 0.637 [3]. These equilibrium results also should apply to suspended particles provided the solvent does not affect the interparticle interaction.

The non-equilibrium properties of hard sphere systems are expected to differ for atomic systems as compared to suspensions, because in addition to particle collisions the solvent will transmit stress in suspensions. Analytic and computer simulation work has been conducted for both atomic systems and suspensions of hard spheres. This work includes calculations of viscosity [4, 5], sedimentation [5, 6], self- and mutual diffusion constants [7].

Results are presented for suspensions of particles which interact with nearly hard sphere interactions. This is evidenced in the phase behaviour [8–10], the equilibrium crystal structure [11] and the sedimentation velocities [9]. These results are important because there are few hard sphere experimental systems. The non-equilibrium microstructure of these suspensions undergoing shear flow is examined by light diffraction techniques [10]. While a simple hard sphere model is presented to interpret observations,



**Figure 1.** Phase diagram showing liquid (L), coexisting liquid and crystal (C), crystal (X) and glass (G) regions as a function of the measured  $\phi$  and rescaled  $\phi^*$  volume fractions.



**Figure 2.** Reduced sedimentation velocity as a function of scaled volume fraction. The symbols are explained in the text.

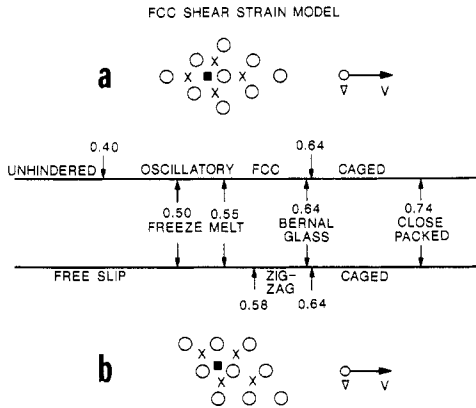
these results provide a new challenge to extend hard sphere theory and simulations to nonsteady non-equilibrium situations.

## 2. Experimental details and results

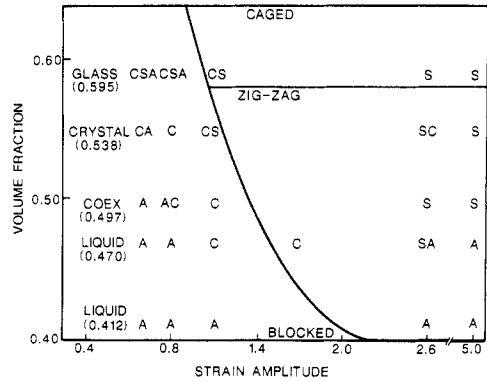
The colloidal particles used in these experiments are  $0.99\ \mu\text{m}$  diameter poly-methylmethacrylate (PMMA) spheres stabilized against aggregation by a surface coating layer of poly (12-hydroxylstearic acid). The particles are suspended in a mixed solvent of tetralin and decalin which has nearly the same index of refraction as the PMMA particles. In this way concentrated samples having volume fractions up to 0.70 are rendered transparent, and light scattering may be used to determine particle micro-structure analogous to x-ray scattering from atomic systems.

Since the particle/solvent density ratio is 1.32, particle sedimentation occurs during the phase equilibration process. The heights of the different layers which result are monitored and extrapolated to zero time to produce the phase diagram in figure 1. This phase diagram shows a transition from liquid to crystalline states with increasing volume fraction. The melting and freezing points are within a few per cent of those values expected for hard spheres, and the width of the coexistence region corresponds to that expected for hard spheres. Reasons for the deviation from accepted hard sphere values are discussed elsewhere, and the volume fraction is scaled ( $\phi^* = (1.04)\phi$ ) such that the freezing volume fraction coincides with the computer simulation value [9].

Hard sphere behaviour also is indicated by light diffraction studies of the most rapidly growing crystallites [11]. While a close packing of particles is expected, it is a randomly stacked structure. There are neither long range attractive forces which favour face-centred cubic crystals nor long range attractive forces which favour hexagonal close packed crystals. Finally we note hard sphere behaviour in the reduced sedimentation rates shown in figure 2. The data for the PMMA spheres (\*) is compared with other data for 'hard spheres' of polystyrene ( $\square$ ) [12] and of silica ( $\circ$ ) [13]. These data are compared with appropriate hard sphere theory elsewhere, and the reduced sedimentation rates of



**Figure 3.** The upper portion shows an FCC crystal structure which is subject to the shear deformation indicated. The allowed motion of (111) layers over one another is indicated as a function of particle volume fraction. The lower portion shows the (sliding) layer orientation, shear deformation, and allowed motion of layers.



**Figure 4.** Observed microstructures as a function of volume fraction and strain amplitude. The symbols correspond to liquid (A), FCC crystal (C), and sliding layer (S). The first symbol in a grouping corresponds to the dominant structure.

the coexisting liquid and crystal phases are found to be 0.026 and 0.016, respectively [11].

Self and collective diffusion constants have been measured for similar PMMA particle suspensions [14] and compare favourably with appropriate hard sphere theory [7]. The rheological properties of PMMA suspensions also have been measured and show hard sphere behaviour, as the ratio of the stabilizing layer thickness to the particle diameter decreases to the value used in our experiments [15]. A limited number of rheological measurements indicate the same viscoelastic behaviour for our samples.

Light diffraction studies of the microstructure under steady and non-steady oscillatory shear flow conditions reveal four basic interparticle orderings: face-centred cubic (FCC), layer, string and liquid-like. The orientation of FCC and layer structures with respect to the velocity and gradient directions is shown in figure 3(a) and 3(b), respectively. The sample cell, experimental conditions and results are given in detail elsewhere [10]. Figure 4 presents the results of oscillatory shear induced ordering studies as a function of volume fraction and maximum strain amplitude. The oscillation frequency is 3.3 Hz. Samples are randomized to show liquid-like light diffraction patterns before each experimental run and then monitored for shear induced order after one minute for a period of up to five minutes. This time period is not sufficient to observe crystallization and the structures must be induced by the shear flow.

It is seen that this nonsteady shear flow can induce an oscillating (between twin) FCC crystal order in a suspension which has an equilibrium liquid-like order ( $\varphi^* = 0.470$ , strain amplitude  $\sim 1.0$ ). The magnitude of the strain amplitude also influences the microstructure tending to the oscillatory FCC structure at small strain amplitudes and a sliding layer structure at large strain amplitudes. The curved line, separating the largely FCC region from the largely layer region in figure 4, represents the maximum strain that a perfect FCC crystal lattice can sustain without particle contact when oriented and sheared as shown in figure 3(a). Figure 3 also indicates the allowed shear strain motions

for the FCC and layer orientations of a perfect hard sphere crystal as a function of volume fraction. The model is consistent with observations but does not explain why the various structures are selected, when both may be allowed. Further details and shear history dependences are discussed elsewhere [10].

### Acknowledgments

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