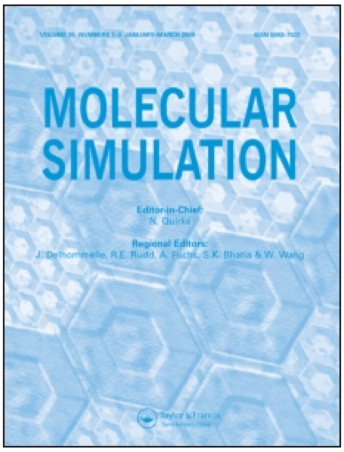

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Hexagonal-String Phases in Suspension Flow

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Preliminary Communication

HEXAGONAL-STRING PHASES IN SUSPENSION FLOW

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Investigations of the structure of flowing colloidal suspensions have seen structures of predominantly hexagonal strings moving in layered arrangements in the direction of the velocity gradient. A combination of computer simulation trajectories and computer graphics show that the predominant "hexagonal string phase" is the BCC lattice sheared along its (111) slip plane and, moreover, that all the common cubic lattice types contain "hexagonal strings".

KEY WORDS: Suspension flow, string phase

In recently reported experiments [1], Pusey and van Megen demonstrated that colloidal suspensions of fine spherical particles, when left to equilibrate, exhibit first-order thermodynamic amorphous-crystal two-phase behaviour analogous to the freezing of atomic liquids. Typical equilibration times increase with particle size and viscosity of medium, as the only source of kinetic energy is Brownian motion. When amorphous colloidal suspensions of dense monodisperse spherical particulates are sheared in laminar Couette flow a transition to an ordered phase is seen on a much shorter time-scale, and is often accompanied by pronounced shear-thinning, i.e. a reduction in the effective viscosity. Hydrodynamic shear forces enhance the particulate kinetic energies and thereby reduce the relaxation times. The ordered phase usually takes the form of hexagonally stacked horizontal strings, when viewed from the flow direction in the plane normal to the flow.

Computer simulations of particulate dynamics have been adapted to investigate the structure of flowing suspensions in the non-Newtonian region for simple hard- and soft-sphere models [2,3]. These models show a transition to an ordered arrangement also; an extrapolation to zero shear rate of the two-phase line for the osmotic coexistence pressure indicates that the order-disorder transition can be described as a shear-perturbation of the static equilibrium phase transition seen by Pusey and van Megen [1]. Subsequent investigations of the structure in the ordered shear-phase also show the structure to be predominantly hexagonal strings moving in a layered arrangement in the direction of the velocity gradient [4]. This characteristic structure of flowing suspensions has come to be known in the reological circles as the "hexagonal-string phase".

Figure 1 shows a typical configuration of the sheared hard-sphere model suspension at the reduced density $\varrho\sigma^3 = 0.9$ $\varrho = N/V$ and σ is the particle diameter), and

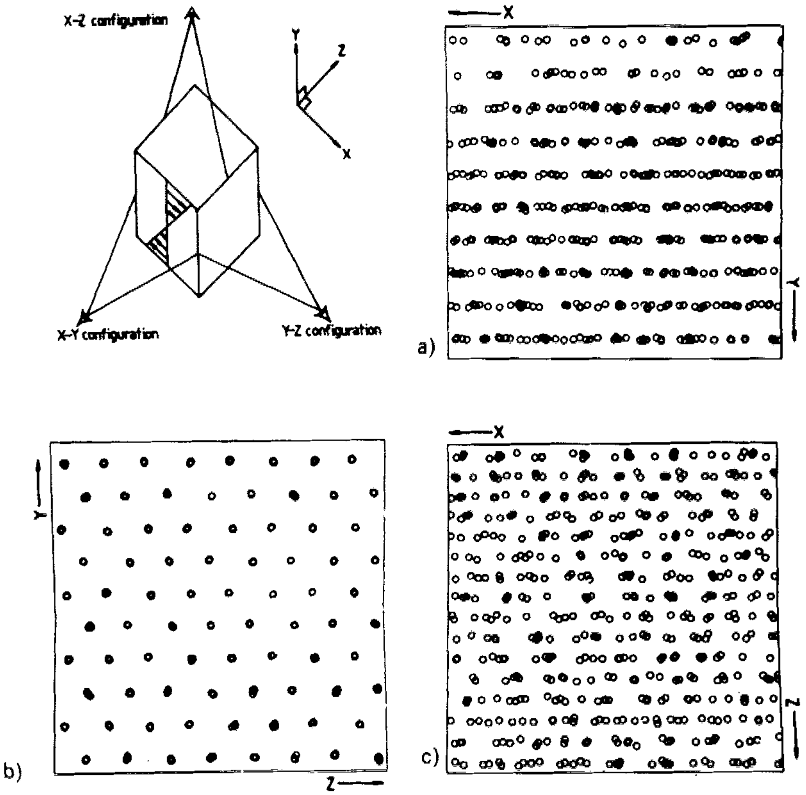

Figure 1 A configuration of hard-spheres in shear flow from a computer simulation calculation in the shear thinning region corresponding to an ordered arrangement of particles: a) projected on to the X-Y plane b) projected on to the Y-Z plane c) projected on to the Z-X plane

reduced shear rate $\gamma(m\sigma^2/E_0)^{1/2} = 10$ (m is mass and E_0 is the kinetic energy per particle): the configuration is from a sheared system of 500 particles using the cross-boundary collision shearing method described by Erpenbeck [5]. The characteristic hexagonal-string-like arrangement is clearly observed in the Y-Z plane with flow in the X-direction; the layering in the X-Y plane facing the shear gradient (Y-direction) is also clear.

The occurance of the hexagonal strings in "isokinetic" computer simulations from an unsteady disordered equilibrium state has no *steady-state* experimental counterpart [6]. In a real suspension shear increases the particle kinetic energies over and above the Brownian motion. Scaling laws for idealised hydrodynamic or granular models, however, show a corresponding states inversion; the "isokinetic" ordering transition at low shear corresponds to the hydrodynamic/granular disordering shear-thickening transition which occurs in the high shear-rate region of the experimental flow curve [6].

The important point in the present context is that all monodisperse suspensions at effective hard-sphere packings exceeding the fluid freezing of 45% will at low shear exhibit hexagonal string phases as perturbations of the equilibrium lattice structures

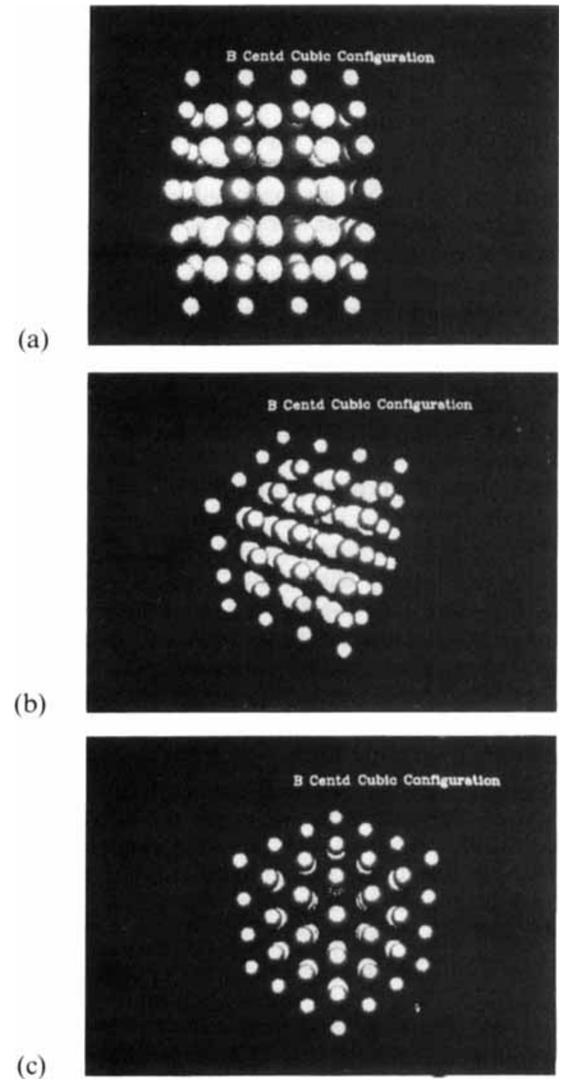

Figure 2 (See Colour Plate XIII at back of this volume.) A computer picture of the body-centred cubic arrangement of particles from three different angles: a) looking down the (111) plane showing the slipping layers of the close-packed BCC lattice b) from a side angle showing the "strings" of particles in the (111) slip plane layers in (a) above c) from a point outside the cube on the cube diagonal line showing the hexagonal arrangement of the strings in (b) above

at the same effective hard-sphere packing and particle kinetic energy and at the corresponding shear-rate. When Brownian motion is negligible and apparent "steady-state" may be defined in its absence, hard-sphere suspensions may exhibit hexagonal string phases at low shear-rates at packing fractions below the equilibrium fluid freezing.

The purpose of this communication is to illustrate:

(i) that the predominant "hexagonal string phase" is merely the body-centred cubic lattice sheared along it's (111) slip plane, i.e. the direction of the cube diagonal.

(ii) that all the common cubic lattice types, i.e. face-centred cubic (FCC), body-centred cubic (BCC) and simple cubic (SC) contian "hexagonal-string phases".

The hard-sphere model in the SC arrangement at close-packing is unstable with respect to slip in all directions of shear stress; it is also unstable with respect to slip in the (111) direction of the BCC lattice at close packing; in the FCC and other maximum packing lattices, however, it is both mechanically stable at low stresses and thermodynamically stable with respect to the more open-structures and the fluid. Under laminar shear flow at steady-state equilibrium, as the shear rate increases at constant density, or as the density decreases at constant shear rate, the (111) flow-plane of the BCC arrangement becomes the preferred structure. In this phase the stress is reduced relative to any of the slip planes of the FCC of HCP lattice types, or hybrids thereof, at a sufficient shear rate or a sufficient dilatancy.

Figure 2 shows a computer graphics picture of the static BCC lattice [6] viewed from three different angles. When a cube (containing 64 particles or 32 units) is viewed down the (111) direction the free-slip planes are clearly evident (top). In the centre picture the side projection clearly shows the "strings". The view from behind the would-be flow direction down the cube diagonal shows the hexagonal arrangement of the strings as commonly observed in flowing colloidal suspensions. Thus, the BCC arrangement, even at zero-shear and close packing, is a "hexagonal-string phase".

Figure 2 shows the BCC phase in the two-component "Caesium Chloride" form, in single component monodisperse suspensions all the particles are deemed equivalent, red or green. One can easily imagine removing one of the component, however; if all the green particles are deleted a simple-cubic arrangement is obtained which, from top to bottom, retains the slipping layers, the strings and hexagons respectively. Thus, the sheared (111) slip-plane of the SC lattice is also a "hexagonal string phase".

If one proceeds further to remove half of the remaining SC (red) particles an FCC lattice is obtained. Here again, in the same slip plane a "hexagonal string phase" with the FCC structure results. In the *close-packed* FCC arrangement, however, the FCC structure (111) — hexagonal string phase, is not amenable to unrestricted slip, unlike the BCC case.

It may be concluded from the foregoing that the overwhelmingly preferred layered structure seen in the flow of sheared colloidal suspensions of spherical particles is the BCC-(111)-slip-plane hexagonal-string phase. It may also noted that at lower densities or higher shear rates two or more structures can become similar as the transverse registry vanishes. In the limit of no transverse registry all the structures would presumably become the "hexagonal-pipe phases" differing only in the ratios of transverse to longitudinal particle concentrations.

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