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Preferred orientation in filtercakes of kaolinite

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Abstract

The orientational order parameter of dense colloidal dispersions of plate-like particles as a function of volume fraction is measured using neutron diffraction. This non-invasive experimental approach directly provides the full particle orientation distribution from which the order parameters can be calculated. The orientation parameters are shown to be linked to the solids fractions of the cakes and the macroscopic permeability of the samples. However, this study suggests that, although orientation can be relevant for a given system, other factors can have a stronger influence, for example, the degree of dispersion or colloidal stability of the clay and may be the principle factor that controls permeability. In addition, we report enhanced ordering of these materials under the influence of an external cross-flow field.

Keywords: Orientational order; Neutron diffraction; Filtercakes; Kaolinite; Clay

1. Introduction

Dense colloidal dispersions, pastes, of plate-like particles are important both industrially, in areas as diverse as paper coating and drilling muds for oil recovery, and academically, where the anisotropic nature of the particles leads to interesting orientational behaviour, particularly liquid crystallinity [1] and the ability of the anisotropic particles to couple with external fields such as flow. Understanding the influence of shape and orientation of particles on the physical properties of such materials is a key goal of current research. However, many of the materials are difficult to investigate in a non-invasive fashion as they are often completely opaque (indeed, in paper coating this opaqueness is a desirable feature) preventing any investigation other than of the surface.

Of particular interest in fields such as paper coating and oil recovery are the formation of filtercakes of such plate-like particles. In many cases plate-like particles, as well as providing other beneficial properties such as desirable rheology in dispersions, also are found to make much more impermeable filtercakes than spherical particles. Such control of permeability is key to avoiding loss of expensive drilling fluids to porous rock or preventing damage caused by the invading fluid in oil producing zones.

Previous work has indicated that the action of platey particles is not simply one of size. Approximately monodisperse spherical particles have maximum density, assuming random close packing, of 64% leaving at least 36% space between them. Polydisperse mixtures of spheres can lead to less permeable structures but achieving and maintaining these particular size distributions can be difficult.

In contrast, plate-like particles, if well oriented and aligned, can fill space much more effectively leaving far less space for fluid to flow between them. Hence, the orientation of these platey particles is expected to play a key role in determining the cake permeability. Only well-aligned plates can be expected to give very impermeable cakes—a cake made with plate-like particles randomly oriented will have a very open array and hence be expected to be exceedingly permeable. Recent theoretical models have attempted to address the diffusive permeability of composites made of plate-like flakes dispersed in a polymer matrix [2]. In these models the flakes are taken to be perfectly aligned, with the

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plate normals in the fluid flow direction, although, of course, real systems have varying extents of preferred orientation. It is important to link preferred orientation of plate-like particles to physical properties of these types of materials.

In this work we will outline a non-invasive neutron scattering procedure that can provide the full 3D orientational distribution function for dense colloidal pastes of platey–clay particles, prepared by a filtration process. Data from a number of materials prepared under a variety of colloidal stability and preparation conditions are presented. The orientational order parameter is determined from this data, and the orientational microstructure of the materials is related to the macroscopic physical properties of the cakes, particularly the permeability.

2. Experimental

2.1. Diffraction

Diffraction has been used to investigate preferred orientation of clay materials for many years. In particular X-ray diffraction has been used to investigate anisotropy of bedding planes of mineral strata with seismic implications [3,4] because the velocities of sound are expected to be anisotropic if the mineral particles show extensive preferred orientation. However, generally in these measurements relatively poor penetration of the X-rays only allows exposed surfaces of the rocks to be used for the orientation studies and pre-treatment often restricts such studies to only very stable materials.

Other techniques, such as optical birefringence, can provide an insight into preferred orientations of dispersions expressed through a single variable, generally referred to as an orientational order parameter, the second-order Legendre polynomial, P_2 or S. The order parameter varies from zero, for completely disordered powders, to unity, for perfectly aligned materials. However, the single value order parameter provides no insight into the actual nature of the particle distribution. P_2 is only the first term of an infinite series of spherical harmonics that describe the full orientation distribution [4]. The approach used here gives the full particle distribution function and hence can be used to calculate all the members of the series. In addition, light birefringence is limited to optically transparent materials.

Determination of the full orientation using small angle scattering from colloidal particles is also not usually possible because of the problem of separating the contributions of the scattering from the external shape of the particles (the 'form factor') from that of the particle arrangements (the 'structure factor'). However, small angle neutron scattering (SANS) can provide important data on the fractal dimensions and surface-to-volume ratio of such dense pastes [5].

The use of neutron diffraction to determine the full orientation distribution function of colloidal dispersions of non-swelling clays and other materials has been reported previously [6]. In these earlier works the materials were fluid dispersions that exhibit orientation under external fields, particularly flow [6]. Among several results reported, the extent of orientational order is seen to increase with increasing flow field, and to align the plate-like particles more closely with the flow–vorticity plane of the flow field. In the work presented here much higher solids fraction materials, pastes or filtercakes, are systems which do not readily flow. Rather it is the method of preparation of these materials that can result in preferred orientation microstructure. Neutron diffraction is a particularly useful technique for the study of the dense, opaque materials of interest here. Generally the transmission of these materials to neutrons is much higher than to light and even to X-rays. This means that the bulk of the material can be probed in a non-invasive fashion, rather than just the surface—the neutron experiment will present an average of all the material illuminated by the neutron beam. The excellent transmission of neutrons to certain other materials (e.g., aluminium) also enable the use of metal sample containers allowing the imposition of pressure, temperature or flow. However, to minimise the incoherent background scattering of H_2O, samples must generally be prepared in D_2O.

The experimental approach to obtain the orientational distribution function for a sample of crystalline clay particles has been presented previously [6] and is only outlined here. The kaolinite clays used here can be thought of as tiny plate-like crystals made of stacks of aluminosilicate layers. The separation of these layers, d, is a characteristic of the material. Braggs Law states that the scattering angle of such a material is given by

$$\lambda = 2d\sin(\theta),$$

where λ is the wavelength of the radiation, 0.455 nm, and θ is half the scattering angle. For intensity to be observed at the detector, the crystal of kaolinite must be in the correct orientation with respect to the incident and scattered beams. Alternatively, for a sample consisting of many tiny crystallites with different orientations, only those crystals which are in the correct orientation, will give rise to intensity on the detector. Hence the intensity measured is directly proportional to the number of crystallites in the sample at each orientation. To obtain the orientation distribution, the number of particles in the sample at each orientation, the sample is rotated in the beam and the intensity counted at each orientation.

Because the technique is based on diffraction peaks where the peak position is characteristic of the material of interest, we can readily extend the approach to multicomponent mixtures and still consider the behaviour of each component separately (provided there is no coincidence of peak positions from different components) [7].

In short, we collect the intensity at a given scattering angle, 2θ, for a diffraction peak characteristic to the material of interest as the sample is rotated in the beam. If the sample is a powder we expect to see no variation in the intensity of the collected signal—any preferred orientation would be reflected by maxima and troughs in the intensity.