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Journal of Colloid and Interface Science 293 (2006) 475–482
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Characterization of the flow of anisotropic colloidal particles using energy-dispersive X-ray diffraction

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Received 24 September 2004; accepted 19 June 2005

Available online 2 August 2005

Abstract

The technique of energy-dispersive X-ray diffraction to study the orientation of microscopic crystalline particles dispersed in a liquid has been described recently. This complements previous neutron diffraction studies by permitting measurements at higher spatial resolution. Work with synchrotron radiation and high-energy X-rays has allowed studies on liquid dispersions flowing in pipes with a thickness of about 1 cm and a spatial resolution of 100 µm. Kaolinite is often found as a dispersion of monocrystalline, microscopic plates. The crystallographic layer structure is commensurate with the particle shape: the 00*l* direction is normal to the plane of the plates. Measurements of diffraction of the flowing liquid dispersion in a pipe oriented in various directions to the incident beam can be used to deduce the average orientation and order parameters of the particles. The competing effects of alignment with walls and in flow fields were observed. Further work has measured the orientation near a bend in a pipe.

Keywords: Kaolinite; Flow alignment; Pipe flow; X-ray diffraction

1. Introduction

Dispersions of solids in liquids are found in many everyday materials such as pastes and colloidal dispersions. For example, they are used in paints, form an important stage in ceramic processing and are used as fillers in polymers to modify mechanical and electrical properties. Rheological properties such as viscosity and the structure that occurs under deformation can both be of crucial importance in determining process conditions and the properties of final products. There is extensive literature on measurement of rheological properties and their relationship with theoretical and semi-empirical constitutive equations (e.g., [1,2]). Interest in relating structure and structural changes to flow is increasing but investigations are restricted to techniques that can be used to access structure in complex fluids such as colloidal dispersions and polymers, and that can be combined with in situ application of flow fields. The orientation of anisotropic colloidal particles is a complex problem in hydrodynamics. It involves interactions between particles as well as with the dispersion medium. The principles of this theory are very well described in the authoritative book by van de Ven [3]. In fluid mechanics [4] it is straightforward to consider certain flow fields such as simple shear. However, most practical applications will involve non-uniform shear or extra deformations such as elongational flow. A common example would be the flow in a cylindrical pipe that will have a non-uniform shear across its diameter and the profile will depend on factors such as slip at walls and the rheological properties of the fluid. The flow in a pipe is therefore best described by the volume flow rate and the geometry. Bends

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2005.06.053

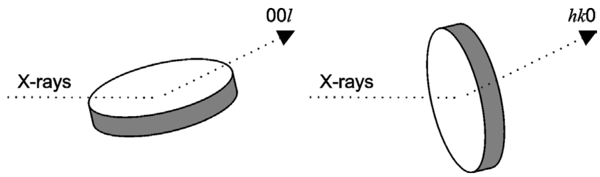

Fig. 1. Diffraction from single-crystal colloidal particles depends on the orientation with respect to the beam. The intensity of $hk0$ and $00l$ diffraction peaks can be used to determine the orientation of particles in a fluid. In energy-dispersive diffraction all peaks are measured simultaneously with a point detector at a single angle, 2θ, typically in the range 2° to 6°. The diffraction angle is exaggerated for clarity in the diagram and thus does not correspond to the crystal lattice spacings and X-ray energies used in the present experiments.

and constrictions will perturb the flow, may cause turbulence that disorders the fluid and also introduce an elongational component to the flow. The calculation of flow patterns for Newtonian fluids with a constant viscosity is straightforward using finite element analysis but for complex fluids such as colloidal dispersions that thin under shear advanced modeling techniques are required.

Diffraction from the internal structure of crystalline particles in a liquid can be used to measure the extent of alignment of anisotropic particles provided that there is a consistent correlation between the shape of the particles and the orientation of the crystal structure. Individual colloidal particles of certain materials are usually found as single crystals. For example, in the case of kaolinite the $00l$ crystal planes lie in the plane of the plate-like particle. The principle of this technique is shown in Fig. 1. Bragg diffraction from the crystal structure within a particle depends on the orientation of the particle with respect to the incident beam. Measurement of the distribution of intensity from diffraction peaks that arise from different crystallographic directions allows the orientation distribution of an ensemble of particles to be determined. Previously neutron diffraction has been used to study the alignment in uniform flow fields with large, thick-walled cells suitable for controlled rheological measurements [5–7]. The long wavelengths allow measurements at high scattering angles and so thinner regions of sample can be probed effectively.

Synchrotron X-ray diffraction with high brilliance sources allows very high spatial resolution in the plane perpendicular to the incident beam. The work described in this paper is a preliminary study that shows how the X-ray measurement of alignment can be used both for studies of the rheology of crystalline particulate dispersions and as a tool to probe complex flow fields such as those near constrictions and bends. In energy-dispersive diffraction experiments, an energy-sensitive detector is placed at a fixed (low) scattering angle and diffraction spectra are obtained as a function of energy from a defined sample volume. The principle of the experimental techniques is that only crystalline particles that are oriented to meet the Bragg condition will give rise to a diffraction peak for a detector placed at a given position relative to the sample. Measurements of peaks with

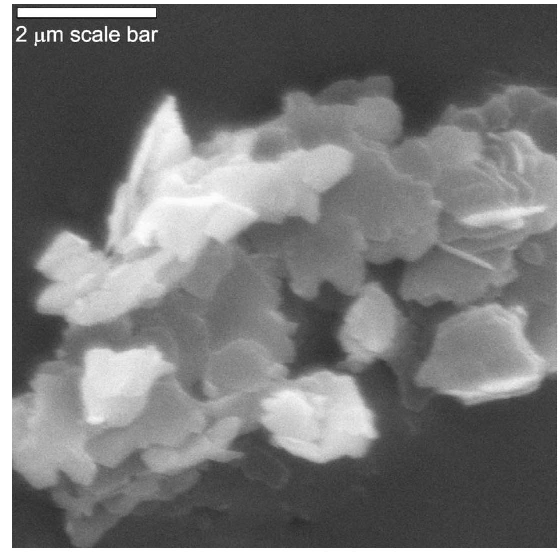

Fig. 2. Scanning electron micrograph of a dried sample of kaolinite taken from the dispersion used for the experiments which shows the crystalline, plate-like nature of the samples.

different conditions relative to the particle morphology and with flow fields in various orientations allow precise maps of alignment to be made. In this paper, studies of kaolinite dispersions flowing in pipes are investigated and the extent to which Legendre polynomials are good order parameters to describe alignment is presented. The experimental methods and sources of error are discussed in some detail so that the potential of the method can be assessed for other problems in colloid rheology.

Rheological properties of clays have been studied extensively (e.g., [8–10]). The behavior is complex, in part because of the interactions between particles that may depend on pH, added electrolytes and the presence of stabilizers [8,11]. In some cases there are aggregation effects that may include the formation of gels. However, even well stabilized dispersions of isolated particles can display unusual features and some of these are evident from recent X-ray [12,13] and neutron scattering experiments [7,14,15].

2. Experimental methods

2.1. Diffraction

The sample used for all these experiments was kaolinite as described in our previous work [7]. A 50% w/w aqueous dispersion of kaolinite stabilized with sodium polyacrylate was used for the experiments described here. As seen in Fig. 2, the kaolinite consists of plate-like crystalline particles. The crystal structure of kaolinite is well known [16]. The diffraction intensities from planes parallel to the large plate faces are described as $00l$ peaks. Intensities from planes perpendicular to the large faces are described as $hk0$ peaks. The X-ray diffraction measurements were made at